Evidence for Methane σ-Complexes in Reductive Elimination Reactions from Tp′Rh(L)(CH$_3$)H

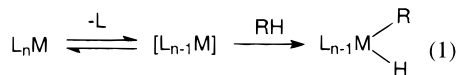**Douglas D. Wick, Kelly A. Reynolds, and William D. Jones***

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Abstract: Two sets of experiments are described that provide indirect evidence for the involvement of alkane σ-complexes in oxidative addition/reductive elimination reactions of Tp′Rh(L)(R)H complexes (Tp′ = tris-3,5-dimethylpyrazolylborate, L = CNCH$_2$CMe$_3$). First, the methyl deuteride complex Tp′Rh(L)(CH$_3$)D is observed to rearrange to Tp′Rh(L)(CH$_2$D)H prior to loss of CH$_3$D. Similarly, Tp′Rh(L)(CD$_3$)H rearranges to Tp′Rh(L)(CD$_2$H)D prior to loss of CD$_3$H. Second, the rate of elimination of methane from Tp′Rh(L)(CH$_3$)H in benzene/perfluorobenzene solvent mixtures is found to be dependent upon the *concentration* of benzene, indicating an associative component to the reductive elimination of methane. Both of these processes, and their rates, are accommodated by the reversible formation of alkane σ-complexes prior to dissociation of alkane.

Introduction

A number of transition-metal systems are now known which oxidatively add alkanes to form relatively stable alkyl hydride complexes.[1] Direct study of the C−H bond insertion step by a coordinatively unsaturated transition-metal fragment has been examined using fast spectroscopic techniques in liquified or supercritical rare gases,[2] low-temperature gas matrices,[3] and hydrocarbon solution.[4] There is now substantial evidence in the literature for the intermediacy of alkane σ-complexes in the activation of alkanes by way of oxidative addition[5] (eq 1) and the studies presented here provide new evidence for their existence.
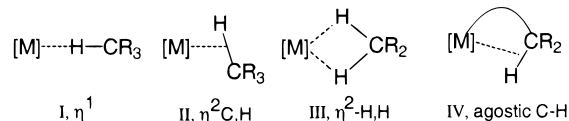
$$L_nM \underset{\longleftarrow}{\overset{-L}{\longrightarrow}} [L_{n-1}M] \overset{RH}{\longrightarrow} L_{n-1}M\begin{smallmatrix}R\\ \\H\end{smallmatrix} \quad (1)$$

An alkane complex consists of a C−H bond of a free alkane that is weakly coordinated to a transition-metal center. In these species, the C−H σ-electrons serve as the electron donor to the

Chart 1

empty metal orbital, and the high-lying C−H σ* orbital serves as a π-acceptor from a filled metal orbital. The structures for these intermediates proposed by several workers are shown as **I−III** in Chart 1, and are analogies of the known agostic structure **IV**. To consider the C−H bond of an alkane, such as methane, to be a σ-type transition-metal ligand would seem to ignore the conventional wisdom concerning the qualities of a good ligand. Low-energy $\sigma_{C−H}$ orbitals and high-energy σ*$_{C−H}$ orbitals should make methane a poor electron donor and electron acceptor, respectively, hence a poor ligand.[6] However, evidence is mounting which suggests that alkane complexes are more common than expected.

Much of the current understanding of C−H bond activation by transition-metal complexes in homogeneous solution has come from mechanistic investigations of alkane reductive elimination from alkyl hydride complexes. Reductive elimination of an alkane from an alkyl hydride complex is the microscopic reverse of oxidative addition of an alkane C−H bond to a coordinatively unsaturated metal center, and hence, studying one in turn provides information about the other. This means that the mechanism of oxidative addition must involve the same intermediates and transition states as in the reductive elimination reaction.

Several lines of evidence have implicated the existence of alkane σ-complexes. One common observation to this effect is that of hydrogen exchange between the hydride and alkyl ligands of isotopically labeled alkyl hydride complexes prior to alkane reductive elimination.[7] Equation 2 depicts the intramolecular

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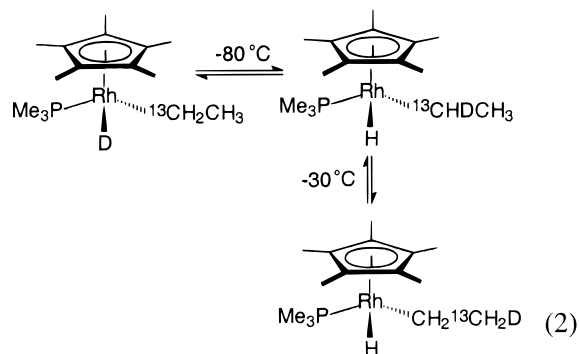(4) Lian, T.; Bromberg, S. E.; Yang, H.; Proulx, G.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 3769−3770. Osman, R.; Pattison, D. I.; Perutz, R. N.; Bianchini, C.; Peruzzini, M. *J. Chem. Soc., Chem. Commun.* **1994**, 513. Lees, A. J.; Purwoko, A. A. *Coord. Chem. Rev.* **1994**, *132*, 155−160.

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rearrangement observed by Periana and Bergman for Cp*Rh-(PMe$_3$)(^{13}CH$_2$CH$_2$)D.[7b] Migration and insertion of the [Cp*Rh-(PMe$_3$)] fragment occurs most rapidly into the α position of the ethyl group followed by migration to the β position. The deuterium label remains attached to the ^{13}C-labeled carbon throughout this rearrangement. This process is competitive with reductive elimination of ^{13}C,^{2}H-ethane. Norton and co-workers have shown that Cp$_2$W(D)(CH$_3$) and Cp$_2$W(H)(CD$_3$) in low concentrations exhibit intramolecular hydrogen exchange between the hydride and methyl ligands prior to methane reductive elimination (eq 3).[7c] In both of the above experiments, mass
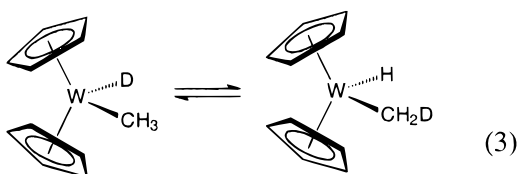
spectroscopy of the reductive elimination products from cross-over experiments further supports the intramolecular nature of the rearrangements.

Girolami has recently observed exchange between the hydrogens of an osmium-bound methyl group and a hydride ligand in (C$_5$Me$_5$)Os(dmpm)(CH$_3$)(H)$^+$.[8] The exchange is rapid enough on the NMR time scale at −100 °C to cause broadening of the resonances, but can be stopped at −120 °C to give distinct methyl and hydride resonances.

Additional support for the intermediacy of alkane complexes comes from the observation of an inverse kinetic isotope effect for alkane reductive elimination from a number of alkyl hydride complexes.[9] For those systems which have shown intramolecular hydrogen exchange an observed inverse kinetic isotope effect for alkane reductive elimination has also been demonstrated. Inverse isotope effects can occur in a single step mechanism with a product-like transition state in which the deuterium experiences a higher force constant in the products relative to that of the reactants, i.e., deuterium favors the stronger bond.[10] This observation can also be accommodated by an inverse *equilibrium* isotope effect (K_H/K_D) involving an intermediate that allows for rapid and reversible migration and insertion to occur prior to the rate-limiting loss of alkane. Formation of an alkane complex from an alkyl hydride complex leads to
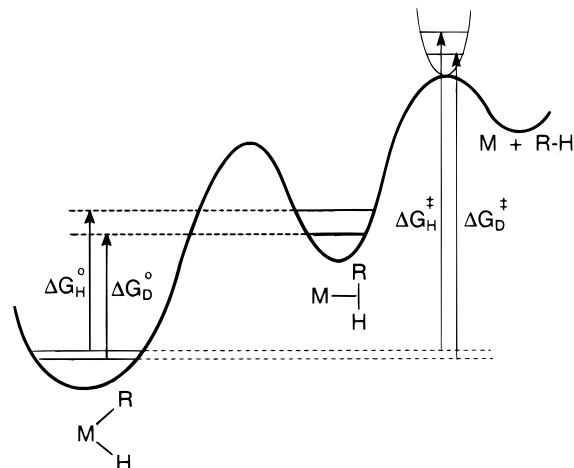

Figure 1. Reaction coordinate which depicts a larger zero-point energy difference between hydrogen and deuterium in the products relative to the reactants. The resulting equilibrium isotope effect is inverse, K_H/K_D < 1.

significant C−H bond formation because hydrogen (deuterium) experiences a higher force constant in a bond with carbon than with the transition metal. The inverse isotope effect results from an increase in the preequilibrium concentration of the deuterio isotopomer compared to the protio isotopomer which leads to a faster rate for reductive elimination for the former compared to the latter.[7d] Furthermore, the inverse effect will exist only if the C−H bond which is formed in the intermediate is not significantly affected in the rate determining step in which alkane is lost. This sequence is shown schematically in Figure 1.

Direct evidence for alkane complexes first came from the study of photochemically generated M(CO)$_5$ (M = Cr, Mo, W) fragments in alkane and alkane/rare gas matrices.[11] While subsequent C−H bond activation was not observed for these complexes, an estimate of the strength of the alkane−metal interaction (∼10 kcal/mol) established the viability of alkane C−H bonds as σ-type electron donors.[12] Agostic C−H interactions (**IV** in Chart 1) in which the C−H bond of a bound ligand interacts with the metal have allowed for a preliminary understanding of the structure of alkane metal complexes.[13] A recent low-temperature observation of the metal fragment [CpRe(CO)$_2$] in cyclopentane even provides direct spectroscopic evidence for the formation of an alkane complex, although no C−H bond cleavage occurs.[14] The equivalence of two hydrogens of the bound methylene group could be interpreted either as structure **III** being the ground state or a fluxional exchange between complexes of structure **II**.

Crabtree used the available structural data for agostic C−H complexes to develop a reaction trajectory for the approach of a free alkane toward a metal center.[15] Initially, the hydrogen

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(9) Representative examples of k_H/k_D include: (a) Cp*Ir(PMe$_3$)(H)-(C$_6$H$_{11}$) in C$_6$D$_6$ at 130 °C, 0.7(1) (ref 7a). (b) Cp*Rh(PMe$_3$)(H)(C$_2$H$_5$) in toluene-d_8 at −30 °C, 0.5(1) (ref 7b). (c) Cp$_2$W(H)(CH$_3$) in CD$_3$CN at 72.6 °C, 0.75(4) (ref 7c). (d) Cp*$_2$W(H)(CH$_3$) in C$_6$D$_6$ at 100 °C, 0.77(7) (ref 7d). (e) [Cp$_2$Re(H)(CH$_3$)][Cl] in CD$_2$Cl$_2$ at 9 °C, 0.8(1) (ref 7e). (f) [CnRh-(PMe$_3$)(H)(CH$_3$)][BAr$_4$] in C$_6$D$_6$ at 75 °C, 0.74(2) (ref 1n). (g) (tmeda)-Pt(CH$_3$)(H)(Cl) in CH$_3$OH at −27 °C, 0.29 (ref 1f).

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end of the C−H bond is directed toward the metal with the carbon end pointed away; this is considered an intermediate structure. Significant C−H bond cleavage occurs in a triangular transition state structure in which the carbon end approaches the metal center more closely. Theoretically, extended Hückel, perturbation theory, and density functional methods have established that an η^1-methane complex (**I** above) between methane and d_6-ML$_5$, d_8-ML$_4$, and d_8-[CpM′L] metal fragments was of optimal energy vs η^2-type structures (**II** above).[16] Recently, Song and Hall have produced second-order perturbation theory calculations for the interaction of methane with the fragment [CpRh(CO)] which predict that a stable η^2-alkane intermediate with the alkane canted as Crabtree describes is viable prior to a triangular transition state in which significant C−H bond breaking occurs.[17] Their calculated energy profile for a reaction of an alkane with a metal center is in agreement with the energetics determined by experiment for the oxidative addition of alkanes by [CpM(CO)] in the gas phase and [Cp*Rh-(CO)] in liquified rare gases.[18,19] Also in line with the experimental results is a computational study of the comparison of methane activation by fragments of the type [CpM(CO)] (M = Co, Rh, Ir), which correlates the electronic structure of the metal to the energies of methane binding as a methane complex and as a methyl hydride complex.[20]

Structural characterization of transition-metal alkane complexes remains an elusive yet realistic goal, especially since these species can apparently be stable in solution.[14] The alkane reductive elimination studies which have provided indirect evidence for an intermediate alkane complex are few in number but have helped to establish alkane complexes as plausible chemical entities. With the exception of [CnRh(PMe$_3$)(H)(CH$_3$)]-[BAr$_4$],[1n] all of the complexes used in the studies referenced contain electron-donating Cp or Cp* ligands. The electron-donating PMe$_3$ ligand is found in the complexes containing late transition metals.

Currently no mechanistic studies of alkane reductive elimination from octahedral alkylhydrido rhodium complexes containing the Tp′ ligand and a π-acid ligand have been reported. The analogy between the Tp′ ligand and the Cp* ligand in their electronic and steric demands has often been assumed. Earlier work in our lab has shown that reductive elimination of benzene from Tp′Rh(L)(Ph)H[21] in the presence of neopentylisocyanide is associative in isocyanide, and that the Tp′ ligand undergoes an η^3 to η^2 interconversion. This behavior is different from that of the related complex Cp*Rh(PMe$_3$)(Ph)H,[22] which shows concerted loss of benzene with no evidence for hapticity changes in the Cp* ligand. Study of alkane reductive elimination from alkyl hydride complexes of the type Tp′Rh(L)(alkyl)H is therefore warranted as it may show marked differences in mechanism compared to that for the related Cp* complexes.

This paper describes an efficient preparation of Tp′Rh(L)-(CH$_3$)H (**2**) from the reaction of Tp′Rh(L)(CH$_3$)Cl (**1**) with Cp$_2$ZrH$_2$. The deuterium-labeled methyl hydride complexes

Tp′Rh(L)(CH$_3$)D (**2-d_1**), Tp′Rh(L)(CD$_3$)H (**2-d_3**), and Tp′Rh-(L)(CD$_3$)D (**2-d_4**) can be prepared from combinations of Tp′Rh-(L)(CH$_3$)Cl or Tp′Rh(L)(CD$_3$)Cl and Cp$_2$ZrH$_2$ or Cp$_2$ZrD$_2$. The synthetic work is followed by a discussion of initial results from an investigation of the mechanism of methane reductive elimination from **2** in benzene. The following observations point toward the intermediacy of an η^2-methane complex and its *associative replacement* by benzene: (1) Intramolecular hydrogen exchange between the hydride and methyl ligands of **2-d_n** is observed by NMR spectroscopy. A preequilibrium step between **2** and an intermediate prior to reductive elimination of methane is indicated by the results of isotopic kinetic experiments. (2) The rate of reductive elimination is also shown to be dependent on both the deuteration of the benzene solvent and the *concentration* of benzene in an inert solvent. These results strongly support the intermediacy of an η^2-methane complex prior to a rate determining step involving methane substitution by benzene.

Results and Discussion

Preparation of Tp′Rh(L)(CH$_3$)H (2). The efficient synthesis of Tp′Rh(L)(CH$_3$)H (**2**, L = CNneopentyl, Tp′ = 3,5-dimethyltrispyrazolylborate) proved not to be so straightforward. Reaction of Tp′Rh(L)(CH$_3$)Cl (**1**) with 1 equiv of LiAlH$_4$ in THF solution followed by evaporation of solvent and extraction with hexanes and a small quantity of wet DMSO allows for the isolation of **2** in variable yields ranging from 30 to 90% as shown by ^{1}H NMR spectroscopy. The DMSO layer traps LiCl and excess salts from the LiAlH$_4$ hydrolysis. **1** does not react with LiHBEt$_3$, NaBH$_4$, Me$_2$SiClH, Et$_3$SiH, or (PhO)$_2$P(O)(H) in THF at ambient temperature. Low yields of **2** are observed when **1** reacts with NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$ (Red-Al) or (*n*-Bu)$_3$SnH in THF.

Quantitative yields of **2** are reproducibly produced by the reaction of **1** with Cp$_2$ZrH$_2$ in benzene (eq 4). The reaction is
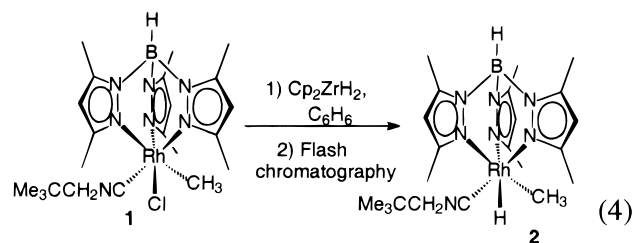
driven thermodynamically by the formation of strong Zr−Cl and Rh−H bonds and is complete within 10 min. The zirconocene products, Cp$_2$Zr(Cl)H and Cp$_2$ZrCl$_2$, along with unreacted Cp$_2$ZrH$_2$ are easily removed by flash chromatography through silica gel to give nearly Zr-free solutions of **2**. A total time of 20 min for reaction and workup allowed for <20% conversion of **2** to Tp′Rh(L)(C$_6$H$_5$)H (**3**) due to reductive elimination. The zirconocene reagent is an attractive alternative to boron and aluminum hydride alkali metal salts for the preparation of alkyl hydride complexes from alkyl halide complexes, as indicated by the synthesis of **2** and the other Tp′Rh(L) alkyl hydride complexes.[23]

Intramolecular Methyl/Hydride Exchange in Tp′Rh(L)-(CH$_3$)D (2-d_1) and Tp′Rh(L)(CD$_3$)H (2-d_3) in Benzene. The

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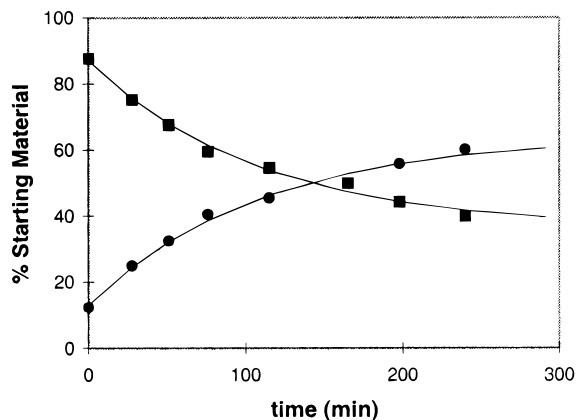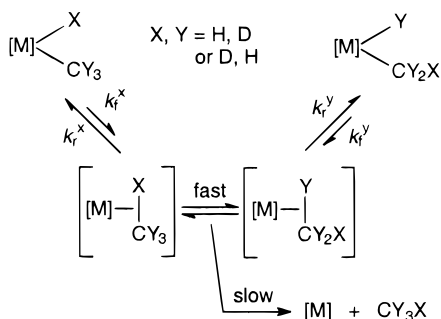(21) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087−6095.

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Figure 2. Methyl ligand region of ^{1}H{^{2}H} NMR spectra ($\sim\delta$ 1.2) at various times (min) f the rearrangement of Tp′Rh(L)(CH$_3$)D (**2-d_1**, ●) to Tp′Rh(L)(CH$_2$D)(H) (**2-d_1′**, ◆) in C$_6$H$_6$ at 22 °C.

isotopically labeled derivatives Tp′Rh(L)(CH$_3$)D and Tp′Rh-(L)(CD$_3$)H were prepared by reaction of the corresponding chloro complexes with Cp$_2$ZrH$_2$ or Cp$_2$ZrD$_2$. Benzene and benzene-d_6 solutions of each compound ($\sim$0.03 M) were prepared and periodically monitored at ambient temperature using ^{1}H{^{2}H} NMR and ^{2}H{^{1}H} NMR spectroscopies to determine the progress of reactions 5 and 6.

Hydrogen exchange in **2-d_1** is clearly shown in a series of ^{1}H{^{2}H} NMR spectra over a 5 h period (Figure 2). At initial time **2-d_1** is not present but is quantitatively produced after 10 min as shown by the appearance of a doublet at δ 1.236 corresponding to the rhodium-bound methyl group of **2-d_1**. Deuterium exchange to give the isotopomer, Tp′Rh(L)(CH$_2$D)H (**2-d_1′**), is demonstrated by the growth of a doublet at δ 1.225 (the chemical shift changes due to an intrinsic isotopic shift) at the expense of the doublet at δ 1.236, and the growth of a hydride resonance at δ −14.818. No intrinsic isotopic shift is observed for the Tp′ and neopentylisocyanide resonances of **2-d_1** vs **2**. The ^{2}H{^{1}H} NMR spectrum of **2-d_1** in C$_6$H$_6$ initially shows a broad singlet at δ −14.699 corresponding to the deuteride ligand. At later time ($\sim$1 h) the deuteride resonance is almost absent and the resonance for the rhodium-bound methyl-d_1 ligand of Tp′Rh(L)(CH$_2$D)H is observed at δ 1.194. Concurrent with this exchange process, yet at a slower rate, is the reductive elimination of methane and the formation of the more stable complex Tp′Rh(L)(C$_6$X$_5$)(X) (X = H or D). At this temperature in benzene, the half-life for methane loss is >5 h. The ^{1}H NMR spectra show the growth of a 1:1:1 triplet at δ 0.143 which is consistent with three protons coupled to one deuterium in CH$_3$D (free CH$_4$ in C$_6$D$_6$ appears as a singlet at δ 0.148). It was not possible to observe the expected 1:2:2:1 quartet for CH$_3$D in the ^{2}H NMR spectrum due to a poor signal-to-noise ratio; a broad singlet at δ 0.114 is observed. The observation of CH$_3$D as the only methane product from reductive elimination indicates that the exchange process is intramolecular.

The isotopic scrambling of **2-d_3** was similarly monitored by ^{1}H{^{2}H} NMR spectroscopy in C$_6$D$_6$. The initial spectrum acquired indicated that partial scrambling had already occurred, as it was not possible to observe **2-d_3**, exclusively. The resonance for the methyl-d_2 ligand of the isotopomer, Tp′Rh(L)(CD$_2$H)D (**2-d_3′**), appears as a doublet at δ 1.199. Over time this resonance increases slightly while the hydride resonance of **2-d_3** at δ

Figure 3. A plot of the percent distribution of Tp′Rh(L)(CH$_3$)(D) (■) and Tp′Rh(L)(CH$_2$D)(H) (●) versus time for the approach to equilibrium at 22 °C. The solid line indicates a nonlinear least-squares fit to an exponential decay to equilibrium.

−14.813 decreases. As an internal check for scrambling, the integral values for the hydride and the methyl-d_2 resonances were compared to that for the single *tert*-butyl resonance at δ 0.654 representing all methyl hydride complexes. With the *tert*-butyl resonance calibrated as 9 protons, the hydride and methyl-d_2 resonances together integrated on average to 1.03(4) protons for all spectra recorded. These data are consistent with a scrambling process which distributes a single hydrogen over two sites to give Tp′Rh(L)(CD$_3$)H and its isotopomer. Eventually, CD$_3$H is lost, appearing as a septet at δ 0.106 as **3-d_6** is formed.

The isotopic scrambling of **2-d_3** was also monitored by ^{2}H{^{1}H} NMR spectroscopy. A broad singlet at δ 1.176, representing the methyl-d_3 and the methyl-d_2 ligands, decreases as a broad singlet at δ −14.717, representing the deuteride ligand of Tp′Rh(L)(CD$_2$H)D, increases. Deuterium scrambling is competitive with reductive elimination, and CD$_3$H appears as a doublet at δ 0.090 in a ^{2}H NMR spectrum and a septuplet at δ 0.106 in the ^{1}H NMR spectrum. This observation is consistent with a single methane product, CHD$_3$, and corroborates the earlier claim that the scrambling mechanism is intramolecular in nature.

Determination of K_{eq} and k_{obs} for the Approach to Equilibrium for the Exchange Reactions of TpRh(L)(CH$_3$)D and Tp′Rh(L)(CD$_3$)H. For the equilibria indicated in eqs 5 and 6, the ratio of the NMR integrals (corrected for number of

$$\text{Tp'Rh(L)(CH}_3\text{)D} \underset{}{\overset{K_1 = 6.3}{\rightleftharpoons}} \text{Tp'Rh(L)(CH}_2\text{D)H} \qquad (5)$$
$$\textbf{2-}d_1 \qquad\qquad\qquad\qquad \textbf{2-}d_1\textbf{'}$$

$$\text{Tp'Rh(L)(CD}_3\text{)H} \underset{}{\overset{K_2 = 1.8}{\rightleftharpoons}} \text{Tp'Rh(L)(CD}_2\text{H)D} \qquad (6)$$
$$\textbf{2-}d_3 \qquad\qquad\qquad\qquad \textbf{2-}d_3\textbf{'}$$

hydrogens) of the product isotopomer to that of the starting isotopomer gives the value of the equilibrium constant (K_1 or K_2) for each exchange process. An approach to equilibrium for **2-d_1** and its isotopomer **2-d_1′** is shown in Figure 3. Statistically, K_1 should have a value of 3, since there are 3 methyl hydrogens exchanging with a single hydride ligand. Assuming that bond stretching modes are dominant in determining isotope effects, the heavier deuterium atom should favor formation of the stronger bond with carbon in Tp′Rh(L)(CH$_2$D)H over that with rhodium in **2-d_1** and K_1 should be expected to be greater than 3.

The observed equilibrium constant K_1 for hydrogen exchange in **2-d_1** at 22 °C is $\sim$5 as seen in the last data point in Figure

Figure 4. A plot of the percent distribution of Tp′Rh(L)(CD$_3$)(H) (■) and Tp′Rh(L)(CD$_2$H)(D) (●) versus time for the approach to equilibrium at 22 °C. The solid line indicates a nonlinear least-squares fit to an exponential decay to equilibrium.

Scheme 1

3. The error is large (~±1) and is due to incomplete resolution of the doublets corresponding to **2-d$_1$** and **2-d$_1$′** in the ^{1}H{^{2}H} NMR spectra. Despite this, the value of the equilibrium constant is significantly different from 3 and is indicative of a shift toward greater product formation, consistent with an isotope effect favoring deuterium on carbon.

An approximate value for K_2 at 22 °C for hydrogen exchange in Tp′Rh(L)(CD$_3$)H, **2-d$_3$**, was determined in a manner similar to that for **2-d$_1$**. Figure 4 shows the approach toward equilibrium for **2-d$_3$** and Tp′Rh(L)(CD$_2$H)D (**2-d$_3$′**). A value of ~1.5 for K_2 indicates that the equilibrium is now shifted to the left (compared to the statistical value of 3) favoring **2-d$_3$** in which deuterium favors bonding with carbon rather than with rhodium in **2-d$_3$′** (eq 6). This value of K_2 may be a minimum value since the loss of **2-d$_3$** and **2-d$_3$′** via reductive elimination made further measurements impossible.

Based on the kinetic plots shown in Figures 3 and 4, an approximate value for the observed rate constant (k_{obs}^i) for scrambling (which includes a statistical factor and an isotope effect) and for K_1 and K_2 in each exchange reaction were determined by fitting the data to an exponential approach to an equilibrium value. For the equilibration of **2-d$_1$** and **2-d$_1$′**, K_1 was 6.3(8) and k_{obs}^1 was 1.8(1) × 10^{-4} s^{-1}. For the equilibration of **2-d$_3$** and **2-d$_3$′**, K_2 was 1.8(6) and the value of k_{obs}^2 was 1.5(6) × 10^{-4} s^{-1} (95% confidence limits).

Isotope Effects for Formation of a Methane Complex from Tp′Rh(L)(CH$_3$)H-d$_n$. The observation of intramolecular hydrogen exchange in **2-d$_1$** and **2-d$_3$** and the ability to measure the rates of scrambling allow for further discussion of the mechanism of this process. Similar observations for other alkyl hydride systems have led to mechanistic proposals which invoked the intermediacy of an alkane σ-complex.[7] For these

systems an inverse *kinetic* isotope effect was observed for reductive elimination of alkane (k_{obs}^H/k_{obs}^D < 1).[9] A fast pre-equilibrium step involving formation of an alkane σ-complex, prior to rate determining loss of alkane, allows for hydrogen scrambling (Scheme 1). In this section the kinetic analysis of the results from the isotopic exchange experiments with **2-d$_1$** and **2-d$_3$** will be presented. This analysis allows for estimation of the kinetic isotope effects on k_f and k_r (Scheme 1) based on the values of K_{eq} and k_{obs} obtained from the isotope scrambling experiments.

First, consider the kinetic expressions for the exchange reactions involving **2-d$_1$** and **2-d$_3$** and their corresponding methane σ-complexes (eqs 7 and 8). Only one η^2-alkane
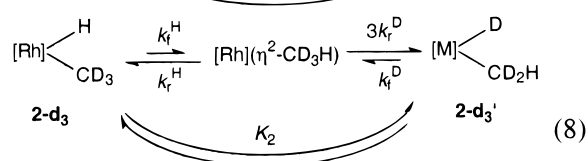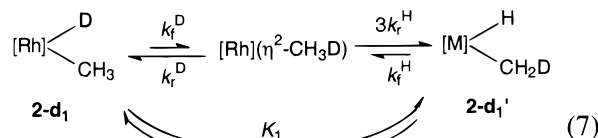
σ-complex is indicated as it is assumed that exchange between η^2-methane isomers is rapid, and therefore kinetically not important. In these reactions, k_f^X (X = H or D) is the forward rate constant which contains an isotope effect for breaking a Rh−X bond and making a C−X bond, k_r^X (X = H or D) is the reverse rate constant which contains an isotope effect for breaking a C−X bond and making a Rh-X bond, and k_f and k_r would be the forward and reverse rate constants free of isotope effects (i.e., X = H, $k_f = k_f^H$, $k_r = k_r^H$). A statistical factor of 3 is added to account for the 3-fold degeneracy of the formation of **2-d$_1$′** and **2-d$_3$′** from their respective η^2-methane complexes.

Furthermore, we can define the variables Z_f and Z_r as the isotope effect factors for breaking a Rh−X bond and making a C−X bond and *vice versa*, respectively, i.e., $k_f^D = Z_f k_f^H$ and $k_r^D = Z_r k_r^H$ (to a first approximation, secondary isotope effects are considered to be negligible). Expressions for the equilibrium constants K_1 and K_2 can be determined by the ratio of the appropriate rate constants to yield a ratio between Z_f and Z_r (eqs 9 and 10). These equations provide only the *ratio* of the

$$K_1 = \frac{\textbf{2-}d_1'}{\textbf{2-}d_1} = \frac{k_f^D 3k_r^H}{k_f^H k_r^D} = \frac{3k_r^H/k_r^D}{k_f^H/k_f^D} = \frac{3Z_f}{Z_r} \quad (9)$$

$$K_2 = \frac{\textbf{2-}d_3'}{\textbf{2-}d_3} = \frac{k_f^H 3k_r^D}{k_f^D k_r^H} = \frac{k_f^H/k_f^D}{k_r^H/3k_r^D} = \frac{3Z_r}{Z_f} \quad (10)$$

isotope effect factors not the individual factors themselves; K_1 and K_2 are simply the inverse of each other related by a statistical factor (i.e., $K_1K_2 = 9$).[7c] Consequently, the two exchange experiments do not provide independent information necessary for determining k_f or k_r explicitly. There are four unknowns (k_f^H, k_r^H, k_f^D, and k_r^D), and four observables (k_{obs}^1, k_{obs}^2, K_1, and K_2), but since K_1 and K_2 are not independent an exact solution cannot be obtained. However, by setting K_1 equal to 6.3 and K_2 equal to 1.8, the ratio of Z_f and Z_r can be determined which allows for the assessment of the consistency of this analysis and of the two experiments. The values of Z_f/Z_r obtained are 2.1 and
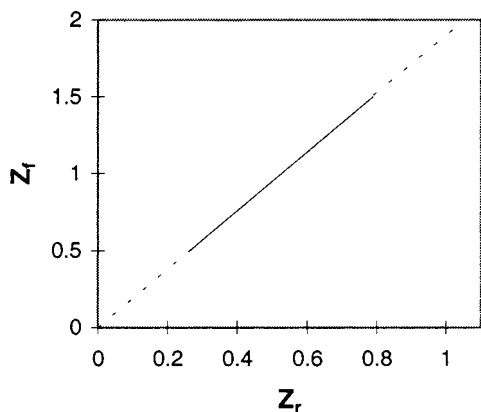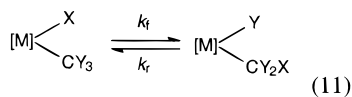
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Figure 5. Possible combinations of isotopic factors Z_f and Z_r for the reactions shown in eqs 6 and 7.

Figure 6. Combined plots of the ln(**2-d_n**) versus time for the reductive elimination of methane from **2-d_0** in C$_6$D$_6$ (▲), **2-d_0** in C$_6$H$_6$ (◆), and **2-d_4** in C$_6$D$_6$ (●) at 36 °C.

Table 1. Summary of Kinetic Data for Reductive Elimination of Methane from Tp′Rh(CNCH$_2$CMe$_3$)(CX$_3$)(X) (X = H or D) in C$_6$H$_6$ and C$_6$D$_6$ at 36 °C

run	compd	solvent	k_{obs}, s$^{-1\ a}$
1	**2-d_0**	C$_6$H$_6$	1.65(1) × 10^{-4}
2	**2-d_0**	C$_6$H$_6$	1.61(2) × 10^{-4}
3	**2-d_0**	C$_6$D$_6$	1.50(2) × 10^{-4}
4	**2-d_0**	C$_6$D$_6$	1.53(3) × 10^{-4}
5	**2-d_4**	C$_6$D$_6$	2.42(5) × 10^{-4}
6	**2-d_4**	C$_6$D$_6$	2.56(12) × 10^{-4}

^{a} Errors are 95% confidence limits.

1.7 based on eqs 9 and 10, respectively, showing reasonable consistency considering the approximations made.

Typical values for isotope effects on alkyl hydride reductive elimination (and σ-complex dissociation) are inverse ($1/Z_f = 0.5-0.8$),[7] whereas values for alkane (σ-complex formation and) oxidative addition are small but normal ($1/Z_r = 1.1-1.4$).[7b] This range of values is consistent with the Z_f/Z_r ratio of ~1.9 observed in the present system, as shown in Figure 5.

Hydrogen exchange in **2-d_1** and **2-d_3** indicates that the forward rates (k_f^X) limit the observed rate of scrambling (k_{obs}^i since k_f^X is much less than k_r^X (the η^2-methane complexes are not directly observed). Since the reaction in eq 7 for the scrambling of **2-d_1** proceeds to near completion (~83% **2-d_1′**), the assumption that k_{obs}^1 is only slightly larger than k_f^D can be made. Given this assumption, eq 7 may be reduced to eq 11 which describes the experimentally observed rate of scrambling, and a simple expression for k_f can be derived (eq 12).[24] With $K_1 = 6.3$ and

$$[M]\begin{smallmatrix}X\\\\CY_3\end{smallmatrix} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [M]\begin{smallmatrix}Y\\\\CY_2X\end{smallmatrix} \quad (11)$$

$$X, Y = H, D \text{ or } D, H$$

$$k_f = \frac{K}{K+1} k_{obs} \quad (12)$$

$k_{obs}^1 = 1.8 \times 10^{-4}$ s^{-1}, $k_f^D \approx k_f = 1.55 \times 10^{-4}$ s^{-1}. For the scrambling of **2-d_3**, since the reaction in eq 8 goes to slightly greater than 50% completion (~60% **2-d_3′**), k_f^H is slightly greater than $k_{obs}^2 /2$. Equations 11 and 12 can also be used to estimate k_f^H. When $K_2 = 1.8$ and $k_{obs}^2 = 1.5 \times 10^{-4}$ s^{-1}, $k_f^H \approx k_f = 0.96 \times 10^{-4}$ s^{-1}. The kinetic isotope effect for the formation of a methane complex, k_f^H/k_f^D ($1/Z_f$) in eqs 7 and 8, is 0.62, inverse as expected. Since Z_f/Z_r is approximately 2, the kinetic isotope effect for the reverse reaction, k_r^H/k_r^D ($1/Z_r$), is 1.2, normal as expected. A similar analysis to determine k_r^H and k_r^D, separately, cannot be done because the methane complex is not observed and therefore these rates are immeasurable under the reaction conditions.[25]

Kinetics of Reductive Elimination of Methane from 2-d_n in C$_6$H$_6$, C$_6$D$_6$, and Mixtures of C$_6$D$_6$ and C$_6$F$_6$. Complex **2**, upon standing in benzene solution, loses methane and forms Tp′Rh(L)(Ph)H, **3**. Logarithmic plots for the reductive elimination of methane from **2** in C$_6$H$_6$ and C$_6$D$_6$, respectively, and of
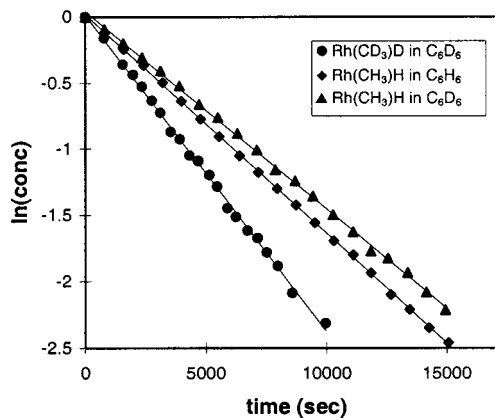
(24) Equation 12 is derived from the following equations: $k_{obs} = k_f + k_r$ and $K = k_f/k_r$.

(25) Assuming that the amount of methane complex is less than 2%, $k_r > 50k_f$.

methane-d_4 from Tp′Rh(L)(CD$_3$)D, **2-d_4**, in C$_6$D$_6$ at 36 °C show good linearity over 3−4 half-lives, which is consistent with the rate of reductive elimination being first order in metal complex (Figure 6). The rate constants for each solvent are shown for runs 1−6 in Table 1. Comparing the rates of runs 3 and 4 with those of runs 5 and 6, an isotope effect of $k_H/k_D = 0.62(4)$ is observed upon full deuteration of both methyl and hydride ligands. Curiously, however, the rate of reductive elimination of methane from **2-d_0** in C$_6$H$_6$ is slightly faster than that from **2-d_0** in C$_6$D$_6$, with $k_{C_6H_6}/k_{C_6D_6} = 1.08(6)$ (95% confidence limits). While this value is nearly unity given the magnitude of the error, the kinetic plots clearly and reproducibly show a difference in rates *depending upon the deuteration of the solvent*. This observation suggests an intriguing possibility that benzene is a necessary component of the transition state prior to reductive elimination of methane and formation of the phenyl hydride complex. The origin of the effect could be due to differences in the binding abilities of the benzene isotopomers or even in the activation of a phenyl C−H(D) bond prior to the rate determining loss of methane.

Flood and co-workers have observed a primary isotope effect for the thermal activation of benzene vs benzene-d_6 by (PMe$_3$)$_4$-OsH(neopentyl) ($k_H/k_D = 2.20(7)$).[26] For the reaction of benzene vs benzene-d_6 with (PMe$_3$)$_4$OsH(CH$_3$) the isotope effect is much smaller ($k_H/k_D = 1.10(5)$). Additional isotopic labeling experiments have led to the conclusion that after rate-limiting loss of phosphine, benzene oxidatively adds to an unsaturated Os(II) center to yield an Os(IV) intermediate containing both C$_6$H$_6$ and neopentane.

The possibility of a solvent isotope effect prompted a study of the rate of reductive elimination as a function of benzene concentration. The use of C$_6$F$_6$ as an inert solvent allows for the preparation of solutions of varying benzene concentration. The fragment Tp′Rh(L) undergoes no observable reaction with C$_6$F$_6$. At very low concentrations of C$_6$D$_6$ (<5%) there appear
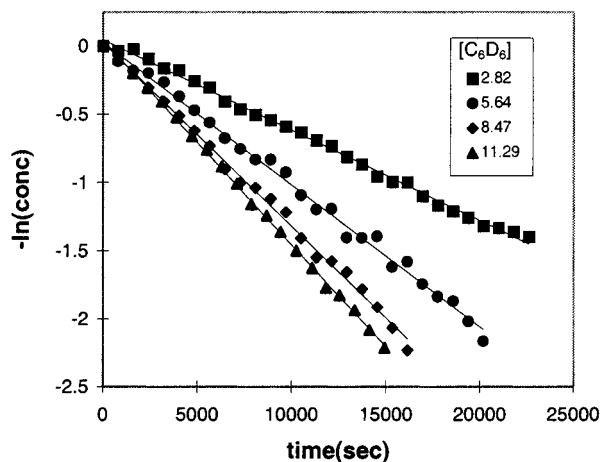
Figure 7. Plot of the $\ln([2\text{-}d_0]/[2\text{-}d_0]_0)$ versus time for the reductive elimination of methane from **2-d_0** in mixtures of C_6D_6 and C_6F_6 at 36 °C.

Table 2. Summary of Kinetic Data for Reductive Elimination of Methane from Tp′Rh(CNCH$_2$CMe$_3$)(CH$_3$)H (**2-d_0**) in Mixtures of C_6D_6 and C_6F_6 at 36 °C

run no.	% C_6D_6, v/v	[C_6D_6], M	k_{obs}, s^{-1} [a]
1	100	11.29	$1.50(4) \times 10^{-4}$
2	75	8.47	$1.34(4) \times 10^{-4}$
3	50	5.64	$1.04(3) \times 10^{-4}$
4	25	2.82	$0.66(2) \times 10^{-4}$
5	0.5	0.06	NA

[a] Errors are 95% confidence limits.

to be side reactions other than the reductive elimination of methane and addition of benzene which diminished the quality of the kinetic measurements. The kinetic plots for reductive elimination of methane from **2-d_0** in varying concentrations of C_6D_6 in C_6F_6 are shown in Figure 7. Table 2 lists the concentrations of C_6D_6 along with the corresponding observed first order rate constants. The observed rates clearly vary as a function of benzene concentration, and a plot of these k_{obs} vs [C_6D_6] data (Figure 8a) does not show the definitive linear behavior expected for a bimolecular reaction under pseudo-first-order conditions. The curvature of the plot is *suggestive* of saturation kinetics.

A mechanism that is consistent with both the observed inverse kinetic isotope effect on the rate of methane reductive elimination and the benzene saturation behavior is depicted in Scheme 2. A preequilibrium between **2-d_0** and an intermediate, methane σ-complex **A**, occurs prior to the rate-limiting step with benzene. To accommodate an associative pathway, and since a d_8 Rh(I) species is involved, the intermediate is postulated to contain an η^2-Tp′ ligand. Displacement of coordinated methane by benzene leads to an η^2-benzene complex, **B**, and subsequent activation of a phenyl C–D bond to give **3-d_6**. Note that earlier studies of the phenyl hydride **3** provided strong evidence for the intermediacy of the η^2-benzene complex **B** in the thermal loss of benzene from **3**.[21] The kinetic expressions for the mechanism depicted in Scheme 2 are given by eqs 13–15.

$$rate = k_2[A][C_6D_6] = \frac{k_1 k_2 [2][C_6D_6]}{k_{-1} + k_2[C_6D_6]} = k_{obs}[2] \quad (13)$$

$$k_{obs} = \frac{k_1 k_2 [C_6D_6]}{k_{-1} + k_2[C_6D_6]} \quad (14)$$

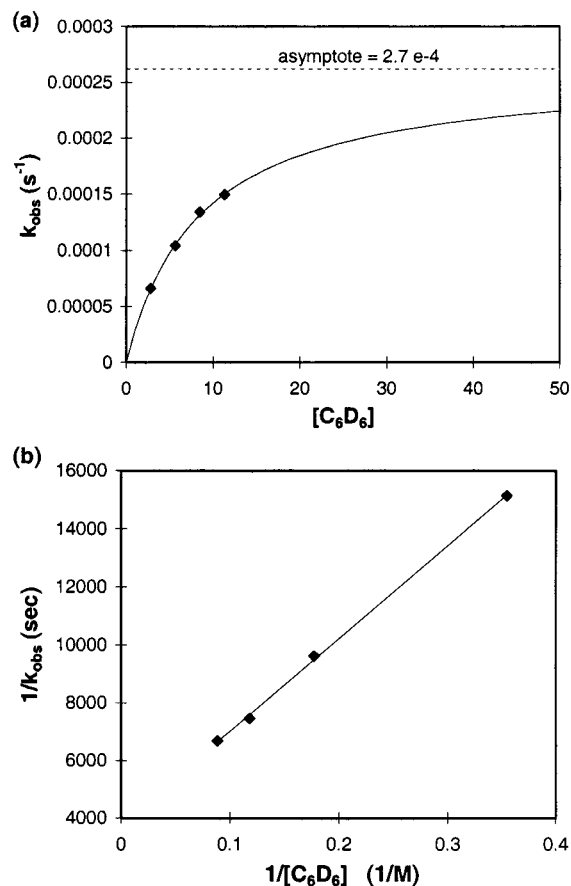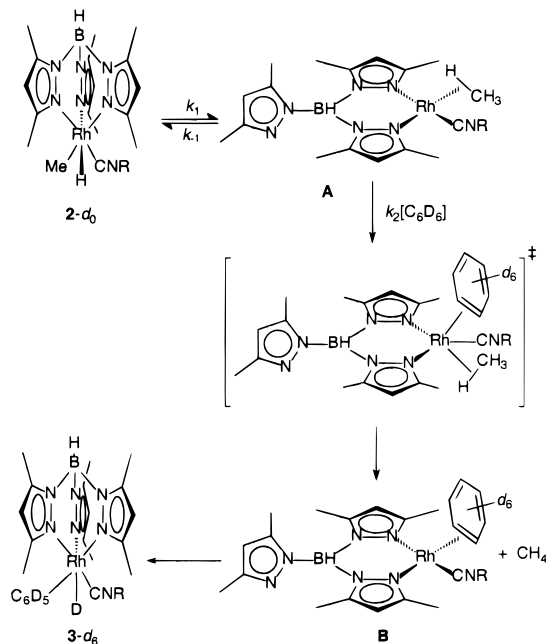$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 [C_6D_6]} \quad (15)$$

Figure 8. (a) Plot of k_{obs} vs [C_6D_6] for the reductive elimination of methane from **2-d_0** in mixtures of C_6D_6 and C_6F_6 at 36 °C. (b) Double reciprocal plot of $1/k_{obs}$ vs $1/[C_6D_6]$.
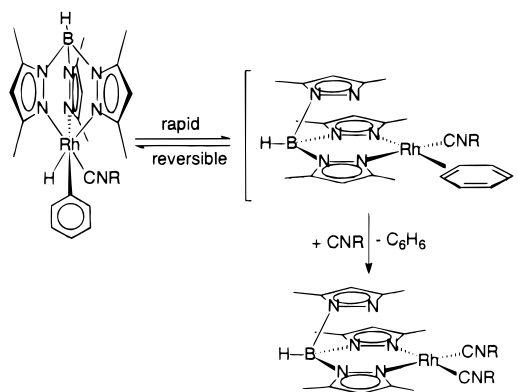
Scheme 2

As eq 15 shows, a linear correlation between $1/k_{obs}$ and $1/[C_6D_6]$ is expected. Indeed the double reciprocal plot of $1/k_{obs}$ vs $1/[C_6D_6]$ is linear (Figure 8b). The forward rate constant (k_1) obtained from the intercept of the plot in Figure 8b is $2.7(4) \times 10^{-4}$ s^{-1}. This value *compares reasonably* with the calculated value obtained from the H/D scrambling experiments using **2-d_1** and **2-d_3** ($k_f^H \approx 1 \times 10^{-4}$ s^{-1}) given that the temperatures

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differed by 14 °C.[27] The value of k_2/k_{-1} obtained from the slope is 0.12(3) M^{-1} which indicates that with a benzene concentration of 1 M the reverse rate constant for the preequilibrium step is approximately 8 times as fast as the rate for the associative displacement of methane by benzene. The associative step only begins to dominate when the concentration of benzene is approximately 8 M. The similarity in the k_1 values for methane complex formation from **2** obtained in these two distinct experiments argues against the variation in rates in Figure 7 being attributed to some sort of general "solvent effect" due to the variation in solvent composition. The observed small solvent isotope effect in C_6H_6 vs C_6D_6 is also consistent with there being an associative reaction even in pure benzene.

Attempts to use trapping ligands other than benzene to displace the coordinated σ-methane adduct failed. Reaction of **2-d$_0$** with PMe$_3$ (0.006−0.29 M) at 22 °C occurs more slowly than reaction with benzene. Reaction with isocyanide leads to multiple substitution and formation of an η^2-trispyrazolylborate product, making it difficult to ascertain which step was rate limiting in the kinetics.

Examination of the literature shows at least one example of a coordinatively induced reductive elimination. Coordination of a neutral 2 electron donor ligand prior to reductive elimination of methane in Cp$_2$ZrH(CH$_3$) has been reported.[28] In contrast, for a number of square-planar or octahedral complexes of 2nd and 3rd row late transition metals dissociation of a ligand prior to reductive elimination is known.[29] On the other hand, concerted reductive elimination of alkanes from complexes of the type Pt(PR$_3$)$_2$(H)(R) is known to occur independent of added phosphine.[30] This is also true of complexes of the type Cp*Ir-(PMe$_3$)(alkyl)H and Cp*Rh(PMe$_3$)(aryl)H.[22,31] A small primary solvent isotope effect has been observed for the reaction of the fragment [Cp*Rh(PMe$_3$)] with benzene ($k_H/k_D = 1.05$), which has been associated with the formation of an η^2-benzene complex.[22] Consequently, the magnitude of the isotope effect observed in the present system is consistent with a mechanism involving the associative substitution of an η^2-benzene ligand for an η^2-methane ligand (Scheme 2). Should the C−H bond of benzene have been cleaved prior to the rate determining step, a larger kinetic isotope effect ($k_H/k_D \approx 1.4−2$) would have been anticipated.[22,26,32] An interesting comparison can be made with the mechanism of benzene reductive elimination from Tp′Rh-(L)(Ph)H, which is *associative in neopentylisocyanide*.[21] An η^2-benzene complex was found to be an intermediate prior to or

(26) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964−7970.

(27) The rate of H/D scrambling in **2-d$_1$** is already rapid at 22 °C, and could not be mearsured at the higher temperature used in the C_6D_6/C_6F_6 experiments (36 °C).

(28) (a) Gell, K. I.; Schwartz, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 3246−3248. (b) Gell, K. I.; Schwartz, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2687−2695. (c) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915−2916.

(29) For Pt(PEt$_3$)$_2$(CH$_2$CMe$_3$)$_2$: (a) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713−6725. For cis-Rh(H)(CH$_2$CHO)-(PMe$_3$)$_3$Cl: (b) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227−5228. For Ir(H)(Cl)(σ-carboranyl)(CO)(PPh$_3$)$_2$: (c) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649−653. For Ir(H)[s-CHCH$_2$C(O)OC(O)](σ-carboranyl)(CO)(PhCN)(PPh$_3$): (d) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972−3976. For Os(PMe$_3$)$_4$(H)(CH$_2$CMe$_3$): (e) Reference 26. (f) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704−713.

(30) (a) Michelin, R. A.; Faglia, S.; Uguagliati *Inorg. Chem.* **1983**, *22*, 1831−1834. (b) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436−1448.

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

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

Scheme 3

during the rate-limiting step (Scheme 3), a sequence similar to that proposed for the replacement of methane by benzene in **2**. Saturation kinetics and a linear double-reciprocal plot of $1/k_{obs}$ vs 1/[CNR] were also seen in this reaction, just as in the present case.

An interesting comparison can be made between the mechanism proposed in the present system and that proposed for the Tp′Rh(CO)$_2$ system in a recent paper by Harris and Bergman. Using ultrafast IR transient absorption, two intermediates with distinct lifetimes of 200 ps and 230 ns were observed. The first intermediate was assigned as the η^2-C,H-cyclohexane complex with an η^3-Tp′ ligand which then rapidly dechelates a pyrazole group to form the η^2-Tp′ σ-alkane complex. This species then more slowly undergoes oxidative addition to the C−H bond and the dangling pyrazole ring snaps shut to give the d_6 octahedral Tp′Rh(CO)(cyclohexyl)H product.[33] This latter σ-complex is analogous to complex **A**, with the oxidative addition product being comparable to **2**. The present work approaches this same reaction coordinate from the opposite direction, and provides support for the formulation of the σ-alkane complex as containing an η^2-Tp′ ligand.

Conclusions

Isotopically labeled methyl hydride complexes of the type Tp′Rh(L)(X)(CY$_3$) (X = Y = H, **2**; X = D, Y = H, **2-d$_1$**; X = H, Y = D, **2-d$_3$**; X = Y = D, **2-d$_4$**) have been prepared in high yield by the reaction of **1** or **1-d$_3$** with Cp$_2$ZrH$_2$ or Cp$_2$ZrD$_2$. Hydrogen exchange between the hydride and methyl ligands of **2-d$_1$** and **2-d$_3$** has been observed and is competitive with reductive elimination of methane. Reductive elimination of methane from **2-d$_1$** produces only CH$_3$D and from **2-d$_3$** only CD$_3$H, as shown by ^{1}H NMR and ^{2}H NMR spectroscopy. These results support the intramolecular nature of the hydrogen exchange process. An inverse kinetic isotope effect with $k_H/k_D = 0.62(4)$ is observed for reductive elimination in **2-d$_0$** vs **2-d$_4$**. These results strongly implicate the intermediacy of a methane complex prior to reductive elimination of methane. Furthermore, the rate of reductive elimination has been shown to be dependent upon the concentration of benzene.

Experimental Section

General. All reactions, recrystallizations, chromatography, and routine manipulations, unless otherwise noted, were carried out at ambient temperature under a nitrogen atmosphere, either on a high vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation Dri-lab. Benzene, C_6D_6, and THF solvents

(33) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260−263.

were distilled under nitrogen or vacuum from dark purple solutions of sodium benzophenone ketyl. All kinetic plots and data fitting were done using Microsoft Excel and the Solver Add-in. Errors are quoted at 95% confidence limits for the appropriate number of degrees of freedom. All kinetic experiments were monitored through a minimum of 3 half-lives. All ^{1}H (400 MHz) and ^{2}H (61 MHz) spectra were recorded on a Bruker AMX-400 spectrometer. Unless otherwise noted, chemical shifts for ^{1}H NMR are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C_6D_6, δ 7.15; THF-d_8, δ 1.73, 3.58). Chemical shifts for ^{2}H NMR were measured in ppm relative to the deuterated solvent resonance of C_6D_6, δ 7.15. All temperatures for kinetic experiments were calibrated relative to the chemical shift differences in the NMR spectra of neat ethylene glycol. Accurate temperature control (± 0.1 °C) was maintained using a Bruker BVT-3000 VT control unit. The LiAlH$_4$ and LiAlD$_4$ solutions were prepared by stirring the solid reagent in THF overnight and filtering through a glass frit funnel. These solutions were titrated just before use using a published iodimetric technique.[34] Anhydrous DMSO was purchased from Aldrich Chemical Co. Wet (H$_2$O) DMSO was made by the preparation of a 1:1000 v/v solution of H$_2$O and anhydrous DMSO, respectively. Wet (D$_2$O) DMSO was prepared as follows: in succession, DMSO was stirred over 4 Å Linde molecular sieves for 24 h, passed through a column of molecular sieves, stirred over CaH$_2$ for 24 h, distilled under vacuum, and wet with D$_2$O (5:1000 v/v, D$_2$O: DMSO). Silica gel (40−140 mesh) was purchased from the Aldrich Chemical Co., dried under vacuum for 24 h at 200 °C, and stored in the dri-lab. Silica gel microcolumns were constructed from cotton plugged Pasteur pipets and a benzene slurry of silica gel. Hexafluorobenzene (C_6F_6) was purchased from the Aldrich Chemical Co, dried over 4 Å Linde molecular sieves for 24 h, degassed using 3 freeze−pump−thaw cycles, and stored in the dri-lab. The zirconium reagents Cp$_2$ZrH$_2$ and Cp$_2$ZrD$_2$ were prepared according to literature methods.[35] Lithium triethylborohydride was purchased from the Aldrich Chemical Co. Resealable NMR tubes with Teflon valves were purchased from the Brunfeldt Co. Complexes Tp′Rh(CNCH$_2$CMe$_3$)(CH$_3$)Cl and Tp′Rh(CNCH$_2$CMe$_3$)(CD$_3$)Cl were synthesized according to literature procedures.[36]

Preparation of Tp′Rh(L)(CH$_3$)H (2). Method 1. To a stirred solution of 25 mg (0.046 mmol) of **1** in 25 mL of THF was added 0.46 mL (0.046 mmol) of a 0.1 M THF solution of LiAlH$_4$. The reaction mixture was stirred for 1 h. Removal of the THF under vacuum yielded a bright yellow solid. The solid was suspended in 30 mL of hexanes, ~1 mL of wet DMSO (H$_2$O for hydrides, D$_2$O for deuterides) was added, and the resulting mixture was stirred for 1 h. Upon standing, the emulsion separated giving a milky hexanes layer and a brown/black DMSO layer. The layers remained undisturbed for 25 min before the hexanes layer was transferred by cannula to a new flask. Two more extractions were done each with 10 mL of hexanes. Hexanes were removed under vacuum to yield a white solid. Benzene was vacuum transferred into the flask and the solid dissolved rapidly to give a pale brown solution. The solution was transferred to a resealable NMR tube using a pipet. The yield of **2** as shown by ^{1}H NMR spectroscopy ranges from 30% to 70%, but a yield as high as 90% has been obtained by allowing the hexanes/DMSO layers to remain undisturbed for at least 2 h under nitrogen. The remaining percentage corresponds to two additional products (vide infra), neither of which have been fully characterized (see Supporting Information). For **2**: ^{1}H NMR (C_6D_6) δ −14.846 (d, J_{RhH} = 24 Hz, 1 H, RhH), 0.669 (s, 9 H, C(CH$_3$)$_3$), 1.221 (d, J = 2 Hz, 3 H, RhCH$_3$), 2.204 (s, 3 H, pzCH$_3$), 2.240 (s, 3 H, pzCH$_3$), 2.308 (s, 3 H, pzCH$_3$), 2.393 (s, 3 H, pzCH$_3$), 2.526 (s, 3 H, pzCH$_3$), 2.530 (s, 3 H, pzCH$_3$), 2.637 (ABq, 2 H, NCH$_2$), 5.609 (s, 1 H, pzH), 5.678 (s, 1 H, pzH) 5.790 (s, 1 H, pzH). The previously reported[1m] chemical shift of the neopentylisocyanide methylene protons (δ 2.745) was incorrect. The correct chemical shift of these protons is δ 2.637.

Method 2. To a stirred solution of 10 mg (0.018 mmol) of **1** in 5 mL of C_6H_6 was added 4 mg (0.018 mmol) of Cp$_2$ZrH$_2$. The reaction

(34) Harris, D. *Quantitative Chemical Analysis*, 2nd ed.; W. H. Freeman: New York, 1987; pp 403−406.

(35) Wailes, P. C.; Weigold, H. *Inorg. Synth.* **1990**, *28*, 257−260.

(36) Wick. D. D.; Jones, W. D. *Inorg. Chem.* **1997**, *36*, 2723−2729.

mixture was stirred for a maximum of 10 min. Removal of all zirconium products was accomplished by flash chromatography through a silica gel microcolumn with C_6H_6 as the eluent. The yield of **2** as shown by ^{1}H NMR spectroscopy was 80%. The phenyl-d_0 hydride complex Tp′Rh(L)(Ph)H constituted the remaining 20%. In the solid state **2** is a white amorphous powder.

Intramolecular Exchange of Hydrogen between the Methyl and Hydride Ligands of Tp′Rh(L)(CH$_3$)D (2-d_1) and Tp′Rh(L)(CD$_3$)H (2-d_3) in Benzene. Determination of K_1 and K_2. The complexes 2-d_1 and 2-d_3 for the exchange reactions were prepared using Method 2, with the flash chromatography step excluded to allow immediate monitoring by NMR spectroscopy. The chemical shifts for the resonances of the neopentylisocyanide and Tp′ ligands of 2-d_1 and 2-d_3 are the same as those of **2**. For 2-d_1: ^{1}H{^{2}H} NMR (C_6D_6) δ 1.236 (d, J = 2 Hz, RhCH$_3$); ^{2}H{^{1}H} NMR (C_6H_6) δ −14.699 (bs, RhD). For 2-d_3: ^{1}H{^{2}H} NMR (C_6D_6) δ −14.813 (d, J_{RhH} = 24 Hz, RhH); ^{2}H NMR (C_6H_6) δ 1.176 (bs, RhCD$_3$). The approach to equilibrium at 22 °C of deuterium scrambling in 2-d_1 was monitored by ^{1}H{^{2}H} NMR spectroscopy (C_6D_6) at regular time intervals. The methyl ligand resonance of the isotopomer Tp′Rh(L)(CH$_2$D)H (2-d_1') appears as a doublet at δ 1.225 (J = 2 Hz). The integrals of the methyl ligand resonance of 2-d_1 and 2-d_1' were corrected for the number of protons present in each ligand. Similarly, the synthesis and approach to equilibrium at 22 °C of deuterium scrambling in 2-d_3 was monitored by ^{1}H{^{2}H} NMR (C_6D_6) at regular time intervals. The methyl ligand resonance of Tp′Rh(L)(CD$_2$H)D (2-d_3') appears as a doublet at δ 1.199 (J = 2 Hz). This resonance and the resonance of the hydride ligand of 2-d_3 were integrated. The corrected integrated areas were used for calculation of the approach to equilibrium as shown in the Supporting Information.

Kinetics of Reductive Elimination of CH$_4$ from 2 in Neat C_6H_6. For runs 1 and 2 in Table 1 10 mg (0.018 mmol) of **1** was weighed out in a vial and dissolved in a minimum volume (0.3 mL) of C_6H_6. The solution was transferred to a resealable 5 mm NMR tube and placed under vacuum to remove solvent. An excess (5 mg, 0.044 equiv) of Cp$_2$ZrH$_2$ was added to the NMR tube, followed by 0.6 mL of C_6H_6, and 0.5 μL of SiMe$_4$ for use as an internal standard. The tube was sealed and vigorously agitated to dissolve the reactants. The sample was immediately placed in a pre-shimmed pre-warmed NMR probe. The solvent resonance was suppressed using the UXNMR solvent peak suppression program zgh2pr. The formation of **2** was complete within 10 min as shown by ^{1}H NMR spectroscopy. Chemical shifts were calibrated by setting the chemical shift of the SiMe$_4$ resonance to zero. For kinetic analysis the singlet resonances at δ 2.315 and 2.354 were integrated periodically. These correspond to a Tp′ methyl resonance for **2** and the phenyl-d_0 hydride complex, respectively. At regular time intervals the percentage of **2** was calculated by dividing the integral value for **2** by the sum of the integral values for **2** and the phenyl-d_0 hydride complex **3**, and this value was used for the determination of the rate of reaction as shown in the Supporting Information.

Kinetics of Reductive Elimination: CH$_4$ from 2 and CD$_4$ from 2-d_4 in Neat C_6D_6. The procedure for runs 3 and 4 was identical to that for runs 1 and 2 above except that C_6D_6 was used as the solvent. Additionally, no solvent suppression was required during the ^{1}H NMR acquisitions. The procedure for runs 5 and 6 was the same as that for runs 3 and 4 except that 1-d_3 and Cp$_2$ZrD$_2$ were used and acquisitions were recorded every 7 min. All runs were made in succession to minimize instrumental variations.

Kinetics of Reductive Elimination of CH$_4$ from 2 in Mixtures of C_6D_6 and C_6F_6. Sample preparation was similar to that described for runs 3 and 4 in Table 1, except that 0.6 mL of a C_6D_6/C_6F_6 mixture was used as the solvent according to the percentages listed in Table 2. Given the change in chemical shifts due to the change in solvent, the resonances at δ 2.395 and 1.961 were integrated for **2** and the phenyl-d_5 deuteride complex 3-d_6, respectively, in run 2. In run 3 these were at δ 2.167 and 1.879. In run 4 two resonances at δ 2.152 and 2.145 were integrated and averaged for **2** and the resonance at δ 1.840 was integrated for 3-d_6.

Reactions with other traps were examined. Reaction of 2-d_0 with PMe$_3$ in the concentration range 0.006−0.30 M occurred at a rate approximately half that for reaction with C_6H_6.[1m] Reaction with

neopentylisocyanide led to the formation of $(\eta^2$-Tp$')$Rh(CNneopentyl)$_2$ as well as other unidentified products, and was unsuitable for kinetic study.