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# Activation of the C–H Bonds in Neopentane and Neopentane-$d_{12}$ by ($\eta^5$-$C_5(CH_3)_5$)Rh(CO)$_2$: Spectroscopic and Temporal Resolution of Rhodium–Krypton and Rhodium–Alkane Complex Intermediates

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**Abstract:** The photoinitiated reaction of Cp*Rh(CO)$_2$ with neopentane and neopentane-$d_{12}$ in liquid krypton has been studied with low-temperature IR flash kinetic spectroscopy. Photolysis of Cp*Rh(CO)$_2$ generates a single transient absorption at 1946 cm$^{-1}$ which is assigned to the Cp*Rh(CO)(Kr) complex. This complex reacts with $(CH_3)_4C$ to form the C–H activated neopentyl hydride product observed at 2008 cm$^{-1}$. Confirming earlier flash kinetic results with cyclohexane, the results are consistent with a pre-equilibrium mechanism in which an initially formed transient krypton complex Cp*Rh(CO)(Kr) is in rapid equilibrium with a transient (uninserted) alkane complex Cp*Rh(CO)($(CH_3)_4C$) which then proceeds to form the neopentyl hydride in a unimolecular step. Under most conditions our mechanism requires that both Cp*Rh(CO)(Kr) and Cp*Rh(CO)(alkane) exhibit unresolved carbonyl stretching absorptions at 1946 cm$^{-1}$. However, use of $(CD_3)_4C$ as the alkane substrate allows us, for the first time, to spectroscopically and temporally resolve both the rhodium–krypton and rhodium–alkane complex intermediates by 1 cm$^{-1}$, lending further support for the pre-equilibrium mechanism proposed to be operative in these systems. As was observed with cyclohexane and cyclohexane-$d_{12}$, a normal isotope effect is observed for the unimolecular C–H(D) insertion step but an unusual equilibrium isotope effect (EIE) is measured for the pre-equilibrium step of the reaction: rhodium is bound an order of magnitude more strongly to $(CD_3)_4C$ than to $(CH_3)_4C$.

## Introduction

Since the discovery that photoproducts of transition metal complexes of the type CpM(L)X or Cp*M(L)X (where Cp = $\eta^5$-$C_5H_5$, Cp* = $\eta^5$-$C_5Me_5$, M = Ir or Rh, L = PMe$_3$ or CO, X = CO or H$_2$) can activate the C–H bonds of alkanes,[1,2] numerous studies have been conducted to elucidate the mechanism of this important reaction.[3–11] However, mechanistic studies of these systems have been hampered by the fact that the C–H insertion step in these reactions is extremely rapid at room temperature. Consequently, direct information about the nature of the intermediates generated at early times during the course of the reactions is difficult to obtain. Kinetic studies are further complicated by the lack of a suitable solvent in which to carry out the reactions since these metal centers also activate the C–H bonds of conventional solvents.

Recently, these difficulties were overcome in our laboratories by the use of liquid rare gases as solvents and low-temperature IR flash kinetic spectroscopy. Weiller and co-workers studied the reaction of Cp*Rh(CO)$_2$ with cyclohexane in liquid krypton over wide temperature and concentration ranges.[12] They were able to detect the C–H activating intermediate generated immediately after photolysis of Cp*Rh(CO)$_2$. Because the observed rate constant saturated at high cyclohexane concentration and was dramatically different when $C_6D_{12}$ was used instead of $C_6H_{12}$, the authors proposed a pre-equilibrium mechanism (Scheme 1) to explain the data. According to this mechanism the initially formed complex Cp*Rh(CO)(Kr) is in rapid equilibrium with an uninserted alkane complex, Cp*Rh(CO)($C_6H_{12}$), which then forms the cyclohexyl hydride, Cp*Rh(CO)(H)($C_6H_{11}$), in a unimolecular step. Because of the limited resolution of the CO probe laser (±4 cm$^{-1}$), a critical assumption of this study was that Cp*Rh(CO)(Kr) and Cp*Rh(CO)($C_6H_{12}$) had very similar (and thus unresolvable) metal–carbonyl stretching frequencies in the IR.

**Scheme 1**

$$\mathrm{Cp^*Rh(CO)(Kr)} + \mathrm{C_6H_{12}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cp^*Rh(CO)(C_6H_{12})} + \mathrm{Kr}$$

$$\mathrm{Cp^*Rh(CO)(C_6H_{12})} \xrightarrow{k_2} \mathrm{Cp^*Rh(CO)(H)(C_6H_{11})}$$

To obtain direct evidence for the presence of the proposed Cp*Rh(CO)($C_6H_{12}$) intermediate, the Cp*Rh(CO)$_2$/$C_6H_{12}$ system was reinvestigated with use of a newly built flash kinetic apparatus in which the CO probe laser was replaced with a higher resolution diode laser.[13] A careful and thorough analysis of the kinetic data verified that the photoinitiated reaction of Cp*Rh(CO)$_2$ with $C_6H_{12}$ in both liquid krypton and xenon proceeds via the pre-equilibrium mechanism outlined above. Unfortunately, attempts to resolve the Cp*Rh(CO)(Kr) and Cp*Rh(CO)($C_6H_{12}$) intermediates with the higher resolution probe laser were unsuccessful. Because the line widths of the CO stretching absorbances are 2–3 cm$^{-1}$ in liquid Kr, the failure to observe both species implies that the CO stretching frequencies of Cp*Rh(CO)(Kr) and Cp*Rh(CO)($C_6H_{12}$) are less than 1 cm$^{-1}$ apart.

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A particularly interesting result of this study was the observation of a large inverse isotope effect on the pre-equilibrium constant ($K_{eq}(H)/K_{eq}(D) \approx 0.1$). This finding implies that $C_6D_{12}$ binds more strongly to the rhodium center than does $C_6H_{12}$. In an effort to discover other alkane substrates that might exhibit the large equilibrium isotope effect (EIE) mentioned above and to delineate the differences in reaction energetics and rates of C-H activation between secondary and primary C–H bonds, we report in this paper the results of a mechanistic study on the photoinitiated reaction of $Cp^*Rh(CO)_2$ with neopentane (2,2-dimethylpropane) and neopentane-$d_{12}$. The results of this study closely mirror the observations with cyclohexane (including the large inverse isotope effect on $K_{eq}$), strongly suggesting that the mechanism in Scheme 1 is general. However, in dramatic contrast to the cyclohexane study, under carefully defined conditions, the use of neopentane as the substrate has allowed us to spectroscopically and temporally resolve the rhodium–krypton and rhodium–neopentane complexes. Thus, we have obtained direct evidence for the existence of an uninserted metal–alkane complex which has been proposed to be an intermediate in C–H insertion reactions by several theoretical and experimental studies.[7,8,14–21]

## Experimental Section

The experimental apparatus has been described in detail previously.[13] The reactions are conducted in a high-pressure cell that can be cooled to 77 K. The reaction is initiated with a 308 nm UV pulse from a XeCl excimer laser (Lambda Physik model EMG-103 run at 2 Hz, pulse fwhm ca. 20 ns, output 60–90 mJ/pulse). The photolysis energy at the cell is approximately 5 mJ/pulse. The time-dependent absorptions of the species generated after the UV pulse are monitored by IR light from a lead salt diode laser (Mütek model MDS 2020, 1896–2070 $cm^{-1}$) and the signal is detected by a liquid $N_2$ cooled InSb IR detector (Cincinnati Electronics model SDD-32EO-S1–05M, 2 mm diameter, 70 ns risetime). Light from the diode laser passes through a monochromator (SPEX model 270M, 0.25 m, grating blazed at 5 $\mu$m, resolution 0.5 $cm^{-1}$ at 5 $\mu$m) to identify the exact wavelength of the IR probe and to isolate a single mode from the multimode laser.

To prepare the photolysis solution, an aliquot of a stock solution of $Cp^*Rh(CO)_2$ in hexanes was injected into the cell and the solvent pumped off. The Kr was introduced into the cell by first flowing it through a stainless steel line containing neopentane vapor. The cell was then pressurized with ≈300 psi of Kr and the temperature lowered to 160 K at which point the Kr condensed. To ensure that the photolysis solution was well mixed, the cell was equipped with a small magnetically driven stirbar. The concentration of the alkane in solution was established by obtaining an IR spectrum with the use of a commercially available FTIR spectrometer (Nicolet 550, 0.5 $cm^{-1}$ resolution, MCT detector). The integrated absorbances of the alkane bands were converted to concentrations by using previously determined band intensities for $(CH_3)_4C$ and $(CD_3)_4C$.[22,23] The peak shapes in the FTIR spectrum at high alkane concentrations were similar to those at low concentrations, indicating that aggregates were not forming in solution at the higher concentrations. All studies were carried out under pseudo-first-order conditions with concentrations of the alkane over 100 times greater than that of $Cp^*Rh(CO)_2$ ($1-2 \times 10^{-5}$ M).

$Cp^*Rh(CO)_2$ was obtained from Strem and used without further purification. Neopentane was obtained from Matheson. Neopentane-$d_{12}$ was obtained from MSD isotopes (98 atom % D) and used without further purification.

## Results

As observed in our earlier studies, in the absence of added alkane, photolysis of a solution of $Cp^*Rh(CO)_2$ in liquid krypton at temperatures from 163 to 193K generates a single transient absorption at 1946 $cm^{-1}$ that decays exponentially with a half life on the order of 1 ms.[12,13,24,25] On the basis of the following observations, we assigned to this transient species the structure of the solvated monocarbonyl complex "$Cp^*Rh(CO)(Kr)$". Because only one CO stretching frequency is observed and the transient at 1946 $cm^{-1}$ is the only one formed immediately after the flash, this species must be a monocarbonyl complex. The rate constant for the reaction of this transient with CO depends on the solvent. In liquid Kr the rate constant is two orders of magnitude larger than in liquid Xe.[25] Since Xe is thought to form a stronger bond with metal centers than Kr,[26] we interpreted the difference in rate constants to be the result of at least one solvent atom being bound to the monocarbonyl. Hence in liquid Xe the species generated at the flash is the more stable $Cp^*Rh(CO)(Xe)$ and, by inference, in liquid Kr the less stable $Cp^*Rh(CO)(Kr)$ complex is formed. This conclusion is supported by earlier studies of CO photodissociation from metal carbonyl complexes in hydrocarbon solutions where the solvent was found to coordinate to the metal center within picoseconds of CO loss.[27–30] In liquid rare gas solvents, Turner and co-workers have identified a relatively long-lived $Cr(CO)_5Xe$ complex which was formed by photolyzing $Cr(CO)_6$ in liquid Xe.[31]

A less plausible but alternative explanation for the solvent dependent reactivity of this transient toward CO is that perhaps different spin states of the monocarbonyl complex are generated when the photolysis is conducted in Xe as opposed to Kr.[32] For example, if the reactive state of the monocarbonyl were a triplet, and an excited singlet state were produced after photolysis, then due to the heavy atom effect,[33] the rate of intersystem crossing to the triplet state would be faster in Xe than in Kr. This argument therefore postulates that the chemistry occurring in liquid Kr is due to a singlet state while that in liquid Xe is due to a triplet state of the monocarbonyl. Consequently, consistent with observation, reaction of the monocarbonyl with singlet CO could be faster in Kr than in Xe because in the latter case the CO would be forced to react less rapidly with the triplet monocarbonyl in a spin forbidden reaction.

To test the variable spin state mechanism, we measured the rate of reaction between the monocarbonyl and triplet oxygen in both liquid Kr and liquid Xe, assuming that if a monocarbonyl triplet were formed in liquid Xe, it would react with triplet $O_2$ faster than the corresponding singlet monocarbonyl presumed to exist in liquid Kr. At 190 K in the presence of 10 mM $O_2$,[34] the 1946 $cm^{-1}$ transient decayed at an observed rate of 13 000 $s^{-1}$ in liquid Kr. A new product absorbance was monitored at 1960 $cm^{-1}$ (presumably $Cp^*Rh(CO)(O_2)$). In liquid Xe, however, the monocarbonyl transient decayed at least an order of magnitude more slowly even though the cell temperature was 30 K higher

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(24) The primary mechanism of this background decay may be the reaction of the photogenerated product, $Cp^*Rh(CO)(Kr)$, with parent to form the dimer, $Cp^*_2Rh_2(CO)_3$.

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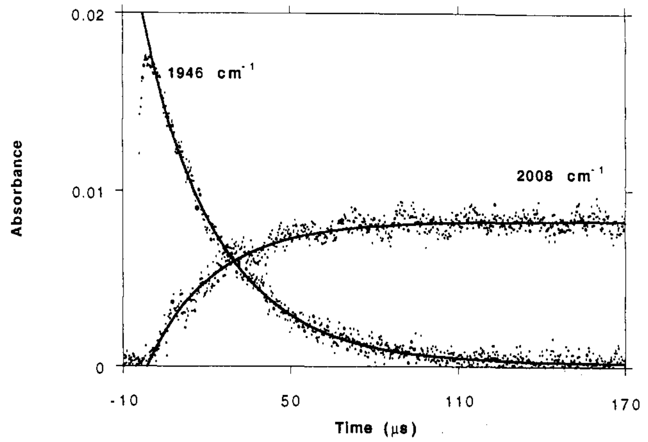

**Figure 1.** Typical traces observed when Cp*Rh(CO)$_2$ is photolyzed in liquid Kr at 193 K in the presence of 3.8 mM neopentane. The transient at 1946 cm$^{-1}$ decays at an observed rateof 37 600 s$^{-1}$ and is presumably due to a mixture of the Cp*Rh(CO)(Kr) and Cp*Rh(CO)((CH$_3$)$_4$C) complexes (see text). The product at 2008 cm$^{-1}$ grows in at a rate of 40 800 s$^{-1}$ and is assigned to the Cp*Rh(CO)(H)(C$_5$H$_{11}$) product. The solid lines represent single exponential fits to the observed traces.

in this case.[35] We therefore rule out the possibility that two different spin states of the monocarbonyl are observed in liquid Kr and liquid Xe. This experiment does not rule out the possibility that we actually observe the chemistry of an excited electronic state of the monocarbonyl complex. However, we believe this is unlikely based on the results of earlier studies which indicate that in hydrocarbon solvents, complexes such as Cr(CO)$_5$, Mo(CO)$_5$, and W(CO)$_5$ decay to their ground electronic states within picoseconds of CO loss from the parent hexacarbonyls.[36,37]

Mirroring its behavior observed earlier with cyclohexane,[13] in the presence of (CH$_3$)$_4$C a transient absorption at 1946 cm$^{-1}$ is again detected which decays exponentially at a rate that increases with alkane concentration. At 2008 cm$^{-1}$ a new species grows in exponentially at a rate that matches the decay rate of the transient absorbing at 1946 cm$^{-1}$. Typical traces are shown in Figure 1. Because product growth is observed at only one CO stretching frequency and the 2008 cm$^{-1}$ stretch is consistent with attachment of the CO ligand to a Rh(III) center,[38] this species is assigned as the neopentyl hydride, Cp*Rh(CO)(H)(C$_5$H$_{11}$). The 2008 cm$^{-1}$ CO stretching frequency for the neopentyl hydride is close to the 2003 cm$^{-1}$ frequency observed for the analogous cyclohexyl hydride described earlier.[13] At 163 K, the neopentyl hydride is stable for a few minutes and can be monitored by FTIR. A plot of the observed rate constant for the formation of the neopentyl hydride versus (CH$_3$)$_4$C concentration (Figure 2) establishes that this system again shows saturation kinetics. If the mechanism in Scheme 1 is postulated, the 1946 cm$^{-1}$ transient is due to a mixture of the alkane complex Cp*Rh(CO)((CH$_3$)$_4$C) and the krypton complex which (as in the cyclohexane system) have unresolved frequencies near 1946 cm$^{-1}$.

In contrast to our observations with cyclohexane-$d_{12}$, however, when (CD$_3$)$_4$C is substituted for (CH$_3$)$_4$C, *two* transient absorbances and the growth of one product absorbance are observed. The concentration–time profiles of these absorbances are shown in Figure 3. At 165 K with 3.8 mM (CD$_3$)$_4$C, the transient at 1946 cm$^{-1}$ exhibits a fast exponential decay followed by a slow one, the observed pseudo-first order rates of which are 11700 and 1900 s$^{-1}$, respectively. This transient is assigned to the Cp*Rh(CO)(Kr) complex which is also observed in the absence of hydrocarbon. The observed rate of growth of the product at 2008 cm$^{-1}$ is 2000 s$^{-1}$. Within experimental error, the slow decay component of Cp*Rh(CO)(Kr) is equal to the growth rate of the product.

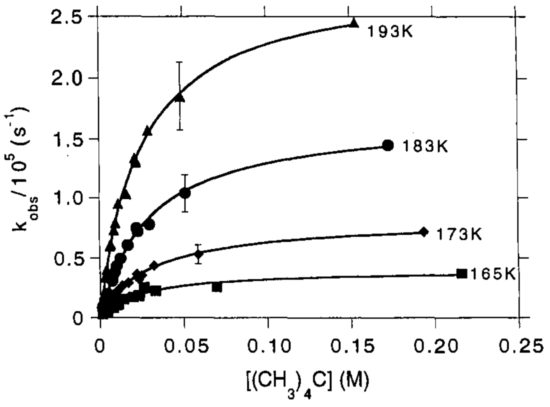

**Figure 2.** Plot of the observed rate versus (CH$_3$)$_4$C concentration at four temperatures. Each data point represents an average of the observed decay and growth rates at 1946 and 2008 cm$^{-1}$, respectively.

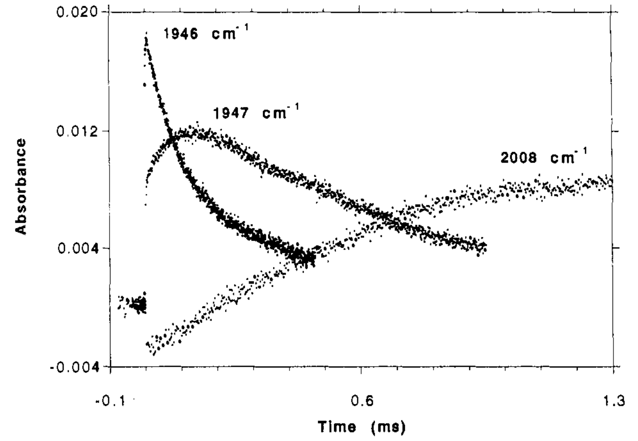

**Figure 3.** The time-dependent absorbances observed when Cp*Rh(CO)$_2$ is photolyzed in liquid Kr at 165 K in the presence of 3.8 mM neopentane-$d_{12}$. The transient at 1946 cm$^{-1}$ shows biexponential behavior with a fast decay followed by a slower one. In marked contrast to the protiated system which shows only one transient absorption, a second transient absorption which grows in and then decays is observed at 1947 cm$^{-1}$ in the deuterated system. The growth at 2008 cm$^{-1}$ is assigned to the Cp*Rh(CO)(D)(C$_5$D$_{11}$) product.

In addition to these two species a third transient is observed at 1947 cm$^{-1}$ that grows in and then decays. Because the line widths of the CO stretching absorbances are 2–3 cm$^{-1}$, there is some overlap with the Cp*Rh(CO)(Kr) transient at 1946 cm$^{-1}$ leading to the observed non-zero absorbance at time zero. To account for this overlap, the time dependence of the observed transient was fit to the following equation: $a \exp(-a_1 t) + b \exp(-a_2 t) + c \exp(-a_3 t) - c \exp(-a_4 t)$. The first two terms describe the biexponential decay of the overlapping 1946 cm$^{-1}$ transient while the last two terms describe the growth and decay of the 1947 cm$^{-1}$ transient in the absence of any overlap. Both $a_1$ and $a_2$ were held at values obtained from the fit to the 1946 cm$^{-1}$ transient while $a_3$ and $a_4$ were allowed to vary. With use of this procedure, values of 11500 s$^{-1}$ for the fast rise ($a_4$) and 1600 s$^{-1}$ for the slow decay ($a_3$) are obtained. The fits are shown in Figure 4. This finding suggests that an intermediate absorbing at 1947 cm$^{-1}$, just barely resolved from the 1946 cm$^{-1}$ species, grows in at a rate similar to that of the fast decay of Cp*Rh(CO)(Kr) and is then consumed at a rate equal to both the slow decay of Cp*Rh(CO)(Kr) and the growth of the neopentyl deuteride. Similar transients are also observed at 173 K although the growth of the 1947 cm$^{-1}$ species is not as evident as at 165 K because the band widths of the CO stretching absorbances increase by ≈1 cm$^{-1}$ as the temperature changes from 165 to 193 K. Consequently, resolution of the two transients becomes more difficult at the higher temperatures. While the growth of the 1947 cm$^{-1}$ transient

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[35] A quantitative value for the rate of reaction in liquid Xe could not be obtained because the reaction was too slow.

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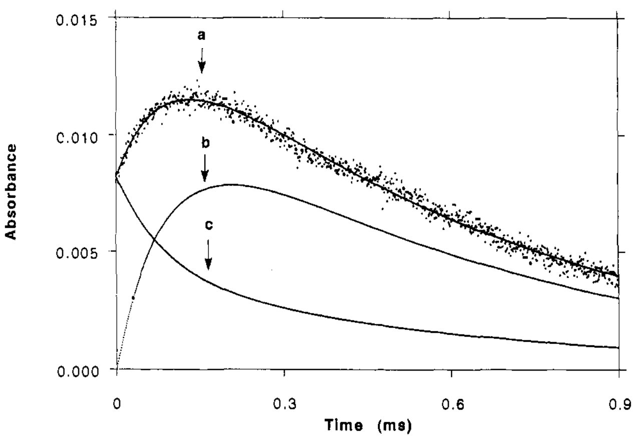


**Figure 4.** The non-zero absorbance of the observed 1947 cm$^{-1}$ transient (trace a) at time zero is due to overlap with the 1946 cm$^{-1}$ transient. Consequently, trace a is fit to the following equation, $a \exp(a_1t) + b \exp(a_2t) + c \exp(-a_3t) - c \exp(-a_4t)$. The first two terms describe the biexponential decay of the overlapping 1946 cm$^{-1}$ transient (shown as trace c) while the last two terms describe the actual transient in the absence of overlap (trace b).

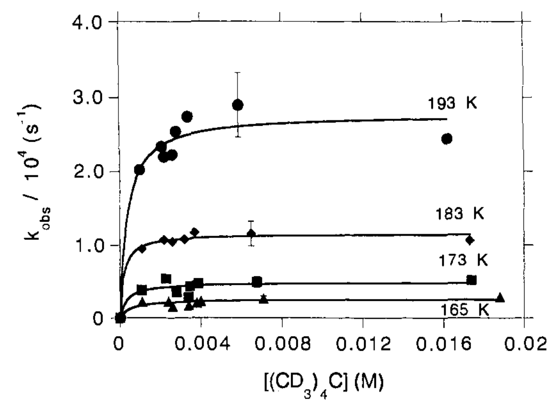


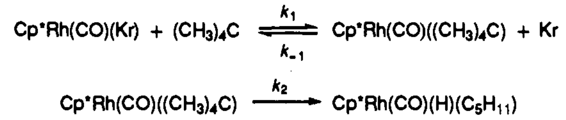
**Figure 5.** Plot of the observed rate versus $(CD_3)_4C$ concentration at four different temperatures. As in Figure 2, each data point is an average of the observed growth and decay rates at 2008 and 1947 cm$^{-1}$, respectively.

is not obvious at 183 K, the concentration–time profile of this transient is still markedly different from the 1946 cm$^{-1}$ transient which decays at a significantly faster rate. At 193 K the absorbances at 1946 and 1947 cm$^{-1}$ no longer exhibit different time profiles. At this temperature both transients overlap closely enough that only a single absorption is observed which exhibits a single exponential decay with a rate constant that matches the growth rate of the product.

A plot of the observed rate constant, $k_{obs}$, versus the $(CD_3)_4C$ concentration is shown in Figure 5. Each data point in this plot represents an average of the observed growth rate of the product and the slow decay rate of the 1947 cm$^{-1}$ transient. In contrast to the $Cp^*Rh(CO)_2/(CH_3)_4C$ system where the observed rate constant saturates at alkane concentrations >50 mM, the observed rate is already saturated at 1 mM when $(CD_3)_4C$ is used. The limiting value of $k_{obs}$ is also approximately 10 times smaller in the case of the deuterated alkane.

It is clear from these results that the intermediate at 1947 cm$^{-1}$ lies on the reaction pathway leading from the reactant, $Cp^*Rh(CO)(Kr)$, to the product, $Cp^*Rh(CO)(D)(C_5D_{11})$. We believe this transient is associated with the uninserted perdeuterioalkane complex, $Cp^*Rh(CO)((CD_3)_4C)$.[39] Thus, in this system we have been able to identify two key intermediates in the photoinitiated reaction of $Cp^*Rh(CO)_2$ with neopentane-$d_{12}$. These results provide strong confirmation of our hypothesis that in the protiated system, the analogous pair of intermediates $Cp^*Rh(CO)(Kr)$ and $Cp^*Rh(CO)((CH_3)_4C)$ are formed, but their CO stretching frequencies are less than 1 cm$^{-1}$ apart and are therefore unresolvable.[40]

**Scheme 2**



$$Cp^*Rh(CO)(Kr) + (CH_3)_4C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cp^*Rh(CO)((CH_3)_4C) + Kr$$

$$Cp^*Rh(CO)((CH_3)_4C) \xrightarrow{k_2} Cp^*Rh(CO)(H)(C_5H_{11})$$

## Discussion

The results presented above are consistent with the mechanism illustrated in Scheme 2. According to this mechanism, the initially formed Kr complex is in equilibrium with an uninserted metal–alkane complex which then goes on, with a unimolecular rate constant $k_2$, to yield the C–H activated product. This mechanism accounts for saturation of the observed rate constant at high alkane concentrations. Furthermore, since the plateau for $k_{obs}$ is equal to $k_2$, the C–H(D) insertion rate constant, a significant isotope effect is expected.[41] Indeed, the dramatic difference in the saturation rates between the deuterated and protiated alkane is consistent with this expectation. However, the strongest evidence for this mechanism comes from the observation of the intermediate alkane complex absorbing at 1947 cm$^{-1}$ that is formed from the $Cp^*Rh(CO)(Kr)$ complex and then goes on to the neopentyl deuteride product. Assignment of the 1947 cm$^{-1}$ transient to a Rh–alkane "$\sigma$-complex" is consistent with recent theoretical studies which indicate that such complexes are intermediates in C–H addition reactions.[14–21] For example, a study by Hall and co-workers on the oxidative addition of methane to CpRh(CO) found that an intermediate with metal–CH dative bond interaction is generated early in the reaction and is bound by 14.8 kcal/mol relative to the monocarbonyl.[21]

The following kinetic analysis was used to extract the relevant rate constants from the experimental data. The differential equations for the kinetic situation depicted in Scheme 2 were solved explicitly by assuming pseudo-first-order behavior in $[(CH_3)_4C]$ (which is certainly the case in this study).[42] The mathematical solutions suggest that $Cp^*Rh(CO)(Kr)$ will decay in a biexponential fashion with a fast decay followed by a slower one. For the case where both $k_1[(CH_3)_4C]$ and $k_{-1}[Kr]$ are larger than $k_2$, the fast decay component represents the approach to equilibrium with the $Cp^*Rh(CO)((CH_3)_4C)$ intermediate while the slow decay reflects the rate of the subsequent step leading to the product. Consequently, the metal–alkane intermediate will grow at a rate equal to the fast decay of the metal–krypton complex and then decay at a rate equal to both the slow decay of the krypton complex and the growth of the product. These qualitative observations match the experimental behavior of the $Cp^*Rh(CO)(Kr)$ and $Cp^*Rh(CO)((CD_3)_4C)$ transients. For the fits, the intramolecular rate constant $k_2$ was set equal to the limiting value of $k_{obs}$, and $k_1$ and $k_{-1}$ were varied to match the experimentally observed rates. The values for these rate constants were further refined by using the kinetic simulation program

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[39] Because spectroscopic evidence for this species is limited to a single CO stretching frequency, we cannot speculate on the actual structure of the complex.

[40] A referee has pointed out that the 1 cm$^{-1}$ increase in $\nu_{CO}$ for the $Cp^*Rh(CO)((CD_3)_4C)$ "$\sigma$-complex" compared to the protiated complex may be due to coupling with the stretching mode of a coordinated C–D bond. Thus, if the CD and CO stretching modes are of the same symmetry and if $\nu_{CD}$ is lower, then coupling between these modes may push the observed $\nu_{CO}$ to a higher frequency than the "pure" CO stretch. In the protiated complex, the coordinated CH stretching frequency is expected to be higher than $\nu_{CO}$, and therefore any coupling between the two modes would lower the frequency of the observed CO stretch relative to the "pure" CO stretch.

[41] Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981.

[42] The exact mathematical solutions for a similar kinetic situation are given in the following: Espenson, J. H. *Chemical Kinetics and Reaction Mechansims*; McGraw-Hill: New York, 1981.

[43] HopKINSIM is a kinetic simulation program for the Macintosh computer written by Daniel Wachsstock, Department of Cell Biology and Anatomy, Johns Hopkins University Medical School. HopKINSIM is based on the original KINSIM program Barshop, B. A.; Wrenn, R. A.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.

**Table 1.** Rate and Equilibrium Constants for the Reaction of Cp*Rh(CO)(Kr) with $(CH_3)_4C$ and $(CD_3)_4C$

| temp (K) | $K_{eq}(D)^a$ | $K_{eq}(H)$ | $10^{-3}k_2(H)$ ($s^{-1}$) | $10^{-3}k_2(D)$ ($s^{-1}$) |
|---|---|---|---|---|
| 165 | $1.6 \pm 0.5 \times 10^4$ | $1180 \pm 400$ | $39.0 \pm 5.0$ | $2.5 \pm 0.4$ |
| 173 | | $1000 \pm 300$ | $81.0 \pm 12.0$ | $4.8 \pm 0.7$ |
| 183 | | $975 \pm 300$ | $170.0 \pm 30.0$ | $12.0 \pm 2.0$ |
| 193 | | $1040 \pm 300$ | $280.0 \pm 40.0$ | $28.0 \pm 4.0$ |

$^a$ $k_1 = 1.8 \pm 0.3 \times 10^6$ $M^{-1}$ $s^{-1}$ and $k_{-1} = 110 \pm 30$ $M^{-1}$ $s^{-1}$ at 165 K.

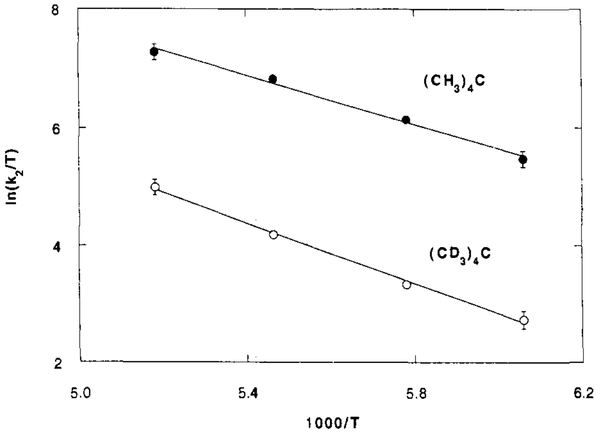

**Figure 6.** Eyring plots for the activation of $(CH_3)_4C$ and $(CD_3)_4C$ by Cp*Rh$(CO)_2$ in liquid Kr.

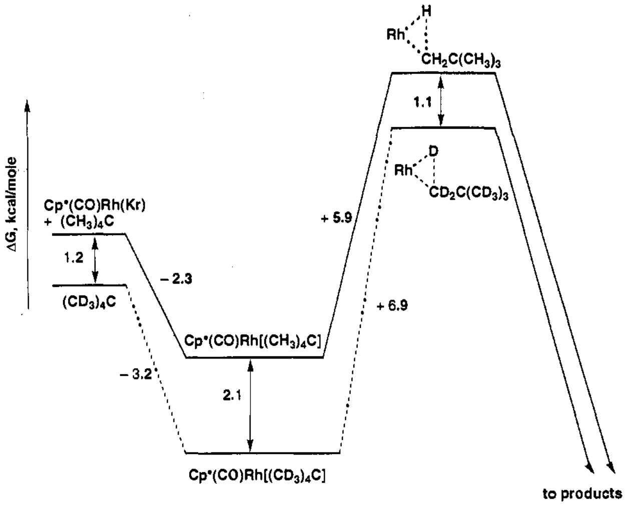

**Figure 7.** Reaction coordinate energy diagram for the activation of $(CH_3)_4C$ and $(CD_3)_4C$ by Cp*Rh$(CO)_2$ in liquid Kr at 165 K. The reaction coordinate is assumed to be the C–H(D) bond being broken.

HopKINSIM[43] and including the background decay rate (in the absence of hydrocarbon) of the Cp*Rh(CO)(Kr) complex.

Because growth of the intermediate alkane complex is not observed in the protiated system, accurate values of $k_1$ and $k_{-1}$ cannot be determined. However, the *ratio* of $k_1$ and $k_{-1}$ ($K_{eq}(H)$) can be obtained from the dependence of $k_{obs}$ on the $(CH_3)_4C$ concentration. A similar procedure cannot be used to obtain the values of $K_{eq}(D)$ since $k_{obs}$ reaches its saturation limit at the lowest alkane concentrations we can achieve. However, because we observe the rise and decay of the Cp*Rh(CO)($(CD_3)_4$) intermediate at 165 K, quantitative values for both $k_1$ and $k_{-1}$ (and thus $K_{eq}(D)$) can be obtained at this temperature. The value of $K_{eq}(D)$ ($k_1/k_{-1}$) at 165 K and the magnitudes of $K_{eq}(H)$, $k_2(H)$, and $k_2(D)$ at a variety of temperatures are listed in Table 1.

The temperature dependence of $k_2(H)$ and $k_2(D)$ allows us to extract activation parameters for the intramolecular step. As shown in Figure 6, Eyring analyses yield $\Delta H^{*} = 4.1 \pm 0.5$ kcal/mol, $\Delta S^{*} = -11.2 \pm 1.4$ eu for $(CH_3)_4C$ and $\Delta H^{*} = 5.1 \pm 0.6$ kcal/mol, $\Delta S^{*} = -10.7 \pm 1.2$ eu for $(CD_3)_4C$. These activation parameters are consistent with the values obtained by theoretical studies on the C–H oxidative addition of methane to CpRh(CO).[18,20] The 1.0 kcal/mol difference in $\Delta H^{*}$ between activation of a C–H versus a C–D bond is consistent with the 1.2 kcal/mol difference in the zero point energies of a C–D versus an equivalent C–H bond. This gives a relatively large $k_H/k_D$ at low temperature (e.g., 10 at −80 °C), which extrapolates to a $k_H/k_D$ of about 4.4 at 25 °C. Within experimental error, the activation parameters for the C–H and C–D insertion steps are identical with those obtained for the cyclohexane system, implying that there is a very small energetic difference between insertion of the Rh center into a secondary versus a primary C–H bond. The absence of a measurable temperature dependence on $K_{eq}(H)$ implies that $\Delta H \approx 0$ kcal/mol for the pre-equilibrium step. However, as in the cyclohexane system, the large uncertainty in the equilibrium constants does not allow us to separate the $\Delta G°$ associated with the equilibrium step into entropic and enthalpic terms. Because several theoretical studies have calculated Rh–alkane binding enthalpies of 15 kcal/mol,[18,19] we think that the large $\Delta G°$ for the binding of the alkane to the metal center is primarily an enthalpic effect.

An important result of the present study is the dramatic difference in the way $k_{obs}$ reaches its saturation limit when $(CD_3)_4C$ is used instead of $(CH_3)_4C$. As shown in Figure 7, this observation implies that $K_{eq}$, and therefore $\Delta G°$, for the conversion of Cp*Rh(CO)(Kr) to Cp*Rh(CO)($(CD_3)_4C$) is significantly greater than that for its conversion to Cp*Rh(CO)($(CH_3)_4C$). Indeed, at 165 K, $K_{eq}(D)$ is ≈14 times larger than $K_{eq}(H)$ ($\Delta\Delta G_{165K} \approx 0.9$ kcal/mol). As discussed in refs 12 and 13, this effect was also observed when cyclohexane was used as the substrate. The magnitude of this unusual and dramatic inverse EIE would be lower at room temperature, but the data definitely point to this conclusion and the effect is relatively difficult to explain. Clearly, vibrational modes other than the C–H(D) bond being broken must make a significant contribution to the zero point energy of the metal–alkane complex, e.g., M–H(D)–C bending vibrations that are absent in the free alkane may lower the zero point energy of the deuterated complex significantly.[44] Whether the observed inverse EIE can be rationalized on the basis of zero point energies requires information about the vibrational frequencies of the rhodium–alkane complexes. Consequently, explanation of this puzzling effect must await further theoretical and experimental investigation. Experiments aimed at discovering other metal–alkane systems that exhibit the large equilibrium isotope effect reported in this paper, as well as understanding its physical basis, are continuing in our laboratories.

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(44) Somewhat analogous inverse EIE's (or inverse contributions to the EIE in association reactions in which translational or rotational modes in the separated fragments are converted into more highly isotope-sensitive modes in the adduct) have been observed in a few other cases; see, for example, (a) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019. (b) Rabinovitch, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353. For the equilibrium $Os_2(CO)_8(C_2H_4) + C_2D_4 \rightarrow Os_2(CO)_8(C_2D_4) + C_2H_4$ at 40 °C in dodecane solvent, the equilibrium constant $K_{eq} = 1.4(1)$; here the observed isotope effect was attributed to the presence of a single isotope-sensitive mode in the ethylene complex that is not present in free ethylene (Bender, B. R., Department of Chemistry, Colorado State University; personal communication). Bender has also calculated an inverse isotope effect for the binding of $D_2$ vs $H_2$ to a metal center in a dihydrogen complex.