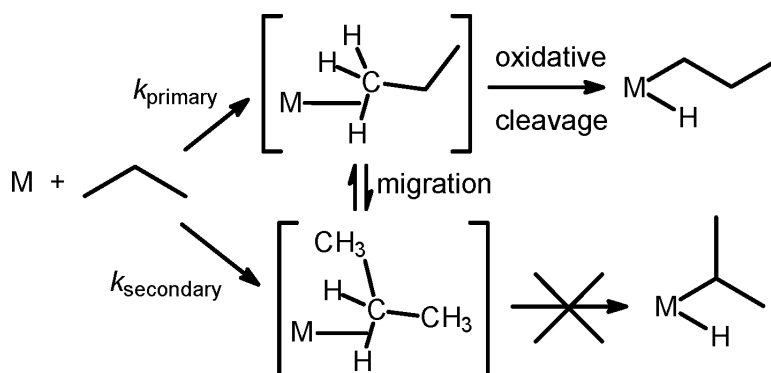## Article

Alkane Coordination Selectivity in Hydrocarbon Activation by [Tp'Rh(CNneopentyl)]: The Role of Alkane Complexes

Andrew J. Vetter, Christine Flaschenriem, and William D. Jones

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Alkane Coordination Selectivity in Hydrocarbon Activation by [Tp′Rh(CNneopentyl)]: The Role of Alkane Complexes

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Abstract: The competitive activation of C−H bonds of linear, cyclic, and branched hydrocarbons using the coordinatively unsaturated 16-electron [Tp′RhL] reactive fragment have been studied (Tp′ = tris-(3,5-dimethylpyrazolyl)borate; L = CNCH$_2$CMe$_3$). Activation of the hydrocarbons leads to the formation of Tp′Rh-(L)(R)(H) alkyl complexes, which were converted to the stable chlorides immediately following the activation of the bonds via photolysis of Tp′Rh(L)(PhN=C=NCH$_2$CMe$_3$) in the solvent mixture. The products were analyzed by ^{1}H NMR spectroscopy. The experiments described provide relative rates for the coordination of primary and secondary C−H bonds to the Rh metal center, indicating a 1.5× preference for the latter.

Introduction

The activation of C−H bonds using coordinatively unsaturated metal complexes has been widely studied.[1] It has been established in many cases that activation of alkanes occurs through a two-step process: formation of a σ-alkane complex followed by oxidative cleavage of the C−H bond to form the metal alkyl hydride.[2] While many studies have been presented that investigate the mechanism involved in the activation of alkanes, the rates at which the primary vs the secondary alkane complex is formed, as outlined in Scheme 1, have not been determined.

The first direct observation of σ-alkane complexes was demonstrated by Turner with photochemically generated M(CO)$_5$ fragments in alkanes and alkane/rare gas matrixes.[3] George and co-workers have directly observed CpRe(CO)$_2$(n-heptane) by time-resolved infrared spectroscopy (TRIR) at room temperature.[4] The complex was reported to have the longest lifetime measured of any known alkane complex at room temperature.

Scheme 1
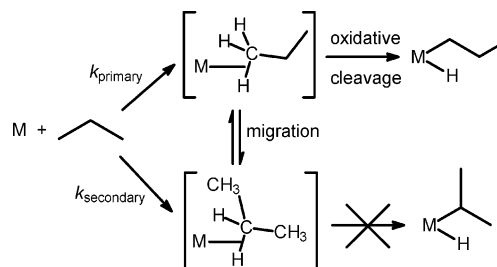
Ball and Geftakis noted the stability of the complex reported by George and were interested in similar experiments using low-temperature NMR spectroscopy to try to observe σ-alkane complexes. The photolysis of CpRe(CO)$_3$ in neat cyclopentane at −80 °C resulted in evidence for the appearance of an alkane complex CpRe(CO)$_2$(cyclopentane).[5] Similarly, Bergman and co-workers used the (C$_5$Me$_5$)Rh(CO)$_2$ complex to study the alkane complex formed in the activation of cyclohexane in liquid Xe and Kr using TRIR.[6]

More recently, Bergman and Harris reported ultrafast studies of C−H activation of hydrocarbons by Tp′Rh(CO)$_2$ (Tp′ = tris-(3,5-dimethylpyrazolyl)borate) in which they were able to observe many intermediates in the reaction.[7] These studies provided a rate constant for the oxidative cleavage of C−H bonds in cyclohexane. In a separate report, as an extension of this work, a comparison in the activation of linear, cyclic, and aryl hydrocarbons was presented.[8] The studies have shown that the process of activation was faster for linear alkanes than with cyclic alkanes once the complex is solvated by a C−H bond to

(1) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (c) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (e) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (f) Seidler, P. F.; Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (g) Baker, M. V.; Field, L. S. *J. Am. Chem. Soc.* **1987**, *109*, 2825. (h) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4276. (i) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (j) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (k) Belt, S. T.; Grevels, F. W.; Klotzbücher, W. E.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8373. (l) Kiel, W. A.; Ball, R. G.; Graham, W. A. G. *J. Organomet. Chem.* **1993**, *259*, 481. (m) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554. (n) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *117*, 10235.

(2) For recent reviews on the formation of alkane complexes in the oxidative cleavage of C−H bonds using transition metal catalysts, see: (a) Hall, C.; Perutz, R. *Chem. Rev.* **1996**, *96*, 3125. (b) *Topics Organometallic Chemistry*; Murai, S., Ed.; Springer: New York, 1999; Vol. 3.

(3) (a) Graham, M. A.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1972**, *34*, C34. (b) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(4) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakoff, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.

(5) Geftakis, S.; Ball, E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.

(6) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.

(7) Harris, C. B. et al. *Science* **1997**, *278*, 260.

(8) Asplund, M. C.; Snee, P. T.; Yeston, J. S.; Wilkens, M. J.; Payne, C. K.; Yang, H.; Kotz, K. T.; Frei, H.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **2002**, *124*, 10605.

Scheme 2
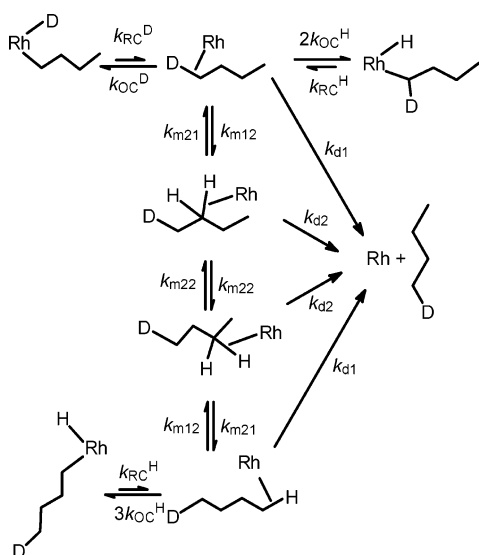
form a σ-alkane complex. However, it was reported that there was little difference in the initial rate of formation of the σ-alkane complex between cyclic and linear alkanes under the reaction conditions of the experiment.

Harris has examined the formation of σ-C−H vs σ-Si−H or σ-O−H adducts by fs-TRIR, as a result of the coordination of silanes and alcohols to $Cr(CO)_5$ upon UV irradiation of $Cr(CO)_6$.[9] They discovered that, during the activation of alcohols, the kinetically formed σ-C−H alkyl complex would rearrange to the more thermodynamically stable O-hydroxyl complex in 1.8 ns in 1-hexanol. The weakly coordinating σ-C−H alkyl complexes were determined to go through an intermolecular pathway when rearranging to the hydroxyl complex and that a chain walk mechanism was not occurring.

The [Tp′Rh(L)] (L = $CNCH_2C(CH_3)_3$) fragment, generated from the irradiation of Tp′Rh(L)(η^2-PhNL) (**1**), has been shown by our group to undergo oxidative cleavage of C−H bonds in a variety of alkanes to give a coordinatively saturated alkyl hydride complex (eq 1).[10] In this system, insertion at the primary C−H bond in linear alkanes occurs exclusively. In-depth kinetic studies have provided insight into the mechanism in which reductive coupling (the microscopic reverse of oxidative cleavage) of alkanes from Tp′Rh(L)(R)H complexes occurs.[11] Deuterium-labeling experiments were used to determine the relative rates of C−H oxidative cleavage, reductive coupling, migration, and dissociation in the alkyl hydride complex during the reductive elimination of the alkane.

(1)
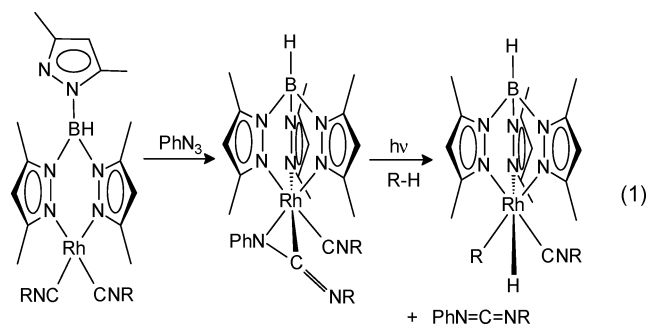
As an example, the processes by which reductive elimination of butane can occur from Tp′Rh(L)($CH_2CH_2CH_2CH_3$)(D) are
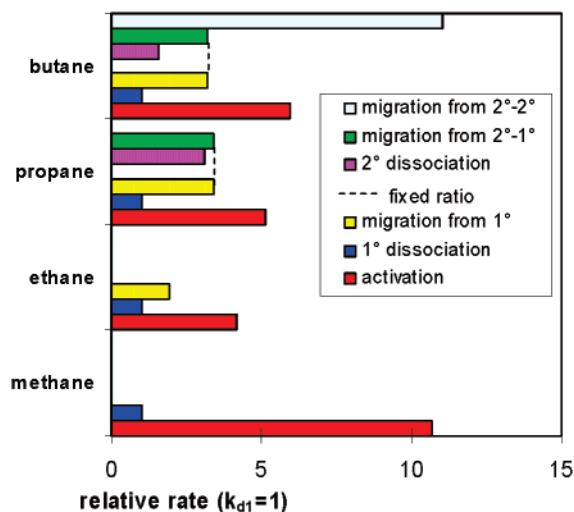
Figure 1. Bar graph showing relative rates of reactions of σ-alkane complexes. For propane and butane, the process for the primary and secondary σ-alkane complexes are separated.

shown in Scheme 2. The reaction can be followed by ^{2}H NMR spectroscopy revealing the relative rates for the pathways shown in the Scheme. Simulation of the data provided rate constants for the above-mentioned processes and provided indirect evidence for the formation of alkane complexes in the activation of hydrocarbons. Figure 1 presents a bar graph of the relative rates of reaction of σ-alkane complexes for several hydrocarbons. It is worthwhile to note that the relative rates of C−H oxidative cleavage, migration, and dissociation all follow the same trend, implying the processes are similar in this series of linear hydrocarbons.

It is believed that insertion into the C−H bond occurs after the formation of the σ-alkane complex. The observation of only primary activation products might suggest preferential coordination to methyl groups over the methylene groups. However, as shown in Scheme 1, the coordinatively unsaturated metal complex could initially form a secondary alkane complex, migrate to the terminus of the alkane chain, and then insert. It did not appear that the relative rate of coordination of the unsaturated metal to primary vs secondary C−H bonds to form alkane complexes could be determined from these studies (vide infra). Though evidence exists for the formation of alkane complexes, there have not been reports on the relative rates of the formation of alkane complexes for primary and secondary coordination in the process of activating C−H bonds. This article presents new data and analyses of these alkane coordination processes.

Figure 2 represents a free-energy diagram for the known possible species that can be formed in the reductive elimination of butane from Tp′Rh(L)(butyl)H based upon our earlier studies. A closer examination of the known rates allows one to *predict* the difference in free energy between formation of a secondary σ-alkane complex vs a primary σ-alkane complex. A difference of 0.3 kcal is calculated for the two processes as outlined below. This predicted value can be tested through a series of competitive activation studies that allow one to investigate the selectivity

(9) Kotz, K. T.; Yang, H.; Snee, P. T.; Payne, C. K.; Harris, C. B. *J. Organomet. Chem.* **2000**, *596*, 183.
(10) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554.
(11) Northcutt, T. O.; Wick, D. D.; Vetter, A. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 7257.
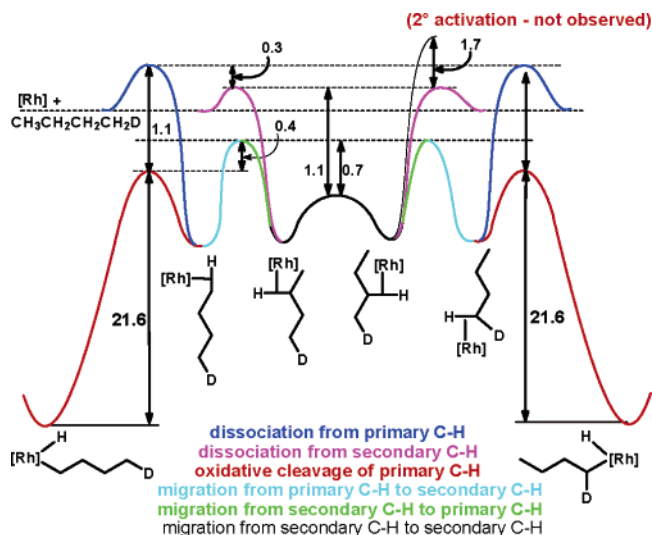
Figure 2. Free-energy diagram for the reductive elimination/oxidative addition for butane showing intermediate σ-alkane complexes. Energy required for secondary activation determined from activation of cyclohexane is superimposed for the butane.

to form σ-alkane complexes for primary and secondary C—H bonds.

Figure 2 has been constructed using the kinetic data obtained previously by fitting the observed rearrangements of Tp′Rh-(L)(D)(CH₂CH₂CH₂CH₃) and Tp′Rh(L)(D)(CH₃CHCH₂CH₃) to the kinetic model shown in Scheme 2. In this study, the absolute rates for reductive coupling of C—H bonds or C—D bonds could be determined but only the relative rates (i.e., *differences* in barrier heights) could be extracted from the kinetic simulations. The ability to extract only relative rates from each σ-alkane complex is a fundamental limitation of these studies, which arises because the absolute (or even *relative*) free energies of the primary or secondary σ-alkane complexes could not be determined experimentally.[12] Nonetheless, the relative barrier heights determine the time-dependent behavior of the various species, which is the critical factor in determining selectivities.
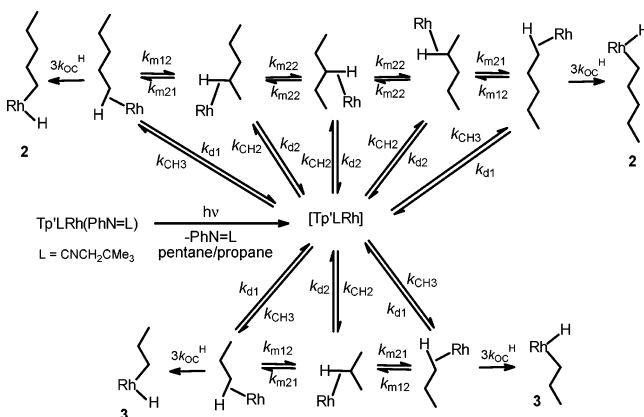
Starting with the primary σ-alkane complex in Figure 2, two relative barrier heights were determined: dissociation vs oxidative cleavage ($\Delta G^{\ddagger}(k_{d1}/k_{OC}{}^{H})$, 1.1 kcal/mol) and primary-to-secondary σ-alkane complex migration vs oxidative cleavage ($\Delta G^{\ddagger}(k_{m12}/k_{OC}{}^{H})$, 0.4 kcal/mol). Likewise, starting from the secondary σ-alkane complex, two different relative barrier heights were determined: dissociation vs secondary-to-secondary σ-alkane complex migration ($\Delta G^{\ddagger}(k_{d2}/k_{m22})$, 1.1 kcal/mol) and secondary-to-primary vs secondary-to-secondary σ-alkane complex migration ($\Delta G^{\ddagger}(k_{m21}/k_{m22})$, 0.7 kcal/mol). By combination of these four free energies, one can determine the relative barrier height for primary σ-alkane complex dissociation vs secondary σ-alkane complex dissociation (eq 2)

$$\Delta G^{\ddagger}(k_{d1}/k_{d2}) = \Delta G^{\ddagger}(k_{d1}/k_{OC}{}^{H}) - \Delta G^{\ddagger}(k_{m12}/k_{OC}{}^{H}) + \Delta G^{\ddagger}(k_{d2}/k_{m22}) - \Delta G^{\ddagger}(k_{m21}/k_{m22}) \quad (2)$$

Figure 2 shows that the top of the barrier corresponding to secondary σ-alkane complex dissociation is lower by 0.3 kcal/

Scheme 3

mol than the top of the barrier for primary σ-alkane complex dissociation, even though the absolute energies of the σ-alkane complexes themselves are not known.[12] As can also be seen in the figure, by microscopic reversibility, this difference represents the difference for *coordination* to the primary vs secondary C—H bonds of the alkane.[13] Therefore, one can predict that binding to the methylene of an alkane should be ∼1.5 times faster than binding to the methyl group of the alkane. It is precisely this barrier difference that will be experimentally determined in this report. We know of no other experimental determinations of this fundamental binding selectivity, and we present here a new method for making such determinations. Extensions of this concept will be made to the coordination and activation of other alkanes.

Results and Discussion

Competitive Selectivity Experiment of Tp′Rh(L) in Pentane/Propane. **1** was irradiated at −20 °C in a 1:1 mixture of pentane:propane resulting in the bleaching of the bright-yellow solution and the formation of a mixture of the two *n*-alkyl hydride products, *n*-pentyl hydride (**2**), and *n*-propyl hydride (**3**). The solution was quenched by condensation of excess carbon tetrachloride at 77 K and allowed to stand at −20 °C for 2 h to form Tp′Rh(L)(*n*-pentyl)(Cl) (**2-Cl**) and Tp′(L)(*n*-propyl)(Cl) (**3-Cl**). The product mixture was analyzed by ¹H NMR spectroscopy. The average product ratio was calculated using resonances that showed no/little overlap, yielding a product ratio of 1.3:1 in favor of activation of pentane over propane (eq 3).

Scheme 3 shows a kinetic model containing all possible pathways of coordination (k_{CH_3}, k_{CH_2}), migration (k_{m12}, k_{m21}, k_{m22}), dissociation (k_{d1}, k_{d2}), and oxidative cleavage ($k_{OC}{}^{H}$) for the competing alkanes. Under the low-temperature reaction conditions, reductive coupling does not occur. Hence, the C—H cleavage is irreversible and the quantity of chloride product observed directly reflects the amount of alkyl hydride product

---

(12) Ball has recently reported observation of an equilibrium mixture of σ-pentane complexes to an unsaturated rhenium fragment, showing a slight preference (0.13 kcal/mol) for secondary coordination. See: Lawes, D. J.; Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **2005**, *127*, 4134.
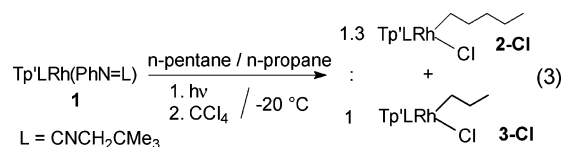
(13) Since all methyl groups contain 3 C—H bonds and all methylenes 2 C—H bonds, we will quote binding on a "per group" basis rather than a "per hydrogen" basis.

formed in the competition. By consideration of limiting cases, if coordination to a methyl C−H bond is the only pathway that occurs, then one would expect the ratio of products to be 1:1 (each alkane has two terminal methyl groups); however, if coordination to a methylene C−H bond is preferred exclusively, one would expect the product ratio to be as large as 3:1 (since pentane has three methylene groups and propane has one). While Scheme 3 may be complicated, most of the relative rates have been determined in the previous studies.[11] In fact, only two new rate constants exist in the scheme, the coordination of the metal to a primary C−H bond (k_{CH_3}) and the coordination of the metal to a secondary C−H bond (k_{CH_2}). In the formulation of a kinetic model, it is assumed that all CH_2 groups coordinate at the same rate and all CH_3 groups coordinate at the same rate. A kinetic simulation can then be performed holding k_{CH_2} constant (and fast) and varying k_{CH_3} until the observed product ratio is attained. The simulation indicated that the relative rate of coordination for a secondary C−H bond (k_{CH_2}) was 1.50 times faster than the relative rate of coordination for a primary C−H bond (k_{CH_3}). Given the observed product ratio, the faster rate of coordination to the secondary C−H bond might not have been expected as the extra methylenes in pentane play a minor role. Yet only with a full kinetic analysis could the importance of methylene coordination be revealed. This relative rate ratio corresponds to a $\Delta\Delta G^{\ddagger}$ of 0.2 kcal/mol, in excellent agreement with the value of 0.3 predicted from the free energy analysis of Figure 2 presented earlier.

The effect of temperature on pentane/propane selectivity was also examined. Three parallel competition experiments were conducted as above at −40, −20, and 0 °C. The pentane/propane selectivities observed were 1.30, 1.30, and 1.27:1, respectively. Therefore, while the detailed dependence of all of the rate constants with temperature has not been determined, the overall effect on selectivity can be seen to be negligible over the range of temperatures studied.

Competitive Selectivity Experiment of Tp′Rh(L) in Pentane/Decane. By application of the rate data from the competition reaction in propane/pentane and the previously mentioned rate studies,[11] one can predict the product ratio for the competitive selectivity reaction of a pentane/decane competition since the rates for all of the possible pathways are known. A kinetic model similar to that in Scheme 3 showing all possible pathways of coordination, migration, dissociation, and insertion into the C−H bond can be used to predict the product distribution, using a coordination selectivity of 1.5 as determined above (see Supporting Information for the scheme and kinetic fit). Given the relative rate of coordination, one might expect the product ratio for pentane:decane to be greater than that which was seen for the propane:pentane experiment since decane has a total of eight methylenes. However, one must take into account the possibility for the occurrence of nonproductive back and forth migration and concomitant dissociation in the longer decane hydrocarbon. If the metal center coordinates to one of the central methylene C−H bonds in decane, it is significantly more likely to dissociate before walking to the end of the chain, where it can insert, considering dissociation can occur from any of the coordinated σ-alkane complexes. This *increase* in the relative amount of dissociation in decane as compared to pentane would most likely result in a *decrease* in the observed selectivity between the activation of the two alkanes. Again, if one assumes

all CH_2s coordinate at the same rate and all CH_3s coordinate at the same rate, the kinetic product ratio for the activation was predicted to be 1.1:1 using the kinetic model established above.

1 was irradiated at −20 °C in a 1:1 mixture of pentane:decane resulting in the bleaching of the bright-yellow mixture and the formation of *n*-pentyl hydride (**2**) and *n*-decyl hydride (**4**). The solution was again quenched with carbon tetrachloride at low temperature and analyzed by ^{1}H NMR spectroscopy, showing a 1:1.1 ratio of Tp′Rh(L)(*n*-pentyl)(Cl) (**2-Cl**) and Tp′(L)(*n*-decyl)(Cl) (**4-Cl**) (eq 4). This excellent agreement supports the validity of the assumptions that were made and further supports the notion that coordination to the methylene C−H bond is 1.5 times faster than coordination to the terminal C−H bond. It is also worth noting that the selectivity between longer chain hydrocarbons is indeed *less* than that seen between shorter chain hydrocarbons. This is in contrast to results reported using [Cp*Rh(PMe₃)] in mixtures of hydrocarbons.[14] In this study, the relative rates of C−H activation in different hydrocarbons was reported to increase linearly as the chain length increased from ethane to *n*-dodecane. This observation can be interpreted in terms of a more "sticky" [Cp*Rh(PMe₃)] fragment, in which dissociation (k_d) is less competitive with migration to the end of the chain. Likewise, the rearrangement of rhodium from one end of a 10-carbon chain to the other reported by Flood is consistent with {[1,4,7-triazacyclononane]Rh[P(OMe)₃]} being a more "sticky" metal fragment.[15] The $Cr(CO)_5$ complexes suggested by Harris are apparently less "sticky" and undergo dissociation during rearrangement.[9]
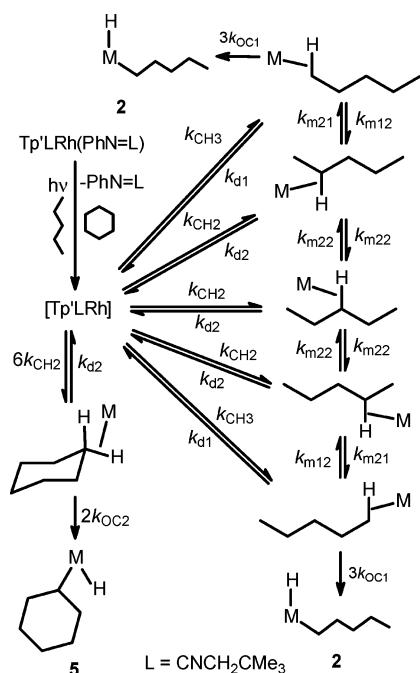

$$(4)$$
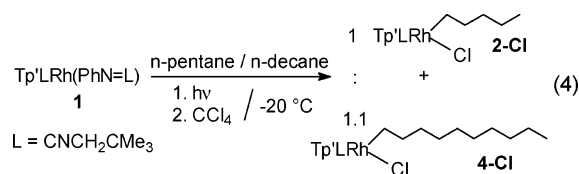
Competitive Selectivity Experiment of Tp′Rh(L) in Pentane/Cyclohexane. Competition experiments in pentane/propane yielded relative rates for the coordination of primary C−H bonds vs secondary C−H bonds and were further supported by the results from the competition experiment with pentane/decane. It was expected that these rates would apply to similar types of bonds in other competition experiments. For example, the methylene C−H bonds of cyclohexane would be expected to coordinate to the [Tp′Rh(L)] fragment at a similar rate as the methylene C−H bonds of pentane, as the methylene groups are in an unstrained conformation, similar to that of a linear alkane. While axial and equatorial C−H bonds in cyclohexane are distinct, their interconversion is facile and can be compared to a linear alkane which does not exist in solution in a single all-trans staggered conformation. If we assume that these methylene groups are comparable, the coordination of pentane and cyclohexane to [Tp′Rh(L)] should be predictable since k_{CH_3}/k_{CH_2} has already been determined. With pentane, coordination to a methylene leads to migration and activation of the terminal methyl group exclusively, i.e., no secondary

(14) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.
(15) Flood, T. C.; Janak, K. E.; Iimura, M.; Zhen, H. *J. Am. Chem. Soc.* **2000**, *122*, 6783.

Scheme 4

Tp'LRh(PhN=L)
1
hv, -PhN=L

[Tp'LRh]

$3k_{OC1}$
k_{CH3}
k_{m21} k_{m12}
k_{d1}
k_{CH2}
k_{d2}
k_{m22} k_{m22}
k_{CH2}
k_{d2}
k_{CH2}
k_{d2}
k_{m22} k_{m22}
k_{CH2}
k_{d2}
k_{CH3}
k_{d1}
k_{m12} k_{m21}
$3k_{OC1}$

$6k_{CH2}$ k_{d2}

$2k_{OC2}$

2

5

L = CNCH$_2$CMe$_3$ **2**

activation occurs. With cyclohexane, however, *only* secondary C−H bonds are available for activation. The lack of observed secondary activation in linear alkanes most likely is a result of the very slow rate of secondary oxidative cleavage (k_{OC2}) as compared to the rate of primary oxidative cleavage ($k_{OC1} = k_{OC}{}^H$). By assumption that the rate of coordination to a secondary C−H bond is the same in linear and cyclic alkanes, a simulation of the observed product ratio in a competitive selectivity experiment with pentane/cyclohexane, the relative rates of oxidative cleavage of the secondary C−H bond (k_{OC2}) vs the primary C−H bond (k_{OC1}) could be determined. These pathways and the corresponding rate constants are shown in Scheme 4.

As before, a 1:1 solution of pentane/cyclohexane and **1** was irradiated at −20 °C to give both *n*-pentyl hydride **2** and cyclohexyl hydride (**5**) complexes and then quenched with carbon tetrachloride. The product ratio of **2-Cl**:Tp′(L)Rh-(cyclohexyl)(Cl) (**5-Cl**) was 6.5:1 (eq 5). Simulation of the product ratio gives a relative rate ratio of $k_{OC1}/k_{OC2} = 64$, assuming that the primary and secondary σ-alkane complexes are at the same free energy. In other words, the rate of oxidative cleavage of a primary C−H bond is 64 times faster than the oxidative cleavage of a secondary C−H bond in this system, all other things being equal. This is consistent with the lack of observation of secondary activation in linear alkanes. Since the kinetic simulation only gives a difference in barrier heights for primary vs secondary activation and we do not know the relative energies of the primary and secondary σ-alkane complexes, the k_{rel} of 64 also contains in it the equilibrium constant between these two species. That is, $k_{rel} = 64(K_{12}) = k_{OC1}/k_{OC2}(K_{12})$, where K_{12} is the equilibrium constant for the formation of the secondary σ-alkane complex from the primary σ-alkane complex. In the kinetic Scheme 4, K_{12} appears as the ratio k_{m12}/k_{m21}, which was arbitrarily set to 1 in the absence of experimental information.

It should also be noted that a large isotope effect exists in the activation of cyclohexane. A 1:1 mixture of pentane:cyclohexane-d_{12} shows *no observable* activation of cyclohexane.

Tp'LRh(PhN=L)
1
L = CNCH$_2$CMe$_3$

1. hv
2. CCl$_4$ / −20 °C

6.5 : 1

Tp'LRh—Cl **2-Cl**
+
Tp'LRh—Cl **5-Cl**

(5)
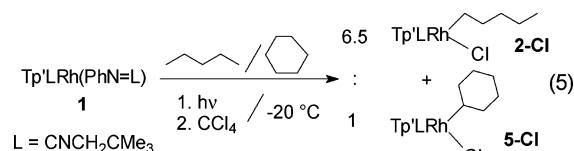
In fact, a 1:4 mixture of pentane:cyclohexane-d_{12} had to be used to observe an appreciable amount of activated C$_6$D$_{12}$. There is a minimal amount of Tp′Rh(L)Cl$_2$ that is formed during the quench in the reaction due to the lability of the activated C$_6$D$_{12}$ product. (In the activation of C$_6$D$_{12}$ in the absence of another alkane, the formation of Tp′Rh(L)Cl$_2$ can be seen upon CCl$_4$ quench.) The quantity of dichloride formed was assumed to represent activation of C$_6$D$_{12}$ in the competition experiment and therefore was combined with Tp′Rh(L)(C$_6$D$_{11}$)(Cl) (**5-Cl**-d_{11}) to determine the correct product ratio. Direct comparison of the product ratios from the separate activation experiments of pentane/cyclohexane and pentane/cyclohexane-d_{12} yields a normal kinetic isotope effect, $k_H/k_D = 3.33$ for the overall process of oxidative addition (alkane coordination plus oxidative cleavage). Many examples exist in the literature where normal kinetic isotope effects for alkane oxidative addition are observed.[6,16] Unfortunately, in the present case we cannot tell if the isotope effect is due to binding of the deutero vs proteo alkane or cleavage of the CH/CD bond.

Competitive Selectivity Experiment of Tp′Rh(L) in Pentane/Cyclopentane. The activation of pentane vs cyclopentane has also been investigated. Because of the rigid and open conformation of the cyclopentane ring, it was not assumed that the rate of methylene coordination is the same as in a linear alkane. Scheme 5 shows the possible pathways for this experiment. The scheme shows different rates for the coordination of the two types of methylene bonds (k_{CH_2} vs $k_{CH_2'}$). However, the same rate for oxidative cleavage of a methylene-alkane complex as in the cyclohexane/pentane experiment (k_{OC2}) was used in the kinetic model.[17] **1** was irradiated in a 1:1 mixture of pentane and cyclopentane at −20 °C to give a mixture of *n*-pentyl hydride (**2**) and cyclopentyl hydride (**6**). The resulting products were quenched with carbon tetrachloride at low temperature showing a 4.5:1 product ratio of **2-Cl**:Tp′(L)(cyclopentyl)(Cl) (**6-Cl**) (eq 6). In the kinetic simulation, $k_{CH_2'}$ was adjusted to match the observed product distribution. The best-fit ratio $k_{CH_2}/k_{CH_2'}$ showed that the rate of coordination to a methylene of cyclopentane was 1.7 times more rapid than the rate of coordination to a methylene of cyclohexane.

Tp'LRh(PhN=L)
1
L = CNCH$_2$CMe$_3$

1. hv
2. CCl$_4$ / −20 °C

4.5 : 1

Tp'LRh—Cl **2-Cl**
+
Tp'LRh—Cl **6-Cl**

(6)
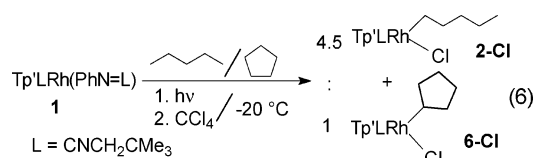
Competitive Selectivity Experiment of Tp′Rh(L) in Cyclopentane/Cyclohexane. From the results of the simulation of the competitive selectivity experiments of pentane/cyclohexane and pentane/cyclopentane, a ratio for $k_{CH_2'}/k_{CH_2} = 1.7$, i.e.,

(16) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585.
(17) Alternatively, one could formulate a model in which binding was the same but the rate of oxidative cleavage was different for the two types of methyl group C−H bond. The *relative* rates would be the same as those found with the present model.

Scheme 5

Scheme 6
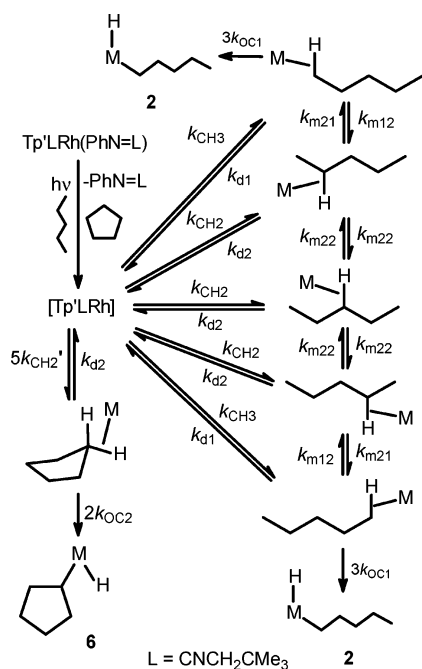
a value representing the relative coordination abilities of cyclopentane vs cyclohexane, was determined. To examine this selectivity experimentally, a direct competition experiment was performed in a 1:1 mixture of cyclopentane/cyclohexane. A product ratio of 1.9:1 in favor of cyclopentane activation was observed (eq 7). Since the rate-determining step in this competition involves coordination to the cycloalkane substrate and the subsequent C–H oxidative cleavage is irreversible under the reaction conditions, this ratio reflects k_{CH_2}/k_{CH_2} for these two substrates.[17] The agreement between the ratios of these independent experiments argues that the kinetic assumptions made in the simulations are reasonable.
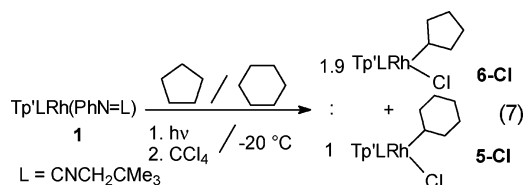

Competitive Selectivity Experiment of Tp′Rh(L) in Pentane/Isobutane. A competition experiment with *n*-pentane and isobutane probed the effect sterics have on the coordination of a methyl group. The two primary methyl groups of pentane compete with the three branched primary methyl groups of isobutane. Scheme 6 shows the possible pathways with one new rate constant, k_{CH_3}' for coordination to the branched methyl group. The rate for k_{CH_3} is known from the previous selectivity experiments. **1** was irradiated in a 1:1 mixture of *n*-pentane: isobutane at −20 °C, and the pentyl hydride (**2**) and isobutyl hydride (**7**) products were quenched with carbon tetrachloride to give the stable alkyl chloride products **2-Cl** and Tp′Rh(L)-(*i*-butyl)(Cl) (**7-Cl**). The products were found to be a 1.35:1 ratio in favor of activation of *n*-pentane (eq 8). Simulation of the results was carried out assuming two different rate constants for coordination to the methyl group of pentane (k_{CH_3}) vs isobutane (k_{CH_3}'). Varying only the ratio of k_{CH_3}/k_{CH_3}' gives a
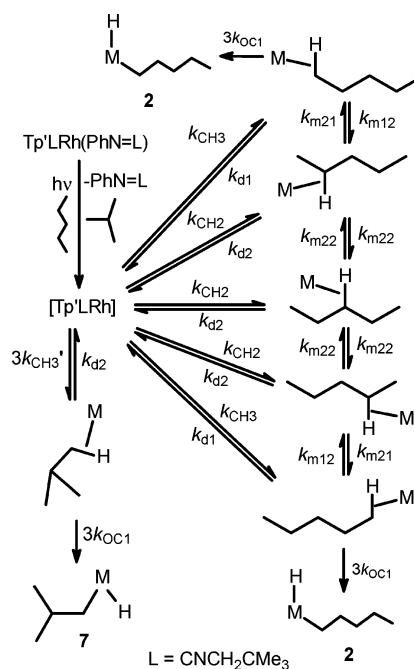
value of 1.2:1, indicating almost no preference for the coordination to the primary C–H bond of a straight chain methyl group vs a branched methyl group.
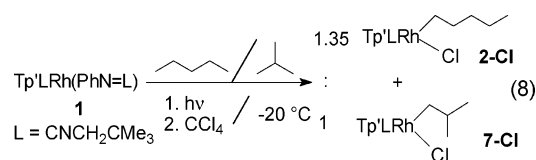
It might have been expected that coordination to isobutane would be statistically favored because of the existence of three primary methyl groups, yet the reverse kinetic preference was observed. However, one must take into account that the preferred coordination is to the methylene C–H bond of the straight-chain alkane of which *n*-pentane has three and *i*-butane has zero. In this experiment, it was assumed that the rate of oxidative cleavage of a primary methyl C–H bond (k_{OC}^{H}) was equal in both alkanes and that no coordination to the tertiary C–H bond had occurred. Observation of tertiary C–H bond activation with the Tp′Rh(L) system has never been observed, so it is assumed that in these compounds coordination to the tertiary C–H bond does not occur.

Evidence for a lack of tertiary C–H σ-complex comes from observation of Tp′Rh(L)(CH$_2$CHMe$_2$)D. This complex scrambles deuterium into the α-position over the course of 15 min to generate Tp′Rh(L)(CHDCHMe$_2$)H, but at no time is scrambling of deuterium into the other methyl groups observed. Such a migration would have proceeded through a [1,3] C–H shift or via an intermediate tertiary σ-alkane complex, but both can apparently be ruled out. An X-ray structure of **7-Cl** shows no unusual interactions of the alkane group with the metal or ligands (see Supporting Information). It is also interesting to note that there is almost no steric effect associated with the rate of binding to a methyl group in a branched vs a linear hydrocarbon. In contrast, Bergman has seen a thermodynamic

Scheme 7
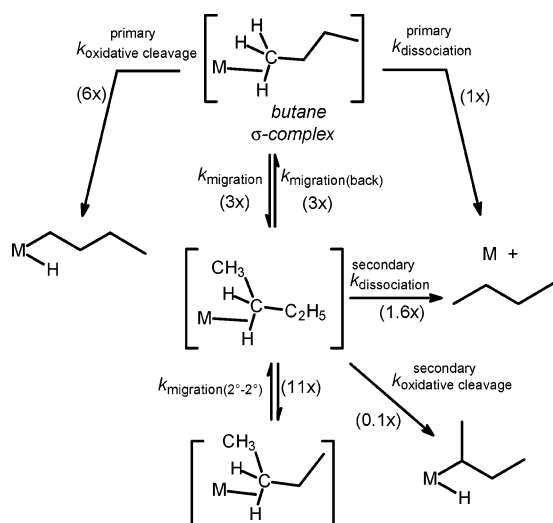
preference for cleavage of C−H bonds in less branched primary C−H bonds.[18]

Conclusion

The activation of hydrocarbon mixtures in neat solution has allowed for the determination of the kinetic selectivity for alkane coordination in the [Tp′Rh(L)] complex. Scheme 7 gives a general picture of the pathways for coordination and activation in the case of butane upon formation of the primary alkane complex. The rates of the processes are given in relation to the rate of primary dissociation (arbitrarily assigned as 1). Upon formation of the primary alkane complex, activation is 6 times more likely to occur than primary dissociation. In addition, migration to form the secondary alkane complex is 3 times more likely to occur than dissociation. Upon formation of the secondary alkane complex, four processes are possible. Dissociation from the secondary position is 1.6 times more likely to occur than dissociation from the primary alkane complex. The secondary alkane complex is twice as likely to migrate back to form the primary alkane complex as to dissociate but is 7 times more likely to migrate to the adjacent secondary position than dissociate. The slowest process is the activation of the secondary C−H bond. The alkane is 16 times more likely to dissociate from the secondary alkane complex than it is to activate and 110 times more likely to migrate to an adjacent secondary C−H bond; hence, no secondary activation is observed.

The studies have shown that there is a slight kinetic selectivity for coordination of a methylene group vs a methyl group of 1.5. The coordination to a methyl group of a branched alkane vs a straight chain alkane occurs at the same rate and the observed product ratio is a result of the preferred rate of coordination to the methylene C−H bonds of the straight chain alkane. The ability to determine these relative rates for coordination in various types of alkane complexes has made it possible to determine the relative rate of the oxidative cleavage of secondary C−H bonds, which had previously been undetermined. With primary and secondary σ-alkane complexes of the same free energy, primary oxidative cleavage is 64 times faster

than secondary oxidative cleavage. The above studies allow for all relative rates involved in the processes of oxidative addition and reductive elimination of an alkane to be determined, thereby expanding the fundamental understanding of the factors involved in alkane activation. The relative energies of the primary and secondary σ-alkane complexes remain to be determined, as do their absolute energies. In addition, it has been determined that a moderate normal isotope effect occurs for the activation of cyclohexane.

It is also interesting to consider the distribution of σ-alkane complexes during these rapid rearrangements that occur prior to C−H oxidative cleavage. Graphs of these distributions are included in the Supporting Information. For the competitions involving linear alkanes (e.g., pentane vs propane) one can see the prevalence of secondary σ-alkane complexes over primary σ-alkane complexes. As a result of this prevalence, the formation of the final activation products occurs at different rates. While initially both propyl hydride and pentyl hydride products form in 1:1 ratio, the longevity of the pentane secondary σ-alkane complexes continues to "feed" the production of the pentyl hydride product, resulting in its net favorability in the competition. A similar propagation is seen in the decane/pentane competition. The competition between pentane and cyclohexane is also quite interesting to monitor. The cyclohexane σ-alkane complex dominates the species present (it has 6 methylenes compared to only 3 in pentane) and persists for a long time, although this is only because many dissociations and reassociations occur without productive C−H oxidative cleavage.

Experimental Section

General. All operations were performed under a nitrogen atmosphere, either in a Vacuum Atmosphere Corporation glovebox or on a high vacuum line using modified Schlenk techniques. Benzene-d_6 was purchased from the Cambridge Isotope Lab and distilled under vacuum from dark-purple solutions of benzophenone ketyl and stored in ampules with Teflon-sealed vacuum line adaptors. Alkanes were made olefin free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water, and distilling from dark-purple solutions of benzophenone ketyl. Preparation of KTp′,[19] Tp′Rh(L)(η^2-PhN=L) (**1**),[20] Tp′Rh(L)(*n*-pentyl)-(Cl),[10] Tp′Rh(L)(*n*-propyl)(Cl),[21] Tp′Rh(L)(c-hexyl)(Cl),[10] Tp′Rh(L)-(c-pentyl)(Cl),[10] Tp′Rh(L)Cl₂,[21] and neopentyl isocyanide (L)[22] have been previously reported. The isobutyl Grignard reagent was purchased from Aldrich Chemical Co. and used as received. All ¹H NMR spectra were recorded on a Bruker AMX400 or Bruker AVANCE400 Spectrometer. All chemical shifts are reported in ppm relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances (benzene-d_6, δ 7.15). Elemental analysis was performed by Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray crystal structure determination of complex **4**. Frieden's KINSIM/FITSIM program was used to carry out the kinetic simulations.[23]

Preparation of Tp′Rh(Cl)(C₁₀H₂₁)(CNCH₂C(CH₃)₃) (4-Cl). An ampule was charged with 10 mg of **1** and dissolved in 2 mL of *n*-decane. The resulting bright-yellow solution was irradiated with $\lambda > 345$ nm for 20 min at −20 °C. The resulting pale-yellow solution was quenched in vacuo with 2 mL of carbon tetrachloride. The solution was allowed

(18) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

(19) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99.
(20) Hessell, E. T.; Jones, W. D. *Organometallics* **1992**, *11*, 1496.
(21) Wick, D. D.; Jones, W. D. *Inorg. Chem.* **1997**, *36*, 2723.
(22) Schuster, R. E. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 772.
(23) Professor Carl Frieden, Department of Biological Chemistry, Box 8231, Washington University School of Medicine, St. Louis, MO 63110. Available on the web; search KINSIM.

to stand at −20 °C for 2 h, after which time excess solvents were removed in vacuo. The resulting yellow oil was isolated. ^{1}H NMR (C_6D_6): Tp′methine, 5.573 (s, 1H), 5.627 (s, 1H), 5.706 (s, 1H); Tp′methyl, 2.093 (s, 3H), 2.156 (s, 3H), 2.228 (s, 3H), 2.407 (s, 3H), 2.779 (s, 3H), 2.991 (s, 3H); CNR, 2.675 (AB$_q$, 2H), 0.732 (s, 9H); $CH_2(CH_2)_8CH_3$ 0.883 (t, 3H), 1.462 (complex mult., 2H), 1.734 (complex mult., 2H), 3.320 (complex mult., 1H), 3.465 (complex mult., 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): 12.27, 12.76, 12.98, 14.32, 14.62, 14.67 (s, pz$C$H$_3$), 18.81 (d, J_{Rh-C} = 19 Hz, Rh(CH$_2$(CH$_2$)$_8$CH$_3$)), 23.05, 27.38, 29.80, 30.11, 30.22, 30.40, 32.30, 33.42, 34.27 (s, Rh(alkyl$C$H$_2$)), 26.63 (NCH$_2$C(CH$_3$)$_3$), 31.94 (s, NCH$_2$$C$(CH$_3$)$_3$), 56.22 (s, N$CH_2$C(CH$_3$)$_3$), 106.65, 107.73, 108.53 (s, pz$C$H), 142.56, 142.83, 144.36, 150.76, 151.12, 153.09 (s, pz$C$q).

Preparation of Tp′Rh(Cl)(C$_4$H$_9$)(CNCH$_2$C(CH$_3$)$_3$) (7-Cl). To a stirred solution of 75 mg (0.132 mmol) of **2** in 15 mL of THF was added, dropwise over a period of 2 min, 80 μL (0.160 mmol) of 2.0 M *i*-butylMgCl in 2 mL of THF. The solution lightened in color upon addition of the Grignard reagent. The mixture was allowed to stir for 15 min, and the excess Grignard reagent was quenched with saturated NH$_4$Cl(aq) until all had reacted to give a clear solution. The solution was extracted with THF (3 × 20 mL) and dried over MgSO$_4$. The mixture was filtered through a cotton plug and concentrated under vacuum to give an orange-yellow solid. The solid was recrystallized from CH$_2$Cl$_2$ at −20 °C and dried under vacuum to give 41 mg (46%) as yellow block crystals. ^{1}H NMR (C_6D_6): Tp′methine, 5.551 (s, 1H), 5.587 (s, 1H), 5.712 (s, 1H); Tp′methyl, 2.099 (s, 3H), 2.161 (s, 3H), 2.216 (s, 3H), 2.376 (s, 3H), 2.823 (s, 3H), 2.976 (s, 3H); CNR, 0.656 (s, 9H), 2.682 (s, 2H); CH$_2$CH(CH_3)$_2$, 1.398 (d, J = 6.5 Hz, 3H), 1.536 (d, J = 6.6 Hz, 3H); CH$_2$CH(CH$_3$)$_2$, 3.35 (complex mult., 1H); CH_2-CH(CH$_3$)$_2$, 2.97 (obs. mult., 1H), 2.80 (obs. mult., 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): 12.31, 12.71, 13.01, 14.78, 14.95, 15.44 (s, pz$C$H$_3$), 25.65, 25.98 (s, RhCH$_2$CH(CH$_3$)$_2$), 26.66 (NCH$_2$C(CH$_3$)$_3$), 28.01 (d, J_{Rh-C} = 19 Hz, Rh(CH$_2$CH(CH$_3$)$_2$)), 31.64 (s, NCH$_2$$C$(CH$_3$)$_3$), 32.60 (s, RhCH$_2$$C$H(CH$_3$)$_2$), 56.43 (s, N$CH_2$C(CH$_3$)$_3$), 106.71, 108.02, 108.70 (s, pz$C$H), 142.55, 142.68, 144.38, 150.55, 151.02, 152.85 (s, pz$C$q). Anal. Calcd for C$_{25}$H$_{39}$BN$_8$RhCl·CH$_2$Cl$_2$: C, 50.91; H, 7.18; N, 16.62. Found: C, 51.24; H, 7.38; N, 15.77.

Sample Preparation and Irradiation Experiments for Competition Reactions. A 5-mm NMR tube was charged with Tp′Rh(L)(η^2-

PhN=C=NCH$_2$C(CH$_3$)$_3$), and the proper ratio of competing alkanes as listed below.[24] The solution was cooled to −20 °C and irradiated with λ > 345 nm for 20 min. The resulting bleached solution was immediately cooled to 77 K, and carbon tetrachloride was added under inert conditions. The solution was warmed to −20 °C and allowed to stand at this temperature for 2 h. ^{1}H NMR spectra were recorded after removal of solvent and dissolution in C_6D_6 and the appropriate resonances (see below) integrated. Ratios of two resonances were compared in each compound. Experiments were done in duplicate, giving identical results in each case. *n*-Pentane/*n*-propane, 2.37, 2.62 mmol/3.21, 3.45 mmol, δ 2.38, 2.99/δ 2.33, 2.97; *n*-pentane/*n*-decane, 0.25 mL/0.42 mL, δ 2.99, 2.38/δ 3.01, 2.41; *n*-pentane/isobutane, 0.5 mL/0.25 g, δ 2.15, 2.23/δ 2.16, 2.21; *n*-pentane/cyclohexane, 0.50 mL/0.47 mL, δ 2.99, 2.38/δ 3.10, 2.48; *n*-pentane/cyclohexane-d_{12}, 0.24 mL/0.89 mL, δ 2.99, 2.38/δ 3.10, 2.48; *n*-pentane/cyclopentane, 0.50 mL/0.41 mL, δ 2.99/δ 2.93; cyclopentane/cyclohexane, 0.43 mL/0.50 mL, δ 2.31/δ 2.48.

Deuterium Migration in Tp′Rh(L)(CH$_2$CHMe$_2$)D. To a resealable NMR tube was added 14 mg of the *i*-butyl derivative **7-Cl** and 22 mg of [Cp$_2$ZrD$_2$]$_2$. Benzene (0.55 mL) was added via a syringe. The mixture was shaken vigorously for 1 min and placed into a preshimmed probe. The isomerization and migration of the deuterium label was monitored by $\{^1H\}^2H$ NMR spectroscopy at 26 °C as described in the text.

Supporting Information Available: Complete ref 7. A summary of the kinetic simulations, schemes, and distributions of species, as well as crystallographic data, intramolecular distances and angles, and positional and thermal parameters for **7-Cl**. NMR spectra for competition experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042152Q

(24) Amounts were measured using volume for all cases because of the volatility of the solvents used, except isobutane and propane, which were measured by difference using mass.