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Deuterium Migration in $\{(1,4,7\text{-Triazacyclononane})Rh(alkyl)D[P(OMe)_3]\}^+$. Evidence for Mobility of Rhodium along Linear Alkane Chains in Inferred Rhodium−Alkane Complexes

Thomas C. Flood,* Kevin E. Janak, Masanori Iimura, and Hongshi Zhen

Department of Chemistry
University of Southern California
Los Angeles, California 90089-0744

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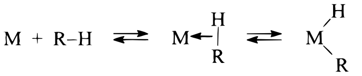
With increasing evidence for the existence of complexes of intact alkanes with transition metals ("σ complexes") as intermediates in many oxidative-addition/reductive-elimination reactions of alkanes (equation 1), there is considerable interest in learning about their structure, bonding, energetics, and dynamical properties.[1−5] Previously, we reported[3d] indirect evidence for the methane complex $[Cn^*Rh(CH_4)(PMe_3)]^+$.[6] We now present indirect evidence that σ complexes of higher alkanes with rhodium in the triamine environment also form as transient intermediates, and that the metal moves along the chain with a barrier that is slightly below the barrier to alkane dissociation.

Alkyl hydride complexes $[CnRh(H)(R)(L)]X$ {Cn = 1,4,7-triazacyclononane;[6] R = Me, Et, Bu, hexyl, and decyl; L = $P(OMe)_3$; $X^- = {}^-OTf$ (triflate, $CF_3SO_3^-$) or $^-BAr_4$ ($^-B[3,5\text{-}(CF_3)_2C_6H_3)]_4$)} have been prepared in 21−32% overall yields from $RhCl_3(H_2O)_n$ by methods completely analogous to those reported for $[CnRh(H)(R)(PMe_3)]X$ (R = Me, Et)[7] and fully characterized. In benzene from 40 to 80 °C, the $[CnRh(H)(R)(L)](BAr_4)$ all react with clean first-order kinetics and quantitative formation of $[CnRh(H)(C_6H_5)(L)](BAr_4)$, which has also been characterized. Arrhenius plots of the benzene reaction give $\Delta H^\ddagger$ ranging from 29.7 to 33.1 kcal/mol and $\Delta S^\ddagger$ from 9.6 to 18.4 eu. Reaction rates of the Et, Bu, hexyl, and decyl derivatives are very similar, while the methyl compound is about 10-fold slower. The size of $\Delta S^\ddagger$ is consistent with a dissociative mechanism for replacement of alkane by benzene, and there is no dependence of the rate of loss of hexane from $[CnRh(H)(hexyl)(L)](BAr_4)$ on benzene concentration in C_6F_6 solution.[8]



$$M + R{-}H \rightleftharpoons M{\leftarrow}\overset{H}{\underset{R}{|}} \rightleftharpoons M\langle^{H}_{R} \qquad (1)$$

Deuteration is effected by reduction of $[CnRh(R)(L)(OTf)](BAr_4)$ with $NaBD_4$ in THF at temperatures between −10 and 10 °C.[9] A Rh-D resonance appears at δ −16.3 to −16.5 ppm in the ^2H NMR spectrum. The initial deuterium content in the alkyl group is variable but generally less than 5%, and is distributed in the α-methylene and slightly into the internal methylene sites (we cannot tell which internal methylenes since they are not resolved) and a small amount on the ω-carbon.[10] The mechanism of the minor incorporation of label into the alkyl group during synthesis is not certain, but after formation of the alkyl deuteride is complete, *the amount in the internal methylenes does not increase* with time at any temperature even during alkane loss. In contrast, the label content of the α-methylene does increase with time and temperature, as anticipated from the results with $[Cn^*Rh(D)(CH_3)(PMe_3)]^+$.[3d] The rate of migration of deuterium to the α carbon at 4 °C $[Rh(H)(CHDC_5H_{11})]$ ($k = 4.3 \times 10^{-4}$ s^{-1})[11] is comparable to the rate of $[Rh(D)(C_6H_{13})]^+$ formation ($k_\alpha[BD_4^-] = 5.5 \times 10^{-5}$ s^{-1}), with the equilibrium constant $K = [Rh(H)(CHDC_5H_{11})]/[Rh(D)(C_6H_{13})]$ close to 1.7, statistically corrected.

Most importantly in the present context, *the deuterium label is also found to migrate into the ω-methyl group*, although more slowly than into the α-methylene (Figure 1). The first-order rate constant for equilibration of deuterium from the α-methylene into the ω-methyl of the rhodium alkyl in C_6H_6 at 39.6 °C is 5.6 (±0.2) × 10^{-6} s^{-1} for the butyl derivative and 3.5 (±0.2) × 10^{-6} s^{-1} for

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[5] Theoretical calculations of alkane complexes: (a) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc*. **1989**, *111*, 9177. (b) Cundari, T. R. *J. Am. Chem. Soc*. **1992**, *114*, 10557. (c) Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118. (d) Koga, N.; Morokuma, K. *J. Am. Chem. Soc*. **1993**, *115*, 6883. (e) Cundari, T. R. *Organometallics* **1993**, *12*, 1998. (f) Margl, P.; Ziegler, T.; Bloechl, P. E. *J. Am. Chem. Soc*. **1995**, *117*, 12625. (g) Zaric, S.; Hall, M. B. *J. Phys. Chem.* **1997**, *101*, 4646. (h) Martin, R. L. *J. Am. Chem. Soc*. **1999**, *121*, 9459.

[6] Informally, 1,4,7-triazacyclononane (tacn) = Cn, and 1,4,7-trimethyl-(tacn) = Cn*. Previously we used the standard abbreviation "tacn", and called 1,4,7-trimethyl(tacn) "Cn." Given that tacn is tractable in organometallic systems, the new abbreviations are more analogous to Cp/Cp* and Tp/Tp*.

[7] Zhou, R.; Wang, C.; Hu, Y.; Flood, T. C. *Organometallics* **1997**, *16*, 434.

[8] Rate constants at 69.6 °C: in neat C_6D_6, 1.97 (±0.07) × 10^{-4} s^{-1}; in 20 vol % C_6D_6 in C_6F_6, 2.03 (±0.04) × 10^{-4} s^{-1}. The rate of loss of methane from $Tp^*Rh(H)(CH_3)(CN\text{-}t\text{-}Bu)$ has been reported to be first order in benzene concentration (ref 3j).

[9] The rate of exchange of the Rh−D on to the α-carbon is very sensitive to the extent of exposure to ambient light, so *all* work with the alkyl hydrides was done with careful exclusion of light.

[10] Methanol solvent provides the best ^1H NMR dispersion of the rhodium butyl, hexyl, and decyl groups, where the ω-methyl resonance is always a second-order triplet at δ 0.8−0.9 ppm. The ^{13}C resonance of the α-carbon in all cases is a doublet of doublets in the range of δ −1 to 8.4 ppm with J_{RhC} = 23−24 Hz and J_{PC} = 13 Hz. In the $^1H-^{13}C$ correlation spectrum of the butyl derivative, this ^{13}C resonance correlates with a ^1H peak at δ 0.9 to 1.1 ppm which is quite broad since the α-protons are coupled to Rh, P, two β-H, and each other (diastereotopic with slightly different δ). All the other alkyl chain protons for all the rhodium alkyls are contained in a broad envelope at δ 1.2 to 1.4 ppm.

[11] Time−concentration data for [Rh](hexyl)(OTf), [Rh](D)(hexyl), and [Rh](H)(hexyl-α-*d*) in the deuteration/α-equilibration experiment ([Rh] ≡ $[CnRh(L)]^+$), and for [Rh](D)(hexyl), [Rh](H)(hexyl-α-*d*), [Rh](H)(hexyl-ω-*d*), and [Rh](H)(Ph) in the α → ω scrambling reaction in neat benzene were fitted to kinetic models based on Scheme 1 using the iterative kinetics program "Gear", copyright 1995 by F. J. Weigert. (a) Stabler R. N.; Chesick, J. *Int. J. Kinet.* **1978**, *10*, 461. (b) Weigert, F. J. *Comput. Chem.* **1987**, *11*, 273.

10.1021/ja000104+ CCC: $19.00

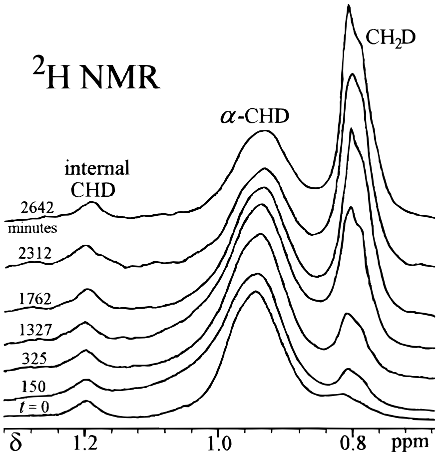


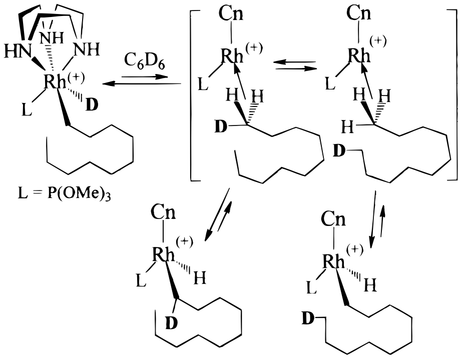
Figure 1. ^{2}H NMR spectra of the butyl region of {CnRh(butyl)(H)-[P(OMe)$_3$]}$^+$-d_1 in CH$_3$OH after the indicated times at 39.6 °C. The ^{2}H C$_2$−C$_5$ resonances at δ 1.2−1.3 are present after synthesis and do not increase in intensity. Complete Rh(D)(butyl)/Rh(H)(CHDC$_3$H$_7$) equilibration and some α → ω scrambling occur during NaBD$_4$ reduction of [CnRh(butyl)(L)(OTf)](BAr$_4$) at 10 °C.

the hexyl.[11,12] These rate constants can be compared with those in the same reactions for formation of [CnRh(H)(C$_6$H$_5$)(L)]$^+$: 1.8 × 10^{-6} s^{-1} from butyl and 1.5 × 10^{-6} s^{-1} from hexyl all in C$_6$H$_6$ at 39.6 °C. The α → ω migration is particularly striking for the decyl complex with 8 intervening methylenes. Work is in progress to determine rates of appearance of deuterium on the ω carbon and rates of [CnRh(H)(C$_6$H$_5$)(L)]$^+$ formation as a function of alkyl group chain length.

Heating [CnRh(H)(Bu)(L)](BAr$_4$) at 50 °C in C$_6$F$_6$ under 13 atm of methane shows a buildup of [CnRh(H)(CH$_3$)(L)]$^+$,[13] but heating [CnRh(H)(hexyl)(L)]$^+$ at 50 °C in 6 vol % of C$_6$D$_6$ in C$_6$F$_6$ under 11 atm of ^{13}CH$_4$ shows no detectable [CnRh(H)-(^{13}CH$_3$)(L)]$^+$ in the ^{13}C NMR spectrum checked after 2 half-lives of clean [CnRh(D)(C$_6$D$_5$)(L)]$^+$ formation. Thus, activation of methane does occur in the absence of benzene, but methane clearly does not compete with benzene in trapping the intermediate.

As shown in Scheme 1, reversible reductive elimination to a coordinated alkane complex readily explains the scrambling results. Within this complex, the metal would migrate along the alkane chain from end-to-end presumably equilibrating among all of the isomeric species with the metal coordinated to each of the methylene/methyl groups in turn. Oxidative addition to form the entire range of *sec*-alkyl hydrides probably occurs, but these would be relatively unstable and so should not be detectable.[14]

Scheme 1



It is unlikely that the α → ω (end-to-end) deuterium migration involves attack of {CnRh[P(OMe)$_3$]}$^+$ on a liberated alkane in view of the competition experiment mentioned above between methane and C$_6$D$_6$. The same observation rules out an α−ω rearrangement by attack of {CnRh[P(OMe)$_3$]}$^+$ on the methyl end of an intact [CnRh(H)(alkyl-α-d_1)(L)]$^+$ followed by reductive elimination from the deuterated end.[15] Another group of mechanisms that must be considered involves intervention of a nitrogen-dissociated intermediate.[16] Coordinative unsaturation in [(κ^2-Cn)Rh(H)(R)(L)]$^+$ would make α- and β-elimination/hydride-readdition mechanisms possible, the α accounting for metal-to-α-carbon equilibration, and the β for end-to-end isomerization. However, a β-elimination path would necessarily scramble deuterium label from the metal onto the β carbon, which is quite inconsistent with the observed clean migration of the Rh−D onto only the α and ω carbons in [CnRh(H)(R)(L)]$^+$-d_1 as shown in Figure 1. A mechanism involving a cyclic intermediate from oxidative addition of the ω carbon to yield the Rh$^{\text{V}}$ intermediate {(κ ^{2}-Cn)-Rh(H)$_2$[η^2-CH$_2$(CH$_2$)$_n$-CH$_2$](L)}$^+$ requires this process to be much faster than β elimination scrambling of deuterium onto the β carbon, and yet much slower than α elimination, all of which seems very unlikely. A more likely nitrogen dissociation permutation would be reductive elimination to an intermediate which would then undergo nitrogen dissociation to square-planar [(κ^2-Cn)Rh(alkane)(L)]$^+$, but this mechanism is still consistent with the inference of a σ-complexed alkane intermediate. With the extant data, we cannot evaluate whether the rearranging rhodium−alkane complex is κ^2-Cn or κ^3-Cn.[17]

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[12] Special care is taken to remove all free alkane from the sample before the ^{2}H NMR analysis.

[13] NMR spectra of [CnRh(H)(R)(L)]$^+$ for R = methyl and butyl are different enough that monitoring reaction progress is clear. In pure C$_6$F$_6$ two dominant as-yet-unidentified, rhodium-containing products are formed, but the reaction is not clean. About 18% of methyl hydride (based on total rhodium) is present at 2 half-lives of butyl hydride disappearance.

[14] A referee has suggested that the CH$_2$D ^{2}H NMR resonance at δ 0.8 in Figure 1 could also contain intensity from Rh(H)(*sec*-alkyl) species. We have not seen any evidence for alkyl isomers in any of the ^{13}C spectra of our Rh-(H)(*n*-R) complexes.

[15] The possibility of liberation of alkane from rhodium followed by re-addition of rhodium to the other end of the alkane *in a solvent cage* cannot be assessed rigorously. However, we believe it is unlikely that butane, hexane, and decane would all have the same efficiency for attack by {CnRh-[P(OMe)$_3$]}$^+$ on the CH$_3$ end of the liberated alkane-d_1 in a benzene solvent cage. For a detailed discussion of the improbability of a solvent-caged mechanism for rearrangement of Cp*Rh(D)(Et)(PMe$_3$), see ref 2b.

[16] Nitrogen-dissociated intermediates have been invoked for Tp*Rh(H)-(R)(L) systems: L = CO, ref 2 g; L = CN-*t*-Bu, ref 3j.

[17] Greater reactivity in reductive elimination and oxidative addition of C−C and C−H bonds between 5-coordinate-d^6 and 3-coordinate-d^8 species compared to 6-coordinate and 4-coordinate species has been know for many years (refs 17a (and references therein)−c). However, these reactions *do occur* between 6-coordinate-d^6 and 4-coordinate-d^8 species (refs 17a,d−f). (a) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (b) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889. (c) References 2g and 3e. (d) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492. (e) Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523. (f) Reference 2b.