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Selective C−H Activation of Haloalkanes using a Rhodiumtrispyrazolylborate Complex

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Abstract: Several halogenated substrates are found to participate in C−H bond cleavage reactions with the photochemically generated fragment [Tp′Rh(CNR)] (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate; R = CH_2CMe_3). Reaction with 1- or 3-chloropentane gives only terminal C−H activation products. Reaction with 2-chloropentane gives a mixture of 4-chloropentyl activation product and Tp′Rh(CNR)HCl, arising from β-chloride elimination of the 2-chloropentyl activation product. Activation of chloromethane gives Tp′Rh(CNR)(CH_2Cl)H, with no activation of the C−Cl bond. Dichloromethane, however, gives only C−Cl cleavage product Tp′Rh(CNR)(CH_2Cl)Cl. By comparing the kinetic stabilities of a series of 1-chloroalkane activation products (C_1−C_5), it was found that the chlorine substituent dramatically decreases reductive elimination rates as the substitution is closer to the metal center. With 1-chloroalkanes, there is evidence for the formation of small quantities of C−H cleavage products α to the chloro substituent. Reactions of neopentyl chloride also showed evidence for small quantities of α-chloro C−H activation product. Reactions with the cyclic substrates 1-chlorocyclopentane and 1,1-dichlorocyclopentane yielded a mixture of diastereomeric activation products.

Introduction

Coordinatively unsaturated metal complexes have been used extensively over the past 40+ years in the activation of typically inert C−H bonds.[1] While early examples of metal complexes displaying this type of reactivity often contained Cp (C_5H_5) and the closely related Cp* (C_5Me_5) ligand frameworks,[2] it has been shown that metal complexes containing other moieties,[3,4] such as 3,5-disubstituted trispyrazolylborate (Tp) ligands,[5] were capable of facilitating similar transformations.[6] Specifically, the reactive fragment [Tp′Rh(CNR)] (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate; R = $CH_2C(CH_3)_3$), which can be generated through solution photolysis of Tp′Rh(CNR)(η^2-PhN=C=NR) (**1**), has been shown to activate aryl and alkyl CH bonds in a number of organic compounds.[7]

Despite the abundance of literature describing CH cleavage reactions of alkanes, examples of analogous reactions with functionalized alkanes are relatively scarce.[8] While concern has arisen about the potential of functional groups to react with metal centers in preference to the targeted C−H bonds, it remains an important goal to activate C−H bonds in the presence of possibly reactive functionalities, since this chemistry could ultimately prove useful in the generation of complicated organic species. Early success has been made mainly in the activation

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(2) Early examples of C−H bond activation chemistry using Cp- and Cp*-based metal complexes: (a) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc D* **1970**, 1677. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (d) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(3) "Pincer complexes" containing a rigid tridentate ligand are one example of a class of compounds being explored for use in intermolecular C−H and C−C bond cleavage reactions. For some examples of their utility, see: (a) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017. (b) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (d) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Shimon, L. J. W.; Martin, J.M. L.; Milstein, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 1949. (e) Novak, F.; Speiser, B.; Mohammad, H. A. Y.; Mayer, H. A. *Electrochim. Acta* **2004**, *49*, 3841. (f) Ben-Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390.

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(5) Trofimenko, S. J. *Scorpionates. The Coordination Chemistrry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(6) Examples of C−H bond activation chemistry using Tp-based metal complexes: (a) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375. (c) Jones, W. D.; Duttweiler, R. P., Jr; Feher, F. J.; Hessell, E. T. *New J. Chem.* **1989**, *13*, 725. (d) Jones, W. D.; Hessell, E. T. *Inorg. Chem.* **1991**, *30*, 778. (e) Slugovc, C.; Padilla-Martínez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

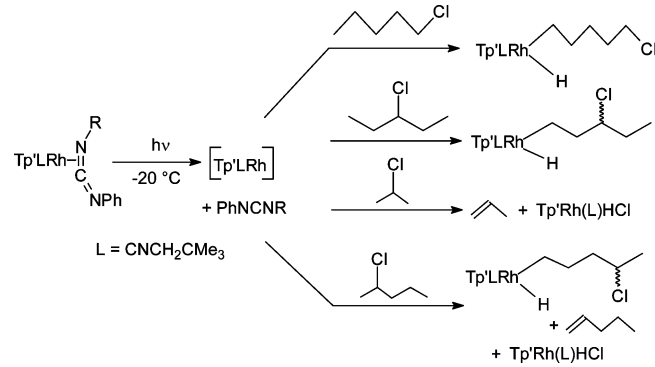
(7) (a) Hessell, E. T.; Jones, W. D. *Organometallics* **1992**, *11*, 1496. (b) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087. (c) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554. (d) Jones, W. D.; Wick, D. D. *Organometallics* **1999**, *18*, 495. (e) Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4484. (f) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974. (g) Northcutt, T. O.; Wick, D. D.; Vetter, A. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 7257. (h) Vetter, A. J.; Flaschenriem, C.; Jones, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 12315.

10.1021/ja9002316 CCC: $40.75

of aryl C−H bonds in functionalized arenes. In particular, Smith[9] and Hartwig[10] have shown that aryl halides could be functionalized through selective cleavage of a C−H bond. This borylation chemistry encompasses an impressive scope of aromatic substrates featuring F, Cl, Br, I, OMe, CF_3, CO_2Et, $CONEt_2$, and CN substituents. Moreover, heterocyclic and asymmetrically substituted compounds have been considered and, depending on the ring substitution pattern and identity of the substituents, functionalization has been observed in positions ortho, meta, and para to ring substitution sites. These borylated arenes serve as effective precursors to useful synthetic targets such as biaryl compounds[11] (via Pd-catalyzed cross-coupling reactions), phenols,[12] diaryl ethers, aryl halides, and *N*-arylanilines.[13] In addition to the above examples, Milstein has shown that iridium "pincer complexes" can be used to cleave selectively the C−H bond ortho to chlorine substitution in aryl chlorides.[14] Also, the use of intermolecular directing groups such as ketones for organic functionalization has been developed, as demonstrated by the work of Murai and Chatani.[15] Legzdins has also seen selective aromatic C−H activation in aryl halides.[16]

While much of the published literature on the activation and functionalization of C−H bonds in compounds containing functional group substitution has centered on aryl substrates, progress has been made in using alkyl substrates in a similar fashion. Specifically, Hartwig has extended his work on borylating substituted arenes to substituted alkanes using $Cp^*Rh(\eta^4\text{-}C_6H_6)$ and $(Cp^*RuCl_2)_2$.[17] In an effort to investigate the reactivity of substituted alkanes with [Tp′Rh(CNR)], we discovered that this reactive fragment does not react with the C−Cl bonds in chloropentanes as indicated in Scheme 1.[18] It

Scheme 1. Major Products in the Reaction of Tp'Rh Fragment with Chloroalkanes



was noted that C−H activation β to a chloro group led to rapid β-chloride elimination, as seen in 2-chloropropane. These results were surprising in light of the fact that the C−Cl bond is weaker than the C−H bond,[19] and 4-coordinate d^8 Rh(I) and Ir(I) complexes are known for their reactivity with alkyl halides.[20] We report here the full study with a variety of halocarbons and the kinetic and thermodynamic stabilities of these products. These studies demonstrate that (1) chlorine substituents dramatically stabilize the alkyl hydride complexes, (2) the C−Cl bond is remarkably unreactive, and (3) a chlorine substituent kinetically disfavors C−H activation at a carbon center.

Results and Discussion

Oxidative Addition Studies. Photolysis of Tp′Rh(L)(η^2-PhN=C=NL) (**1**) (Tp′ = tris-(3,5-dimethylpyrazolyl)borate, L = $CNCH_2CMe_3$) in neat chloromethane solvent at −20 °C results in the formation of Tp′Rh(L)(CH_2Cl)H (**2**) in 70% yield by ^{1}H NMR spectroscopy. A rhodium hydride resonance was observed at δ −14.03, indicating C−H bond activation, with a small J_{Rh-H} = 20 Hz compared to other Tp′Rh(L)(R)H complexes[7] (typical J_{Rh-H} = 24 Hz). Three Tp′ methine resonances were also observed along with six distinct Tp′ methyl resonances indicating an asymmetric Tp′Rh(X)(Y)(Z) complex. In addition, a pair of doublet of doublets were observed at δ 4.77 and 4.99, and assigned as a pair of diastereotopic methylene hydrogens with coupling to each other and to rhodium. The complex was easily converted to the chloroderivative **2-Cl** upon addition of carbon tetrachloride. In addition, **2** was found to be exceptionally stable compared to the nonchlorinated analogue Tp′Rh(L)(CH_3)H (vide infra), which loses methane after a few hours at RT. A minor product was also formed during the photolysis (30%), but it did not contain any metal hydride resonances and was also of the type Tp′Rh(X)(Y)(Z) (see Experimental Section). While this complex could not be identified, it is *not* the C−Cl activation product Tp′Rh(L)(CH_3)Cl.[21] Upon addition of carbon tetrachloride, this complex was completely converted to Tp′Rh(L)Cl_2.

The fragment [Tp′Rh(L)] was reported to react selectively with the terminal C−H bonds of a series of chloropentanes.[18] Upon further examination of other chloroalkanes, reaction with 1-chlorobutane also gives a single major product identified as

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(10) For examples of borylation of mono- and polysubstituted arenes from Hartwig, see: (a) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (b) Ishiyama, T.; Takagi, J.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056. (c) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *J. Chem. Soc. Chem. Commun.* **2003**, 2924.

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

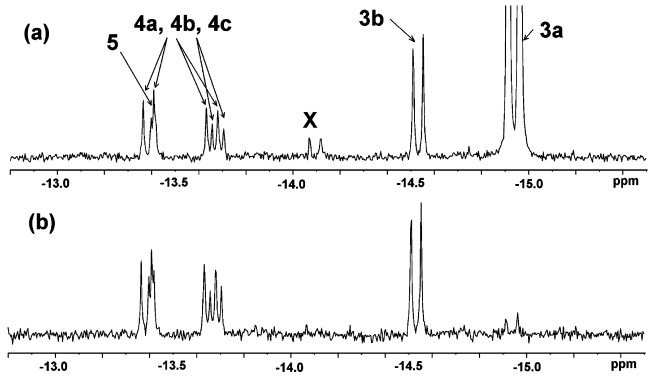
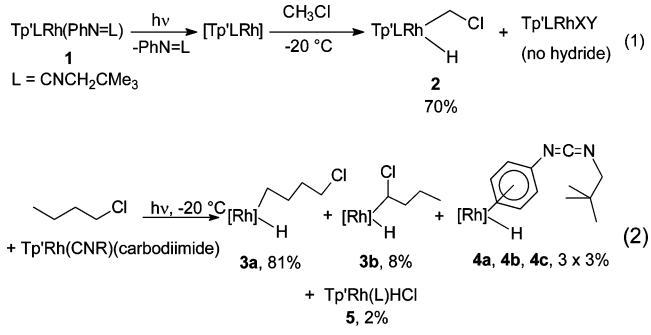


Figure 1. ^{1}H NMR spectrum (hydride region) for the activation of 1-chlorobutane by Tp′Rh(L) (a) immediately after photolysis following replacement of C_4H_9Cl by C_6D_6, and (b) after 10 h at RT.

Tp′Rh(L)($CH_2CH_2CH_2CH_2Cl$)H (**3a**), with a characteristic hydride resonance at δ −14.9 and a value for J_{Rh-H} = 24 Hz that is typical of aliphatic C−H activation products (Figure 1a).[7] No interaction with the C−Cl bond was observed. Traces (3−4%) of other products could be detected based upon their known hydride signals, including the *m*-, *o*-, and *p*-aryl carbodiimide activation products (**4a**, **4b**, and **4c**),[7a] and Tp′Rh(L)HCl (**5**)[18] (eq 2). Another species that appeared at δ −14.53 with J_{Rh-H} = 20 Hz was assigned as the α-chloro activation product Tp′Rh(L)($CHClCH_2CH_2CH_3$)H (**3b**), based upon the low value of its Rh−H coupling constant and its long life in solution at RT. While **3b** could form as a mixture of diastereomers, only one stable species is observed. It is possible that the hydride complex labeled **X** in Figure 1a is the other diastereomer (for **X**, J_{Rh-H} = 20 Hz), but this species disappears after 10 h at RT and is therefore less stable than **3b** (Figure 1b). The presence of hydrido chloride **5** can be accounted for by activation of a C−H bond in the 2-position of chlorobutane (secondary C−H activation is known to be unfavorable[7h]), which would lead to rapid, irreversible β-chloride elimination.



Similar to the observations with 1-chlorobutane, reactions of **1** with both 1-chloropropane and 1-chloropentane produced mostly terminal C−H activation products. With 1-chloropropane the 3-chloropropyl hydride complex **6a** dominated, and small quantities of a stable product (**6b**, ∼4%) with J_{Rh-H} = 20 Hz was assigned to activation of a C−H bond at the α-carbon bearing the chlorine. Small quantities of **4a**−**c** and **5** were seen, as was the minor product at δ 14.1 with J_{Rh-H} = 20 Hz possibly due to a less stable diastereomer of **6b** (Figure 2, eq 3). With 1-chloropentane, the 5-chloropentyl hydride (**7a**) dominates, and a significant quantity of the α-chloro product **7b** (13%) is now seen at δ −14.53 (J_{Rh-H} = 20 Hz), along with the possible other diastereomer. A few percent of two unidentified hydride

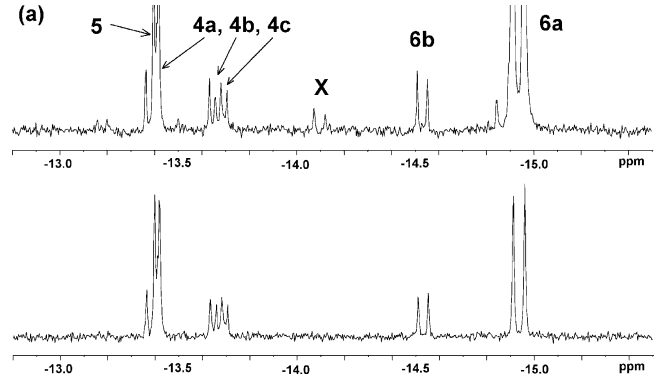


Figure 2. ^{1}H NMR spectrum (hydride region) for the activation of 1-chloropropane by Tp′Rh(L) (a) immediately after photolysis following replacement of C_3H_7Cl by C_6D_6, and (b) after 10 h at RT.

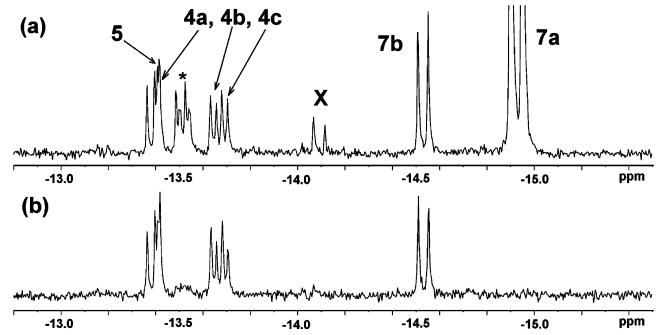
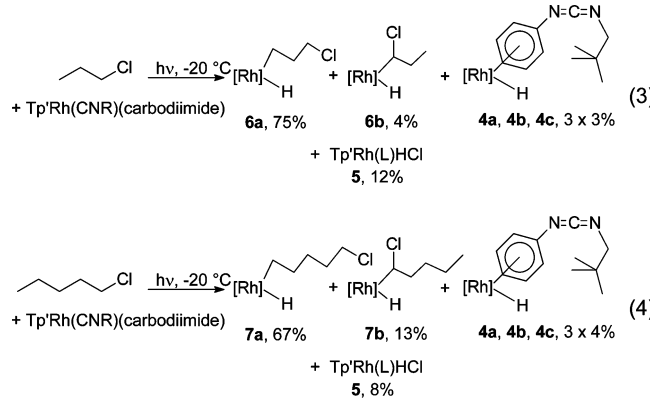


Figure 3. ^{1}H NMR spectrum (hydride region) for the activation of 1-chloropentane by Tp′Rh(L) (a) immediately after photolysis following replacement of $C_5H_{11}Cl$ by C_6D_6, and (b) after 10 h at RT. The asterisk represents an unidentified side product.

products was also noted in this experiment, in a region for aryl hydride products (Figure 3, eq 4). Consequently, the longer the chloroalkane chain, the more of the α-chloroalkyl hydride product is seen, with the ratio of ω-chloroalkyl: α-chloroalkyl product changing from 5:1 to 10:1 to 19:1 as one progresses from chloropentane to chlorobutane to chloropropane. Product **6a** was also characterized by reaction with CCl_4 to give the chloro derivative, **6a-Cl**, for which an X-ray structure was obtained (see Supporting Information).



In an attempt to increase the amount of α-chloroactivation product, a sample of **1** was irradiated in 1-chloropentane and allowed to stand at RT for 2 days. Under these conditions, reductive elimination of chloropentane from **7a** should occur many times, allowing the metal to find the thermodynamically most preferable product. As shown in eq 5, substantial quantities

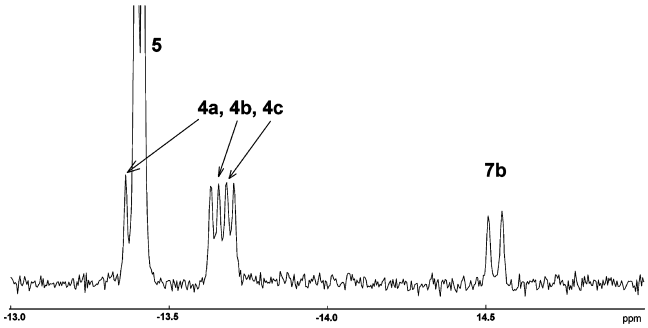
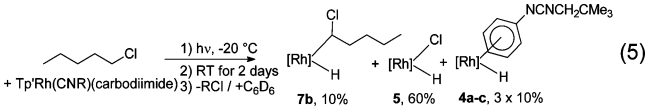


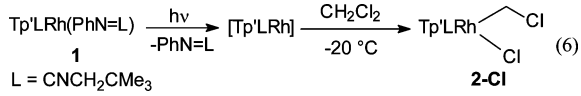
Figure 4. ^{1}H NMR spectrum (hydride region) for the activation of 1-chloropentane by Tp′Rh(L) after standing for 2 days at RT.

of **5** are formed, providing evidence for the activation of the secondary C−H bonds at the 2-position of 1-chloropentane (irreversible as a result of rapid β-chloride elimination). Only 10% of the stable α-chloropentyl hydride product is seen, indicating that activation of the C−H bonds on the carbon bearing the chloro-substituent is kinetically disfavored (Figure 4).



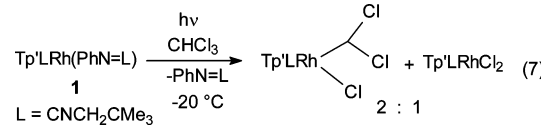
(5)

In contrast to the activation of chloromethane and the other chloroalkanes, irradiation of a neat solution of **1** in methylene chloride did not result in the activation of a C−H bond. Instead C−Cl activation product **2-Cl** is produced cleanly (eq 6). The structure was confirmed by solid state X-ray crystallography of **2-Cl** (see Figure 5a). The results were somewhat surprising considering the strong preference seen for C−H bond activation with the other chlorocarbon substrates. However, C−Cl oxidative addition of dichloromethane to Rh(I) metal centers is well documented in the literature.[22]



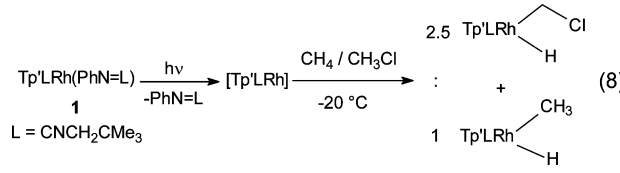
(6)

The photolysis of a yellow solution of **1** dissolved in chloroform produces a red-brown solution, in contrast to the normal bleaching that is observed upon photolysis in the previously mentioned activations. A ^{1}H NMR spectrum in C_6D_6 showed two products in a 2:1 ratio. The minor product was easily recognized as Tp′Rh(L)Cl_2 (red). The resonances for the major product appeared as three distinct Tp′ methine resonances and six Tp′ methyl resonances, indicating a Tp′Rh(L)(X)(Y) complex. A doublet was observed at δ 8.61 (1 H) with a $J_{\text{Rh-CH}}$ = 3.4 Hz (the doublet is absent in the activation of $CDCl_3$), allowing the product to be assigned as Tp′Rh(L)$(CHCl_2)$Cl (eq 7), the structure of which was confirmed by X-ray analysis (Figure 5b). The formation of the dichloride during the reaction could result from the known reactivity of chloroform with the excited states of metal complexes.[23] However, if **1** is allowed to sit in chloroform for 30 min in the dark, complete conversion to the dichloride occurs. The amount of dichloride present in the reaction mixture is dependent on the time that **1** is exposed to chloroform prior to photolysis. Once C−Cl cleavage of the chloroform occurs in the reaction, the product is stable. Subsequent attempts to convert Tp′Rh(L)$(CHCl_2)$Cl to Tp′Rh(L)Cl_2 with excess chloroform in the dark showed that it was unreactive. The carbonyl analogue of this compound has been reported.[24]



(7)

The ability to successfully C−H activate chloromethane allowed for the direct competition experiment to determine if the activation of a C−H bond of CH_4 was preferred over the activation of a C−H bond of CH_3Cl. A 1:1 ratio of methane/chloromethane was condensed into a thick-walled high pressure NMR tube containing **1** dissolved in cyclohexane-d_{12}. The ratio of the gases dissolved in the cyclohexane was recorded by ^{1}H NMR spectroscopy after allowing the gases to equilibrate in solution for 20 min. The mixture was irradiated at RT for 15 min, and a ^{1}H NMR spectrum was recorded immediately following irradiation. The ratio of the two hydrides resulting from activation of each substrate was analyzed and corrected for the initial concentrations of substrate. The kinetic product ratio indicated that chloromethane is 2.5 times more reactive than methane toward C−H activation (eq 8); that is, chlorine substitution now renders α-C−H bond activation to be kinetically favored (vide infra)!



(8)

In blocking the primary C−H bonds at both ends of a linear alkane via chlorine substitution, one might expect that C−Cl bond cleavage or α-chloro C−H activation might be preferred over activation of the interior secondary C−H bonds of the alkane, as earlier studies showed secondary C−H activation to be extremely unfavorable.[7h] However, the photolysis of 1,4-dichlorobutane in the presence of **1** gave Tp′Rh(L)(H)(Cl) (**5**) as the only observable product, and 4-chloro-1-butene was detected in the volatile materials by GCMS (eq 9). No direct C−Cl oxidative addition product was observed in the reaction. In light of the earlier observations, the formation of **5** is interpreted as a result of initial C−H activation of the methylene C−H bonds of the chain, followed by rapid β-chloride elimination. Additionally, irradiation of **1** in 1,2-dichloroethane showed no evidence of the "α-activation" product being present. Rather, only **5** was observed, implying that β-chloride elimination was

(22) For recent reports of dichloromethane activation, see: (a) Tejel, C.; Ciriano, M. A.; Lopez, J. A.; Jimenez, S.; Bordonaba, M.; Oro, L. A *Chem.—Eur. J.* **2007**, *13*, 2044. (b) Wright, J. A.; Danopoulos, A. A.; Motherwell, W. B.; Carroll, R. J.; Ellwood, S.; Sassmannshausen, J *Eur. J. Inorg. Chem.* **2006**, 4857. (c) Ito, J.; Miyakawa, T.; Nishiyama, H. *Organometallics* **2006**, *25*, 5216. (d) Ho, J. H. H.; Black, D. S. C.; Messerle, B. A.; Clegg, J. K.; Turner, P. *Organometallics* **2006**, *25*, 5800. (e) Burkill, H. A.; Vilar, R.; White, A. J. P. *Inorg. Chim. Acta* **2006**, *359*, 3709.

(23) (a) Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **2002**, *5*, 730. (b) Plyusnin, V. F.; Grivin, V. P.; Larionov, S. V. *Coord. Chem. Rev.* **1997**, *159*, 121.

(24) Teuma, E.; Malbosc, F.; Etienne, M.; Daran, J.-C.; Kalck, P. *J. Organomet. Chem.* **2004**, *689*, 1763.

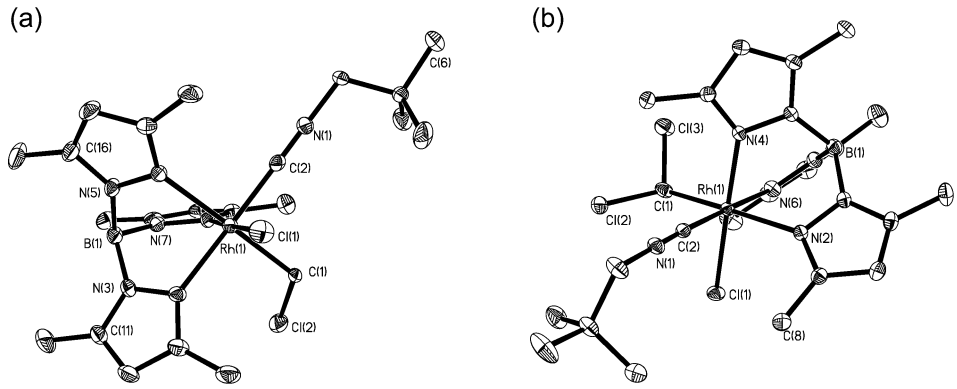
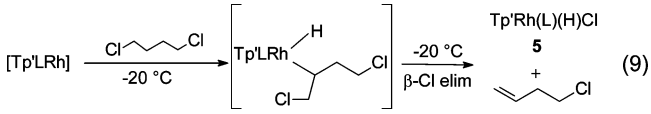


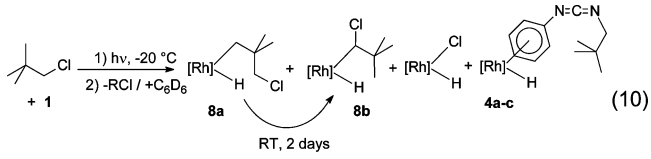
Figure 5. ORTEP drawing of (a) Tp′Rh(CNCH$_2$CMe$_3$)(CH$_2$Cl)Cl, **2-Cl**, and (b)Tp′Rh(CNCH$_2$CMe$_3$)(CHCl$_2$)Cl.

preferred in a case where an α-activation product was also capable of β-chloride elimination.



(9)

C−H bond activation of neopentyl chloride was investigated in an attempt to generate the α-activation product as the major species formed following photolysis. The activation of neopentyl chloride resulted in the formation of mostly the terminal C−H activation product Tp′Rh(L)(CH$_2$CMe$_2$CH$_2$Cl)(H) (**8a**), evidenced by a doublet at δ −14.94 (J_{Rh-H} = 25 Hz). A small amount of Tp′Rh(CNR)(CHClC(CH$_3$)$_3$)(H) (**8b**) was also present at δ −14.53 (J_{Rh-H} = 21 Hz), a chemical shift and coupling constant consistent with the location of a minor species in each reaction with the 1-chloroalkanes discussed earlier (eq 10). After standing for 3 days at RT, **8a** had disappeared, and carbodiimide activation products **4a**, **4b**, and **4c** were observed (Figure 6a,b). A small amount of Tp′Rh(L)(H)Cl (**5**) was also seen. Upon heating to 80 °C, **4a** and **4c** were observed to convert to the more stable ortho isomer **4b**, and the quantity of **8b** increased slightly.



(10)

Reactions of [Tp′Rh(CNR)] with Cyclic Chloroalkanes. In addition to the work done with the linear chloroalkanes, the activation and elimination of two chlorinated cyclic alkanes were also investigated. In the case of 1-chlorocyclopentane, the initial ^{1}H NMR spectroscopic data revealed a complex mixture of species present in the Rh−H region of the spectrum (Figure 7a). Interpretation of the spectrum hinges on the idea that C−H bond cleavage can occur at any of the three distinct carbon atoms present in the free substrate. In addition to the three carbodiimide activation products **4a**−**c**, the presence of **5** (from C−H activation at the 2-position of the ring) and five additional doublets can be observed. The doublet at δ −14.67 (J_{Rh-H} = 22 Hz) was assigned to the α-chloro adduct **9a**, and the remaining four doublets near δ −15.3 can be assigned to the four diastereomers (two pairs) **9b**−**e** arising from activation at the 3-position of the chlorocyclopentane (eq 11). Additional evidence for this assignment comes from the observation that

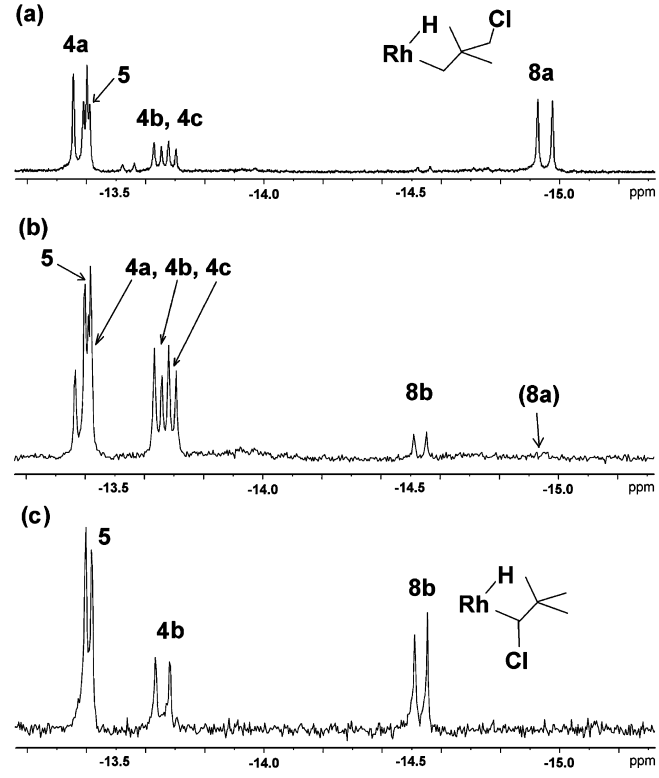
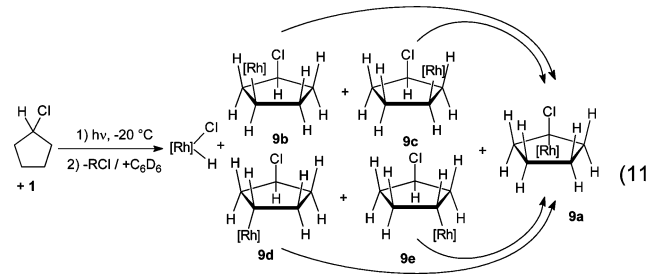


Figure 6. ^{1}H NMR spectrum (hydride region) for the activation of neopentylchloride by [Tp′Rh(L)] (a) after photolysis of **1** in neopentyl chloride, (b) after standing 3 days at RT, and (c) after heating to 80 °C for 2 days.

all 4 of these isomers disappear after standing for 4 h at RT (Figure 7b), leaving only **9a** as the stable 1-chlorocyclopentyl adduct.



(11)

Further evidence supporting the above assignments comes from examination of the reaction of **1** with 1,1-dichlorocyclo-

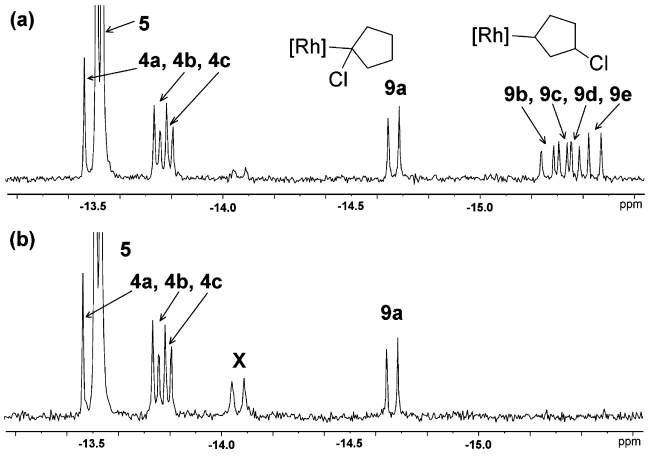


Figure 7. ^{1}H NMR spectra (C_6D_6) for the photochemical reaction of **1** with chlorocyclopentane by [Tp′Rh(CNR)] ([Rh] = Tp′Rh(CNR)) (a) immediately after photolysis and (b) after 4 h at RT.

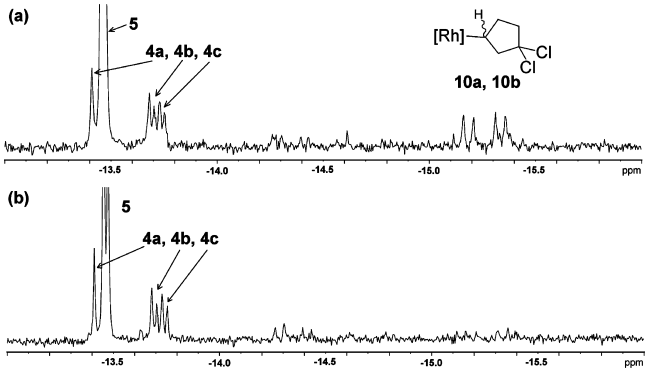


Figure 8. Reaction of **1** with 1,1-dichlorocyclopentane (a) immediately after photolysis and (b) after 12 h at RT.

pentane. Again, the major species present is the β-chloride elimination product **5** arising from activation of a C−H bond in the 2-position. Because the two faces of the ring are now equivalent, only one pair of diastereomers, **10a**−**b**, is formed upon activation of the C−H bond at the 3-position. No α-chloro activation product is possible. The two diastereomers disappear from the ^{1}H NMR spectra after 4 h, consistent with the instability of this type of alkyl hydride complex (Figure 8).

Reactions of [Tp′Rh(L)] with Fluoro- and Iodoalkanes. In an attempt to extend the scope of the activation of haloalkanes, [Tp′Rh(L)] was also shown to activate fluoropentane. The activation of 1-fluoropentane was monitored by ^{1}H NMR spectroscopy. A bright yellow solution of **1** dissolved in 1-fluoropentane bleached rapidly upon irradiation at −20 °C. ^{1}H NMR spectroscopy showed clean formation of a single product, with a hydride resonance at δ −14.91 (J_{Rh-H} = 24 Hz). A set of complex multiplets was observed at δ 4.2 for the pendant CH_2F group. Three distinct Tp′ methine resonances and six Tp′ methyl resonances were seen, indicating a single C−H activated product assigned as Tp′Rh(L)($CH_2(CH_2)_3CH_2F$)H (**11**, eq 12). The chloride derivative, **11-Cl**, showed similar resonances to **11**. The solid-state X-ray crystallographic structure of **11-Cl** confirmed the activation of the terminal C−H bond of fluoropentane (Figure 9).

Iodobutane was also activated by [Tp'Rh(L)]. Irradiation of **1** in neat iodobutane at −20 °C, followed by removal of solvent and dissolution in C_6D_6, showed two products in a 2:1 ratio by ^{1}H NMR spectroscopy (eq 13). The spectrum did not show any

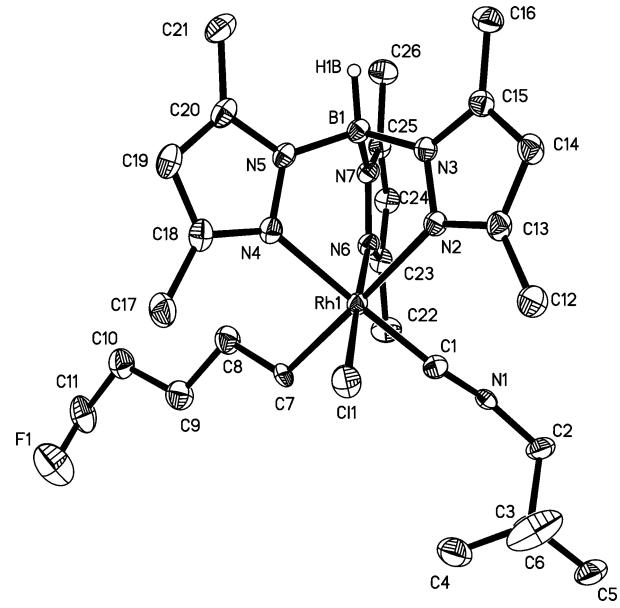
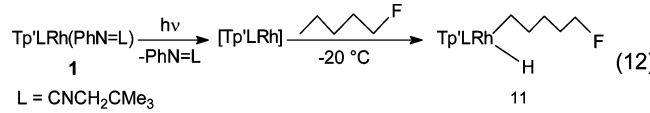
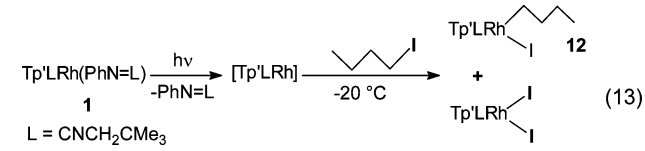


Figure 9. ORTEP drawing of complex **11-Cl**.



metal hydride resonances that would have resulted from C−H bond activation. A distinct triplet was observed at δ 1.0 integrating to 3H, indicating the existence of a terminal methyl group. The major product was assigned as Tp′Rh(L)($CH_2CH_2CH_2CH_3$)I (**12**), arising from C−I oxidative addition, and was confirmed from its independent synthesis by refluxing Tp′Rh(L)(butyl)Cl in the presence of NaI. The minor product showed resonances characteristic of $TpRh(L)I_2$.



Reductive Elimination Studies. In order to compare the relative thermodynamic stability of **2** with the analogous methyl hydride complex produced from the activation of methane, attempts were made to quantify the rate of reductive elimination of CH_3Cl from **2**. **2** did not reductively eliminate CH_3Cl in benzene at 26 °C. Furthermore, it was found that complete disappearance of **2** was not observed even after 2 days at 80 °C. The decay of **2** was *not* observed to follow a smooth first- or second-order rate law.[25] Therefore, the reductive elimination of CH_3Cl from **2** must occur with a higher barrier than the decomposition pathway (the details of which remain unknown) by which **2** is observed to disappear. While the barrier for chloromethane reductive elimination from **2** could not be determined from these experiments, it must be >28 kcal/mol, based on the rate of the observed decomposition process.

(25) The quality of the data was not improved by adding CH_3Cl scavengers such as pyridine, $(PPh_3)_2Ir(CO)Cl$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylphosphine. Moreover, changing the solvent and temperature did not improve the quality of the data obtained, nor did elimination in the presence of pentafluorobenzene at 70 °C despite the strong driving force to form Tp′Rh(CNR)(C_6F_5)(H).

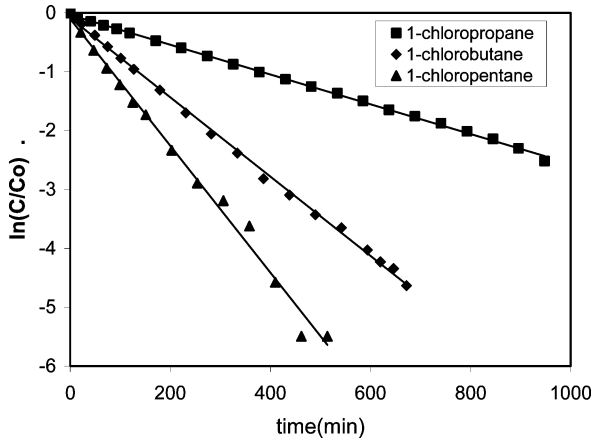


Figure 10. First-order plots showing the relative stability of a series of Tp′Rh(CNR)((CH$_2$)$_n$CH$_2$Cl)(H) complexes as judged by their relative rates of RCl elimination at 26 °C in C_6D_6.

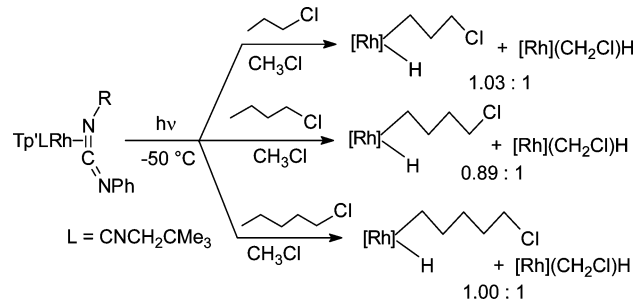
Table 1. Relative Rates for Reductive Elimination from Tp′Rh(L)(R^{Cl})H and Tp′Rh(L)(R)H in C_6D_6

R	T (°C)	k_{obs}, RCl, s^{-1}	k_{obs}, RH, s^{-1} [7]	k_{rel}
methyl	80	$\sim 4 \times 10^{-5}$	–	–
methyl	26	$\sim 2 \times 10^{-8}$[a]	$4.51(3) \times 10^{-5}$	~2000
ethyl	26	β-Cl eliminates	$1.82(7) \times 10^{-4}$	–
propyl	26	$4.21(3) \times 10^{-5}$	$2.63(7) \times 10^{-4}$	6.3
butyl	26	$1.12(1) \times 10^{-4}$	$2.77(14) \times 10^{-4}$	2.5
pentyl	26	$1.80(5) \times 10^{-4}$	$2.70(8) \times 10^{-4}$	1.5

[a] Estimated assuming $\Delta G^{\ddagger}$ is temperature independent.

The reductive elimination of the 1-chloroalkanes **3a**, **6a**, and **7a** was studied in order to determine the relative stability of the Tp′Rh(CNR)((CH$_2$)$_n$CH$_2$Cl)(H) complexes produced from substrate activation. The substrates studied were all activated at −20 °C and the elimination of the 1-chloroalkane from its respective activation product was monitored at 26 °C in C_6D_6. The results are summarized in Figure 10 showing the first order decay of each complex, and Table 1 lists rate constants for reductive elimination in comparison with the parent hydrocarbon elimination rate. It can be readily seen that the complexes with chloride closer to the metal are the slowest to undergo reductive elimination, providing evidence for a strong inductive effect on the stability.[26] An electron-withdrawing group in close proximity strengthens the metal−carbon bond, due to the anticipated increased ionic contribution to the M−C bonding, thereby making it more resistant to decomposition via reductive elimination. Remarkably, chloro-substitution has a noticeable effect on the resultant product stability even five carbon atoms removed from the metal center. A similar inductive effect on the strength of the metal−carbon bond was noticed in the activation of alkyl nitriles by [Tp′Rh(L)].[27] Closely related to the experimental studies presented here, Cundari et al. have calculated the kinetic and thermodynamic preference for C−Cl vs C−H activation in chloromethane at the 14 e$^-$ Ir^I fragment [Ir(PH$_3$)$_2$H].[28] They found a strong kinetic preference for CH activation over C−Cl activation, in agreement with our findings.

Scheme 2



In addition, the C−Cl oxidative addition product was predicted to be strongly thermodynamically favored, consistent with our knowledge of the stability of Tp′Rh(CNR)(CH$_3$)Cl.[21] Unfortunately we could not observe Tp′Rh(CNR)(CH$_2$Cl)H convert to Tp′Rh(CNR)(CH$_3$)Cl (or vice versa) experimentally, but it is hard to imagine that the latter methyl chloride complex with a metal-chloride bond is not preferred thermodynamically. Consequently, the Cundari calculations are in good agreement with these experimental observations.

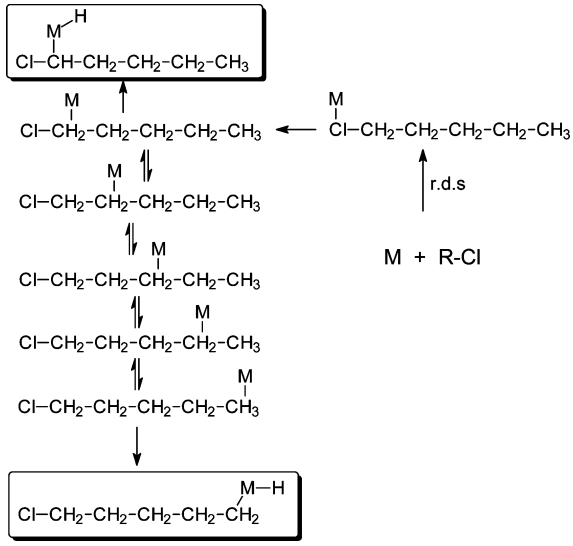
Competition Experiments of Chloromethane vs 1-Chloroalkanes. Expanding on the study in which it was shown that chloromethane activation was favored over methane activation by a factor of 2.5, a series of experiments were conducted in which the [Tp′Rh(CNR)] fragment was generated in a 1:1 molar mixture of chloromethane and a 1-chloroalkane in order to determine which substrate is kinetically preferred. In competitions involving 1-chloropropane, 1-chlorobutane, and 1-chloropentane it was found that the observed product distributions showed no substrate chain length dependence, i.e., all substrates are activated at about the same rate (Scheme 2). This result was surprising when compared to analogous competition experiments with alkylnitriles, in which it was found that longer-chained alkylnitriles were activated preferentially over acetonitrile.[27] For nitriles, the observed selectivity was rationalized by suggesting that the longer alkyl chains provide more coordination sites at which σ-alkane complexes could form. Chain migration to the primary C−H bonds would then occur before oxidative cleavage, resulting in a preference for the longer substrates.

With chloroalkanes, the observed selectivity suggests a different selection mechanism is operating. The kinetic similarity of the substrates suggests that binding to the chlorine may determine the selectivity, and that once bound the metal migrates to the terminal methyl group where C−H activation takes place. Halogen-bound alkyl and aryl halide complexes are known.[29] This hypothesis is also supported by the calculations by Cundari for chloromethane activation, in which the σ-chlorine adduct of CH$_3$Cl was found to be ~5 kcal/mol more stable than the σ-C−H adduct.[28] Bickelhaupt noted a similar (calculated) stabilization in a chloro-bound adduct with palladium.[30] The rate-determining chloro-binding hypothesis also explains why chloromethane activation is kinetically preferred over methane activation.

Rate-determining binding to chloride during chloroalkane activation can also explain an earlier observation made regarding the formation of more α-chloro C−H activation product with

(26) σ_I values fall off with chain length: −CH$_2$Cl (0.13),−CH$_2$CH$_2$Cl (0.07),−CH$_2$CH$_2$CH$_2$Cl (0.02),−CHClCH$_3$ (0.15). See Hansch, C.; Leo, A.; Taft, R. W *Chem. Rev.* **1991**, *91*, 165.
(27) Vetter, A. J.; Rieth, R. D.; Jones, W. D. *Proc. Nat. Acad. Sci.* **2007**, *104*, 6957.
(28) Cundari, T. R.; Vaddadi, S. *Inorg. Chim. Acta* **2004**, *357*, 2863.
(29) (a) Albietz, P. J.; Cleary, B. P.; Paw, W.; Eisenberg, R. *J. Am. Chem. Soc.* **2001**, *123*, 12091. (b) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831.
(30) de Jong, G. T.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2006**, *2*, 322.

Scheme 3



increasing chain length. It was observed that with 1-chloropentane, 1-chlorobutane, and 1-chloropropane that 13%, 8%, and 4% α-chloro activation products were observed, respectively. If the metal really does first bind to chlorine and then migrate up and down the chain randomly prior to oxidative addition at the methyl group, then there is a greater chance that the metal will spend time attached to C−H bonds near the chlorine, resulting in an increase in the α-C−H σ-complex. With shorter chains, the metal migrates to the methyl group more rapidly, and therefore has fewer opportunities to activate an α-C−H bond. Consequently, one would predict the observed trend based upon the relative migration/dissociation/activation rates established for σ-alkane complexes in this series (Scheme 3).[7g,h]

From these selectivities and rates of chlorocarbon reductive elimination, we can construct a qualitative free-energy picture for chlorocarbon activation. The chloromethyl hydride product **2** is the most stable species observed, and from its lack of elimination of chloromethane we can estimate the barrier to be ≥28 kcal/mol. The barrier for elimination of the other chloroalkanes is about 23 kcal/mol. Consequently, **2** must be at least 5 kcal/mol more stable than **3a**, **6a**, or **7a**. Furthermore, the α-chloro effect can be quantified by comparing the activation of methane vs chloromethane. As indicated in Figure 11 (taking the C−H bond strength in CH_3Cl as 103 vs 105 kcal/mol in CH_4[31]), the α-chloro substitutent can be seen to increase the Rh−C bond strength by at least 3 kcal/mol (=ΔG − (105 − 103). While not shown explicitly, if formation of such a M-ClR adduct does occur during CH activation, then by microscopic reversibility, reductive elimination of chloroalkane should also occur by way of this species. The presence of this intermediate does not effect the overall energetics of the oxidative addition.

Finally, at this point we can only speculate as to why activation at an α-C−H bond of a chloroalkane should be kinetically slow yet thermodynamically preferred. In essence, addition to this C−H bond is comparable to addition to a secondary C−H bond in terms of the crowding that occurs at the metal. Perhaps the chlorine is just too large to permit the metal to achieve the proper transition state geometry for the α-C−H cleavage. The transition state for secondary activation of propane by this Rh fragment has been calculated earlier using

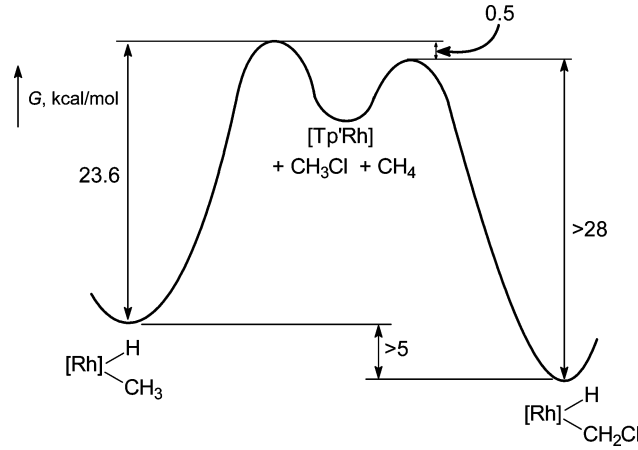


Figure 11. Net free-energy diagram comparing the activation of methane and chloromethane by [Tp′Rh(CNR)].

DFT, and it shows significant steric interactions between the methyl groups and the metal center.[32] One can expect similar severe steric interactions between the metal center and the chlorine atom. However, in the unique case of chloromethane, one has both a chlorine atom to favor coordination and a 'primary' C−H bond, resulting in a kinetically preferred (and thermodynamically preferred) α-C−H activation.

One surprising aspect of the studies done earlier with nitriles[27] was the lack of observation of an η^2-C,N-nitrile adduct, which one would assume to be more stable than a σ-Cl−R complex as proposed here. This was indeed found to be the case for another low-valent metal complex, [Ni^0(dippe)], which made η^2-nitrile complexes with a variety of nitriles.[33]

Conclusions

In conclusion, [Tp′Rh(L)] has been shown to activate selectively terminal C−H bonds in chloro substituted alkanes. C−H bond activation was also observed in the photolysis of chloromethane. However, the attempted activation of methylene chloride and chloroform result exclusively in C−Cl cleavage to give stable rhodium chloride complexes. Even in the absence of primary C−H bonds, activation of secondary C−H bonds is still preferred over the cleavage of the C−Cl bond as was shown in the activation of 1,4-dichlorobutane. Chlorine substituents have a dramatic effect on stabilization of an alkyl hydride via an inductive effect that can be noticed even five carbons removed from the metal center. An α-chloro substituent strengthens the M−C bond by at least 3 kcal/mol. Activation of C−H bonds α to the chloro substituent appears to be kinetically disfavored compared to the other reactions available. Competition studies with linear chloroalkanes show little selectivity as a function of chain length, and consequently suggest that binding of the chlorine precedes C−H activation as the rate determining step. This binding, however, does result

(31) Weissman, M.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 243.

(32) Clot, E.; Eisenstein, O.; Jones, W. D. *Proc. Nat. Acad. Sci.* **2007**, *104*, 6939.

(33) (a) Garcia, J. J.; Jones, W. D. *Organometallics* **2000**, *19*, 5544. (b) Garcia, J. G.; Brunkan, N. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 9547. (c) Brunkan, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 3627. (d) Garcia, J. J.; Arevalo, A.; Brunkan, N. M.; Jones, W. D. *Organometallics* **2004**, *23*, 3997. (e) Atesin, T. A.; Li, T.; Brennessel, W. W.; Lachaize, S.; Garcia, J. J.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 7562. (f) Atesin, T. A.; Li, T.; Lachaize, S.; Garcia, J. J.; Jones, W. D. *Organometallics* **2008**, *27*, 3811.

in higher selectivity for activation of a chloroalkane (e.g., CH_3Cl) over an alkane (e.g., CH_4).

Experimental Section

General Considerations. Unless mentioned elsewhere, all experimentation was carried out using high-vacuum techniques under a nitrogen atmosphere or using a Vacuum Atmospheres glovebox under a nitrogen atmosphere. Reactions were performed in oven-dried glassware cooled under vacuum. Tetrahydrofuran (THF), cyclohexane, and pentane were dried over sodium (MCB Chemical)/benzophenone (Acros) ketyl and were distilled prior to use. Dichloromethane was dried over activated alumina and was distilled prior to use. Methyl chloride was purchased from Aldrich and was used as received. $(PPh_3)_2Ir(CO)Cl$ was purchased from Alfa Aesar and was used as received. Hexamethyldisiloxane, 1,4-dioxane, 1-chloropropane, 2-chloropropane, 1-chloropentane, chlorocyclopentane, 1,4-dichlorobutane, pentafluorobenzene, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and carbon tetrachloride were purchased from Aldrich and were dried and degassed prior to use. Triethylphosphine was purchased from Strem and was dried and degassed prior to use. 1-Chlorobutane was purchased from Fluka and was dried and degassed prior to use. 1,2-Dichloroethane was purchased from Fisher Scientific and was dried and degassed prior to use. Neopentyl chloride was purchased from TCI and was dried and degassed prior to use.[34] *N*-phenyl-*N*′-neopentylcarbodiimide,[7a] 1,1-dichlorocyclopentane,[35] and Tp′Rh(CNR)(η^2-PhN=C=NR)[7a] (**1**) were prepared by using adaptations of procedures previously published in the literature. 4-chloro-1-butene was independently synthesized following the literature procedure.[36] Tp′Rh(L)I_2 was independently synthesized by heating Tp′Rh(L)Cl_2 in the presence of NaI in acetone.

C_6D_6 was purchased from Cambridge Isotope Laboratories and was dried over sodium/benzophenone ketyl prior to use. C_6D_{12} was purchased from Cambridge Isotope Laboratories and was dried over sodium/benzophenone ketyl followed by green titanocene[37] prior to use. ^{1}H NMR spectra were recorded on Bruker 400 MHz and Bruker 500 MHz spectrometers, with chemical shifts reported relative to residual solvent. A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low-temperature unit was used for X-ray crystal structure determination. All photolyses were conducted with an Oriel arc source using a 200-W Hg(Xe) bulb. The light was filtered using a water IR filter and Pyrex glass.

Activation of Chloromethane. 1 (5 mg, 0.007 mmol) was placed in a sealable NMR tube. To this 0.6 mL of chloromethane was added in vacuo. The solution was kept at −35 °C and photolyzed for 15 min. The solvent was removed at 0 °C under vacuum and C_6D_6 was condensed in. A ^{1}H NMR spectrum (RT) showed two products, a single C−H activated product in roughly 70% yield by NMR assigned as Tp′Rh(L)(CH_2Cl)H (**2**) and a second product observed in about 30% yield. This second product could not be isolated. Treatment of the solution with CCl_4 leads to the formation of Tp′Rh(L)(CH_2Cl)Cl (**2-Cl**) and Tp′Rh(L)Cl_2. For **2**, ^{1}H NMR (C_6D_6): δ Rh−H: −14.03 (d, J = 20 Hz, Rh−H); Tp′ methyl: 2.127 (s, 3H), 2.160 (s, 3H), 2.242 (s, 3H), 2.315 (s, 3H), 2.595 (s, 3H), 2.679 (s, 3H); Tp′ methine: 5.570 (s, 1H), 5.613 (s, 1H), 5.781 (s, 1H); $CNCH_2C(CH_3)_3$: 0.695 (s, 9H), 2.660 (s, 2H); CH_2Cl: 4.770 (dd, J = 7.2, 2.7 Hz, 1H), 4.99 (dd, J = 7.1, 2.6 Hz, 1H). For the byproduct, ^{1}H NMR (C_6D_6): δ Tp′ methyl: 2.062 (s, 3H), 2.181 (s, 3H), 2.185 (s, 3H), 2.267 (s, 3H), 2.470 (s, 3H), 2.538 (s, 3H); Tp′ methine: 5.401 (s, 1H), 5.591 (s, 1H), 5.607 (s, 1H); remaining resonances were obscured. The addition of two drops of acetonitrile to the photolysis solution prior to photolysis results in the formation of **2** in 95% yield.

Activation of Methylene Chloride. An ampule was charged with 48 mg (0.07 mmol) of **1** and 5 mL of CH_2Cl_2. The bright yellow solution was cooled to −20 °C and photolyzed for 20 min. The solvent was removed from the resulting pale yellow solution under vacuum to give Tp′Rh(L)(CH_2Cl)Cl (**2-Cl**) in quantitative yield by ^{1}H NMR spectroscopy. **2-Cl** was crystallized from methylene chloride/hexanes at RT to give light yellow crystals. ^{1}H NMR (C_6D_6): δ Tp′ methyl: 2.044 (s, 3H), 2.095 (s, 3H), 2.177 (s, 3H), 2.522 (s, 3H), 2.704(s, 3H), 3.052 (s, 3H); Tp′ methine: 5.538 (s, 1H), 5.625 (s, 1H), 5.665 (s, 1H); $CNCH_2C(CH_3)_3$: 0.654 (s, 9H), 2.580 (s, 2H); CH_2Cl: 5.63 (dd, 1H), 5.84 (dd, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.22, 12.66, 12.85, 14.27, 14.66, 14.68 (s, pzCH_3), 26.49 (s, $CNCH_2C(CH_3)_3$) 31.85 (s, $CNCH_2C(CH_3)_3$), 35.33 (d, J_{Rh-C} = 23.4 Hz, Rh(CH_2Cl)), 106.97, 107.84, 108.70 (s, pz*C*H), 142.82, 142.95, 144.32, 151.20, 151.47, 153.47 (s, pz*C*q). Anal. Calcd. for $C_{22}H_{35}N_7RhBCl_2$: C, 45.39, H, 6.06, N, 16.84. Found: C, 45.30, H, 5.73, N, 15.76.

Activation of Chloroform. The activation procedure was followed as for activation with methylene chloride except that 25 mg of **1** was dissolved in 6 mL of chloroform. The solution was photolyzed at −20 °C for 20 min. The solution changes color from light yellow to orange upon photolysis. The solvents were removed in vacuo to give an orange solid. The ^{1}H NMR spectrum showed two products in a 2:1 ratio. The minor product was easily recognized as Tp′Rh(L)Cl_2 (**4**). The major product was assigned as the C−Cl activated product, Tp′Rh(L)($CHCl_2$)(Cl) (**3**). ^{1}H NMR for **3** (C_6D_6): δ Tp′ methyl: 2.020 (s, 3H), 2.039 (s, 3H), 2.106 (s, 3H), 2.679 (s, 3H), 2.889 (s, 3H), 2.913 (s, 3H); Tp′ methine: 5.450 (s, 1H), 5.610 (s, 1H), 5.701 (s, 3H); $CNCH_2C(CH_3)_3$: 0.664 (s, 9H), 2.625 (AB_q, 2H); CHCl$_2$: 8.614 (d, J = 3.4 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.23, 12.67, 12.87, 14.27, 14.93, 15.91 (s, pzCH_3), 26.72 (s, $CNCH_2C(CH_3)_3$), 31.65 (s, $CNCH_2C(CH_3)_3$), 56.46 (s, $CNCH_2C(CH_3)_3$), 66.72 (d, J_{Rh-C} = 32.7 Hz, Rh($CHCl_2$)), 107.36, 108.16, 109.23(s, pz*C*H), 143.02, 143.94, 144.46, 151.89, 152.40, 153.20 (s, pz*C*q).

Competitive Activation of Chloromethane and Methane. A high-pressure NMR tube (Wilmad no. 522-PV) was charged with 5 mg of **1** dissolved in C_6D_{12}. Under inert conditions, chloromethane (charged 7.4 mL known volume with 150 mmHg of chloromethane and condensed into tube, repeated) and methane (charged tube with 45 psi) were added to the tube. The tube was shaken vigorously for 20 min after which time a ^{1}H NMR spectrum was recorded to determine the ratio of the two gases in solution. The sample was irradiated at RT for 10 min and a ^{1}H NMR spectrum was recorded immediately. The ratio of the resulting hydrides from activation of chloromethane and from activation of methane was measured. The product ratio was corrected for the initial concentrations of the two gases in solution. In triplicate runs, ratios of 2.7:1, 2.5:1, and 2.1:1 were observed favoring CH_3Cl activation.

Activation of 1-Chloropropane, 1-Chlorobutane, and 1-Chloropentane. 1 (6 mg) was placed in a resealable NMR tube and was treated with roughly 0.5 mL of 1-chloroalkane. The resulting dark yellow solution was kept at −20 °C and was photolyzed for 30 min. The resulting pale yellow solution was allowed to warm to RT under vacuum. The remaining residue was dissolved in 0.6 mL C_6D_6 and 0.5 μL of an internal standard (hexamethyldisiloxane) added. The resulting solution was placed in a 26 °C NMR probe and was monitored by ^{1}H NMR spectroscopy overnight. Disappearance of the resonances assigned to the terminal C−H activation products, Tp′Rh(CNR)((CH_2)$_n$$CH_2$Cl)(H), were observed to follow a smooth first-order decay producing Tp′Rh(CNR)(C_6D_5)D. Other

(34) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth: Boston, 1996.
(35) Dakkourit, M.; Typke, V.; Schauwecker, T *J. Phys. Chem. A* **2004**, 108–4658, In order to aid in the isolation of the product, bromine was added to the reaction mixture to react with 1-chlorocyclopentene—a byproduct formed in significant quantity—in order to form the relatively heavy 1,2-dibromo-1-chlorocyclopentane. In at least one instance, prolonged storage of the products from the activation of 1,1-dichlorocyclopentane at−20 °C—dissolved in THF and layered with pentane—led to the formation of crystals characterized as Tp′Rh(CNR)X_2 (X = Cl or Br).
(36) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509.
(37) Hazari, S. K. S.; Dhar, D. *J. Bang. Acad. Sci.* **1992**, *16*, 241.

minor products were observed in these reactions as described in the text. For Tp'Rh(CNR)((CH$_2$)$_2$CH$_2$Cl)(H) (**6a**), ^{1}H NMR (C_6D_6): δ Rh−H: −14.94 (d, J_{Rh-H} = 24 Hz, 1 H); Tp′Me: 2.19 (s, 3 H), 2.20 (s, 3 H), 2.29 (s, 3 H), 2.35 (s, 3 H), 2.45 (s, 3 H), 2.53 (s, 3 H); Tp′-H: 5.62 (s, 1 H), 5.65 (s, 1 H), 5.82 (s, 1 H); CNR: 0.65 (s, 9 H), 2.63 (s, 2 H); CH$_2$CH$_2$CH$_2$Cl: 3.00 (t, J_{H-H} = 7.3 Hz, 2 H, CH$_2$CH$_2$C*H*$_2$Cl), 3.54 (m, 1 H, CH$_2$C*H*$_2$CH$_2$Cl), 3.63 (m, 1 H, CH$_2$C*H*$_2$CH$_2$Cl), 4.31 (m, 2 H, C*H*$_2$CH$_2$CH$_2$Cl). For Tp′Rh(CNR)((CH$_2$)$_3$CH$_2$Cl)(H) (**3a**), ^{1}H NMR (C_6D_6): δ Rh−H: −14.94 (d, J = 24 Hz, 1 H); Tp′Me: 2.21 (s, 6 H), 2.30 (s, 3 H), 2.37 (s, 3 H), 2.52 (s, 3 H), 2.56 (s, 3 H); Tp′-H: 5.66 (s, 2 H), 5.84 (s, 1 H); CNR: 0.67 (s, 9 H), 2.70 (s, 2 H); CH$_2$Cl: 3.41 (m, 2 H). For Tp′Rh(CNR)((CH$_2$)$_4$CH$_2$Cl)(H) (**7a**), ^{1}H NMR (C_6D_6): δ Rh−H: −14.93 (d, J_{Rh-H} = 25 Hz, 1 H); Tp′Me: 2.21 (s, 3 H), 2.22 (s, 3 H), 2.31 (s, 3 H), 2.38 (s, 3 H), 2.55 (s, 3 H), 2.57 (s, 3 H); Tp′-H: 5.67 (s, 2 H), 5.85 (s, 1 H); CNR: 0.68 (s, 9 H), 2.68 (s, 2 H); CH$_2$Cl: 3.24 (t, J_{H-H} = 7.4 Hz, 2 H). Any remaining resonances were obscured. Treatment of a THF solution of Tp′Rh(CNR)((CH$_2$)$_2$CH$_2$Cl)(H) with an excess of carbon tetrachloride at −20 °C and allowing the resulting light yellow solution to stand at low temperature for ∼2 h in the dark resulted in the effective conversion to Tp′Rh(CNR)((CH$_2$)$_2$CH$_2$Cl)(Cl). X-ray quality crystals of Tp′Rh(CNR)((CH$_2$)$_2$CH$_2$Cl)(Cl)·CH$_2$Cl$_2$ were obtained by allowing a dichloromethane solution of the complex to evaporate slowly at −20 °C for roughly 3 weeks.

Activation of *N*-Phenyl-*N*′-Neopentylcarbodiimide. 1 (6 mg) was placed in a resealable NMR tube and was treated with roughly 0.5 mL of a mixture consisting of five drops of carbodiimide in cyclohexane. The resulting mixture of light-colored solid in yellow liquid was kept at 10 °C and was photolyzed for 20 min. The resulting mixture was allowed to warm to RT under vacuum. The remaining orange gel containing light-colored solid was treated with 0.4 mL of C_6D_6. The resulting solution was placed in a 26 °C NMR probe and was monitored by ^{1}H NMR spectroscopy over the course of 3.5 h. The obtained spectra appeared to contain a mixture of activation products, which were assigned to the three possible aromatic activation products of the carbodiimide based on the Rh−H chemical shift and coupling constant of the doublet corresponding to Tp′Rh(CNR)(H)(C_6H_5).[7c] For **4a**−**c**, ^{1}H NMR (C_6D_6): δ Rh−H: −13.48 (d, J_{Rh-H} = 23 Hz), −13.76 (d, J_{Rh-H} = 24 Hz), and −13.78 (d, J_{Rh-H} = 24 Hz).

Activation of 1,4-Dichlorobutane. 1 (5 mg) was placed in a resealable NMR tube. To this 0.6 mL of 1,4-dichlorobutane was added. The solution was cooled to −20 °C and photolyzed for 15 min. The volatile materials were removed at 0 °C under vacuum and analyzed by GCMS showing the formation of 4-chloro-1-butene as a result of β-chloride elimination. A ^{1}H NMR spectrum of the resulting pale yellow solid showed a single product previously characterized as **5**. ^{1}H NMR for **5** (C_6D_6): δ Rh−H: −13.40 (d, J = 11.5 Hz, 1 H); Tp′methyl: 2.074 (s, 3H), 2.120 (s, 3H), 2.207 (s, 3H), 2.286 (s, 3H), 2.862 (s, 3H), 2.869 (s, 3H); Tp′methine: 5.499 (s, 2H), 5.803 (s, 1H); CNCH$_2$C(CH$_3$)$_3$: 0.655 (s, 9H), 2.554 (s, 2H).

Activation of Neopentyl Chloride. 1 (6 mg) was placed in a resealable NMR tube and treated with roughly 0.5 mL of neopentyl chloride. The resulting dark yellow solution was kept at −20 °C and photolyzed for 30 min. The resulting pale yellow solution was allowed to warm to 0 °C under vacuum. The remaining residue was treated with 0.6 mL of C_6D_6 and 0.5 μL of an internal standard (hexamethyldisiloxane). The resulting solution was placed in a 26 °C NMR probe and monitored by ^{1}H NMR spectroscopy overnight. The spectra obtained contain a mixture of activation products as described in the text, the dominant species assigned to the product of primary C−H activation, Tp′Rh(CNR)((CH$_2$)C(CH$_3$)$_2$CH$_2$Cl)(H) (**8a**). ^{1}H NMR (C_6D_6): δ Rh−H: −14.94 (d, J_{Rh-H} = 24 Hz). This product was observed to convert to Tp′Rh(CNR)((CHCl)C(CH$_3$)$_3$)(H) (**8b**) over the course of several days while heating to 80 °C.

Activation/Elimination of 1-Chlorocyclopentane. 1 (6 mg) was placed in a resealable NMR tube. Roughly 0.3 mL of chlorocyclopentane was condensed onto **1** in vacuo. The resulting dark yellow solution was kept at −20 °C and photolyzed for 30 min. The resulting pale yellow solution was allowed to warm to 0 °C under vacuum. The remaining residue was dissolved in 0.6 mL of C_6D_6 and 0.5 μL of an internal standard (hexamethyldisiloxane) added. The resulting solution was placed in a 26 °C NMR probe and monitored by ^{1}H NMR spectroscopy over the course of 5 h. The spectra obtained showed a mixture of activation products as described in the text. ^{1}H NMR (C_6D_6): δ Rh−H: −13.52 (d, J_{Rh-H} = 11 Hz, Tp′Rh(CNR)(H)(Cl)); −14.67 (d, J_{Rh-H} = 22 Hz, Tp′Rh(CNR)(*c*-CCl(CH$_2$)$_4$)(H)).

Activation/Elimination of 1,1-Dichlorocyclopentane. 1 (6 mg) was placed in a resealable NMR tube and was treated with roughly 0.6 mL of a mixture consisting of three drops of 1,1-dichlorocyclopentane in cyclohexane. The resulting dark yellow solution was kept at 10 °C and photolyzed for 20 min. The resulting mixture was allowed to warm to RT under vacuum. The remaining residue was dissolved in 0.6 mL of C_6D_6 and 0.5 μL of an internal standard (hexamethyldisiloxane) added. The resulting solution was placed in a 26 °C NMR probe and was monitored by ^{1}H NMR spectroscopy overnight. The spectra obtained showed a mixture of activation products as described in the text. ^{1}H NMR (C_6D_6): δ Rh−H: −13.46 (d, J_{Rh-H} = 11 Hz, Tp′Rh(CNR)(H)(Cl)).

Competition Experiments of 1-Chloroalkane Substrates vs Chloromethane. 1 (6 mg) was placed in a resealable NMR tube and was treated with roughly 150−300 μL of a liquid substrate (1-chloropropane, -butane, or -pentane). Chloromethane (charged 0.579 L volume with pressure appropriate to make a 1:1 molar mixture upon condensation of the gas into the NMR tube) was added to the tube. The resulting mixtures were analyzed by ^{1}H NMR spectroscopy at the temperature to be used for photolysis (typically −50 °C), which established the ratio of substrates in solution. The samples were irradiated at −50 °C for 45 min and were analyzed by ^{1}H NMR spectroscopy immediately after excess substrate was removed in vacuo and the remaining residue was dissolved in C_6D_6. The ratios of the resulting hydrides from activation of chloromethane (δ −14.05) vs the other substrate (δ −14.94) were measured and corrected based on the molar ratio of substrates present in the NMR spectrum measured before photolysis. Results are presented in Scheme 2.

Activation of 1-Fluoropentane. 1 (30 mg) was dissolved in 5 mL of 1-fluoropentane. The solution was cooled to −20 °C and irradiated for 15 min, during which time the bright yellow solution became colorless. The solvent was removed immediately at low temperature on the vacuum line. The resulting solid was dissolved in C_6D_6 and a ^{1}H NMR spectrum was taken immediately showing a single hydride. For **11**, ^{1}H NMR (C_6D_6): δ Rh−H: −14.91 (d, J_{Rh-H} = 24 Hz); Tp′methine: 5.653 (s, 1H), 5.662 (s, 1H), 5.841 (s, 1H); Tp′methyl: 2.196 (s, 3H), 2.212 (s, 3H), 2.296 (s, 3H), 2.377 (s, 3H), 2.549 (s, 3H), 2.568 (s, 3H); CNCH$_2$C(C*H*$_3$)$_3$: 0.655 (s, 9H), 2.650 (s, 2H); CH$_2$(CH$_2$)$_3$CH$_2$F: 4.28 (m, 2H), 2.00 (complex. m, 1H), 1.86 (complex m, 1H), 1.71 (complex m, 1H), the remaining alkyl resonances are highly split and obscured.

Activation and Quench of 1-Fluoropentane. A solution of **11** was prepared as described above. The resulting bleached solution was quenched with carbon tetrachloride and allowed to stand at −20 °C for 2 h. The solvents were removed resulting in a brown solid. A ^{1}H NMR spectrum showed the clean formation of Tp′Rh(L)(CH$_2$(CH$_2$)$_3$CH$_2$F)Cl (**11-Cl**). The solid was recrystallized from THF/hexanes mixture at −20 °C, yielding a light yellow solid. ^{1}H NMR (C_6D_6): δ Tp′methyl: 2.089 (s, 3H), 2.154 (s, 3H), 2.221 (s, 3H), 2.341 (s, 3H), 2.783 (s, 3H), 2.960 (s, 3H); Tp′methine: 5.571 (s, 1H), 5.622 (s, 1H), 5.705 (s, 1H); CNCH$_2$C(CH$_3$)$_3$: 0.708 (s, 9H), 2.616 (s, 2H); CH$_2$(CH$_2$)$_3$CH$_2$F: 4.202 (m, 1H), 4.09 (m, 1H), 3.376 (m, 1H), 3.216 (m, 1H), 2.04 (m, 1H), 1.93 (m, 1H), 1.39 (m, 2H), the remaining alkyl resonances are highly split and obscured. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.27, 12.74, 12.97, 14.55, 14.61, 14.63 (s, pz*C*H$_3$), 18.00 (d, J = 19 Hz, *C*H$_2$(CH$_2$)$_3$CH$_2$F), 26.60 (s, CNCH$_2$C(*C*H$_3$)$_3$), 28.34 (d, J = 4.6, CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$F), 30.69 (d, J = 19 Hz,

$CH_2CH_2CH_2CH_2CH_2F$), 31.93 (s, $CNCH_2C(CH_3)_3$), 33.66 (s, $CH_2CH_2CH_2CH_2CH_2F$), 56.19 (s, $CNCH_2C(CH_3)_3$), 83.94 (d, J = 165 Hz, $CH_2CH_2CH_2CH_2CH_2F$), 106.68, 107.74, 108.53 (s, pz*C*H), 142.57, 142.85, 144.37, 150.75, 151.16, 153.06 (s, pz*C*q). Anal. Calcd for $C_{26}H_{43}N_8RhBClF$: C, 50.22, H, 6.97, N, 15.77. Found: C, 49.97, H, 6.64, N, 15.26.

Activation of 1-Iodobutane. A bright yellow solution of **1** (5 mg) dissolved in 1-iodobutane was irradiated at −20 °C for 15 min. The solution became deep orange upon irradiation. The volatile materials were removed under vacuum leaving a dark red-orange solid. A ^{1}H NMR spectrum was recorded immediately following removal of the solvent and showed the formation of two products, neither containing a metal hydride. The first product was identified as the C−I activated product Tp′Rh(CNneopentyl)(*n*-butyl)I (**12**) and the symmetric product was assigned as Tp′Rh(CNneopentyl)I_2. ^{1}H NMR for **12** (C_6D_6): δ Tp′ methyl: 2.071 (s, 3H), 2.146 (s, 3H), 2.210 (s, 3H), 2.370 (s, 3H), 2.816 (s, 3H), 3.023 (s, 3H); Tp′ methine: 5.607 (s, 2H), 5.700 (s, 1H); $CNCH_2C(CH_3)_3$: 0.774 (s, 9H), 2.753 (s, 2H); $CH_2CH_2CH_2CH_3$: 3.19 (m, 1H), 3.54 (m, 1H) 1.02 (t, J = 7.3 Hz, 3H), 1.63 (m, 2H), 1.71 (m, 1H), remaining alkyl resonance is obscured. ^{13}C NMR (C_6D_6): δ 12.45, 12.95, 14.30, 14.42, 17.23, 17.39 (s, pz*C*H_3), 12.95 (s, Rh($CH_2CH_2CH_2$-*C*H_3), 15.23 (d, J = 18.5 Hz, Rh*C*$H_2CH_2CH_2CH_3$), 26.54 (s, $RhCH_2CH_2CH_2CH_3$), 26.76 (s, $CNCH_2C(CH_3)_3$), 32.27 (s, $CNCH_2C(CH_3)_3$), 38.22 (s, $RhCH_2CH_2CH_2CH_3$), 56.43 (s, $CNCH_2C(CH_3)_3$), 106.98, 107.70, 108.68 (s, pz*C*H), 142.86, 143.31, 143.94, 150.31, 151.54, 153.94 (s, pz*C*q). ^{1}H NMR for Tp′Rh(CNneopentyl)I_2 (C_6D_6): δ Tp′ methyl: 2.013 (s, 6H), 2.109 (s, 3H), 2.770 (s, 6H), 3.341 (s, 3H); Tp′ methine: 5.519 (s, 2H), 5.601 (s, 1H); CNR: 0.870 (s, 9H), 2.841 (s, 2H). ^{13}C NMR (C_6D_6): δ 12.53, 18.42, 21.45 (s, pz*C*H_3), 26.82 (s, $CNCH_2C(CH_3)_3$), 32.90 (s, $CNCH_2C(CH_3)_3$), 56.79 (s, $CNCH_2C(CH_3)_3$), 108.41, 109.12 (s, pz*C*H), 143.54, 144.24, 153.07, 157.01 (s, pz*C*q).

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Supporting Information Available: Tables of kinetic data and X-ray crystallographic data for complexes **6a-Cl**, **2-Cl**, Tp′Rh(CNR)($CHCl_2$)Cl, and **11-Cl**. This material is available free of charge via the Internet at http://pubs.acs.org.

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