

**PROGRESS REPORT
and
CONTINUATION REQUEST
SUBMITTED TO
THE U.S. DEPARTMENT OF ENERGY**

BY

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FOR

**TRANSITION METAL ACTIVATION AND
FUNCTIONALIZATION OF CARBON-HYDROGEN BONDS**

William D. Jones, Principal Investigator
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Current Project Period: December 1, 2004 - November 30, 2005 (year 1)

Total Project Period: December 1, 2004 - November 30, 2007

Total Award Amount (3 years): \$ 405,000

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Continuation Request Amount (year 2): \$135,000

Unexpended Balance from Previous Year: \$0

Abstract of FY 2005 Research in the Chemical Sciences

Title: Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds

Grant# FG02-86ER13569

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Total Grant Period: 12/1/04-11/30/07, \$405,000 for three years

Current Grant Period: 12/1/04-11/30/05, \$135,000 for year one

Coworkers: Dr. Sébastien Lachaize (postdoc), Ahmet Gunay (graduate student), Brett Swartz (graduate student), Andrew Vetter (graduate student).

Collaborators: Prof. Juventino Garcia, Universidad Nacional Autonomas de Mexico, Mexico City.
Prof. Odile Eisenstein and Dr. Eric Clot at the University of Montpellier, France

Overview of Research Goals and Accomplishments:

This project has as its overall goal improvement in the intelligent use of our energy resources, specifically petroleum derived products, and is aimed at the development of new routes for the manipulation of C-H and C-C bonds. During the first year of this 3 year project period, our research has focussed on the following specific goals: (1) fundamental studies of C-H bond cleavage reactions of trispyrazolyl-boraterhodium complexes, including binding and activation, (2) C-C bond activation in aryl-alkynes, aryl-nitriles, and allyl-nitriles, (3) C-H bond activation reactions in functionalized substrates, and (4) carbon-fluorine bond activation with hafnium and zirconium. This year we have made progress in each of these areas, as described in the following report.

The specific accomplishments of the current grant period include: (1) we have successfully measured and quantitatively modeled the processes available to metal alkyl hydride complexes in a trispyrazolylborate-rhodium complex, including both linear and cyclic hydrocarbons; (2) we have preliminary results that measure *for the first time* the selectivity for a metal fragment binding to methyl vs methylene groups in a linear hydrocarbon; (3) we have cleaved C-C bonds in aryl-acetylenes, aryl-nitriles, and alkyl-nitriles, expanding tremendously the breadth of C-C cleavage; (4) we have established that Cp*HfH₂ can effect C-F bond cleavage of fluorocarbons; (5) we have discovered new C-H and C-C functionalizations that allow introduction of reactive boronate and olefin functional groups; (6) we have cleaved C-C bonds in allyl nitriles, leading to isomerization of the C-C skeleton. This reaction is critical to the DuPont synthesis of Nylon from butadiene; (7) we have measured C-H activation selectivities in chloroalkanes, showing a preference for activation of the terminal methyl groups and the facile β -chloride elimination reaction, (8) we have measured C-H activation selectivities in aliphatic nitriles, showing a preference for activation of the terminal methyl groups.

A wide variety of chemistry has been examined, resulting in publication of several manuscripts. The work has been communicated at both national and international meetings. DOE funds have been used for the partial support of 4 graduate students (Andrew Vetter, Ahmed Gunay, Brett Swartz, and Ryan Reith) and 1 postdoc (Sébastien Lechaize) during the current grant period, as well as several undergraduates (Susanne Golisz, Mike Sweeney). The C-CN work has been done in collaboration with Professor Juventino Garcia at the Universidad Nacional Autonomas de Mexico, and calculations on the C-F activation have been carried out in collaboration with Prof. Odile Eisenstein and Dr. Eric Clot at the University of Montpellier, France.

The continued success of this work will lead to the development of new techniques and processes for the manipulation of petroleum-based hydrocarbons. These new processes will be based upon the new methods for making and breaking strong bonds in organic molecules of the type studied here. The work has the potential to have a significant impact in science and in technologies of interest to DOE as the chemistry relates to the petroleum industry and chemicals derived from petroleum.

A detailed report follows, followed by a listing of the DOE supported publications.

Detailed Progress Report for the Project Period Dec. 1, 2004- Nov. 30, 2005 (year 1).

This report summarizes research that has been performed during the first year of the current 3-year grant, as well as work that will be completed and published by the end of the prior grant period.

1. Tris-pyrazolyborate Rhodium Alkane Binding and Activation Studies.

Our rhodium-trispyrazolyborate studies on hydrocarbon activation make use of the reactive 16-electron fragment $[\text{HB}(3,5\text{-dimethylpyrazolyl})_3]\text{Rh}(\text{CNCH}_2\text{CMe}_3)$, abbreviated herein as Tp'RhL. In the prior 3-year project period, we established that the Tp'RhL fragment coordinates an alkane to give a σ -complex. A series of labelling studies *allowed the determination of the relative rates of the processes available to the alkane σ -complex*, specifically: (1) C-H activation (called oxidative cleavage), (2) migration down the alkane chain, or (3) simple dissociation. These experiments involved modelling of the scrambling of deuterium in complexes such as $\text{Tp}'\text{Rh}(\text{L})(\text{CH}_2\text{CH}_2\text{CH}_3)\text{D}$ before loss of propane- d_1 . Figure 1 shows the relative rates of these processes for methyl, ethyl, n-propyl, and n-butyl derivatives. For methane, C-H activation is strongly preferred over dissociation, whereas for ethane, the rates of these two processes are closer. End-to-end migration in ethane is intermediate. For propane, terminal C-H activation is favored over dissociation to a lesser extent than methane, but comparable to ethane. Migration from the end to the middle of propane is slightly slower than C-H activation. For the secondary propane complex, migration to the end and dissociation occur at about the same rate. Interestingly, migration down a butane chain (secondary to secondary) is the fastest process, accounting for the observed kinetic preference for terminal C-H activation.

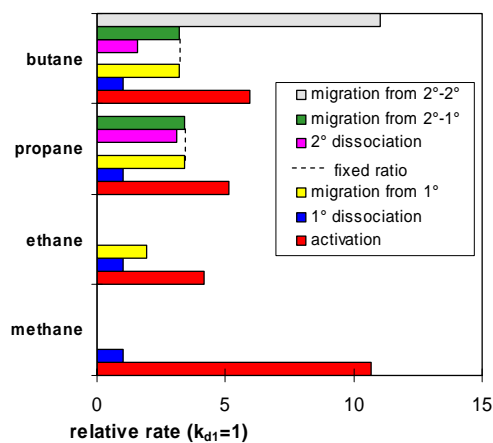
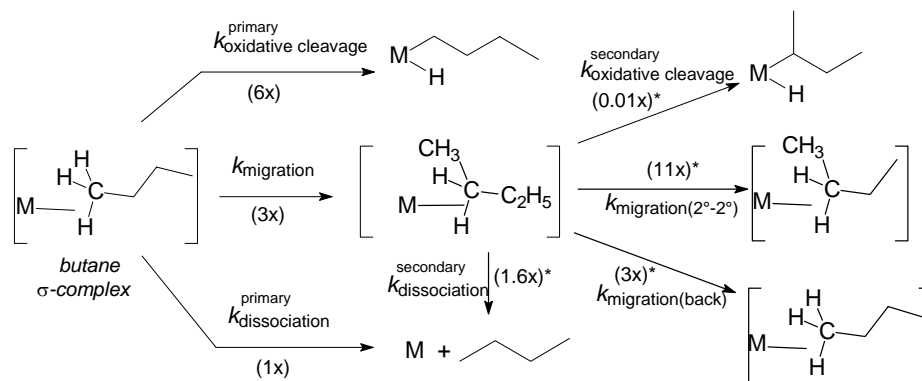


Figure 1. Relative rates of σ -alkane processes.

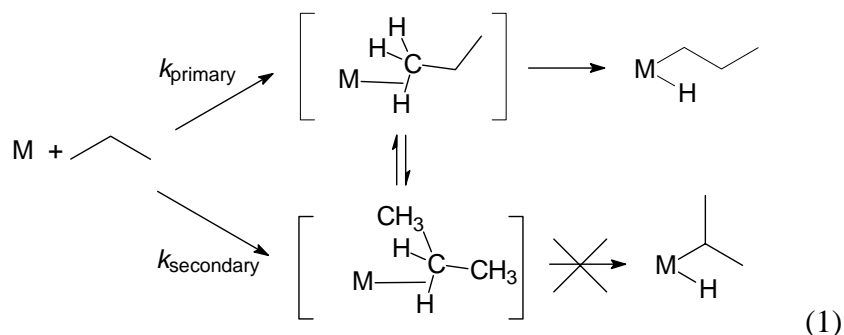
These conclusions can be expressed in a schematic fashion as shown in Scheme 1. Our studies do not permit the determination of either the absolute or relative energies of the primary and secondary alkane complexes, so we cannot establish the relative rates of processes between these two intermediates. Relative rates are shown assuming the energies of the two alkane complexes are equal.

Scheme 1: Relative rates of processes available in primary (1°) and secondary (2°) alkane complexes.



*Assuming 1° alkane σ -complex is at the same energy as the 2° alkane σ -complex

With the relative rates of all of these processes now known for any linear alkane, we have completed studies to determine *which C-H bond of an alkane first binds to the TpRhL fragment*. The execution of this experiment is not completely obvious, as reaction of the fragment with any linear hydrocarbon only gives a single product, the n-alkyl hydride (eq 1). One cannot determine how the alkane initially bound if a single product is observed.

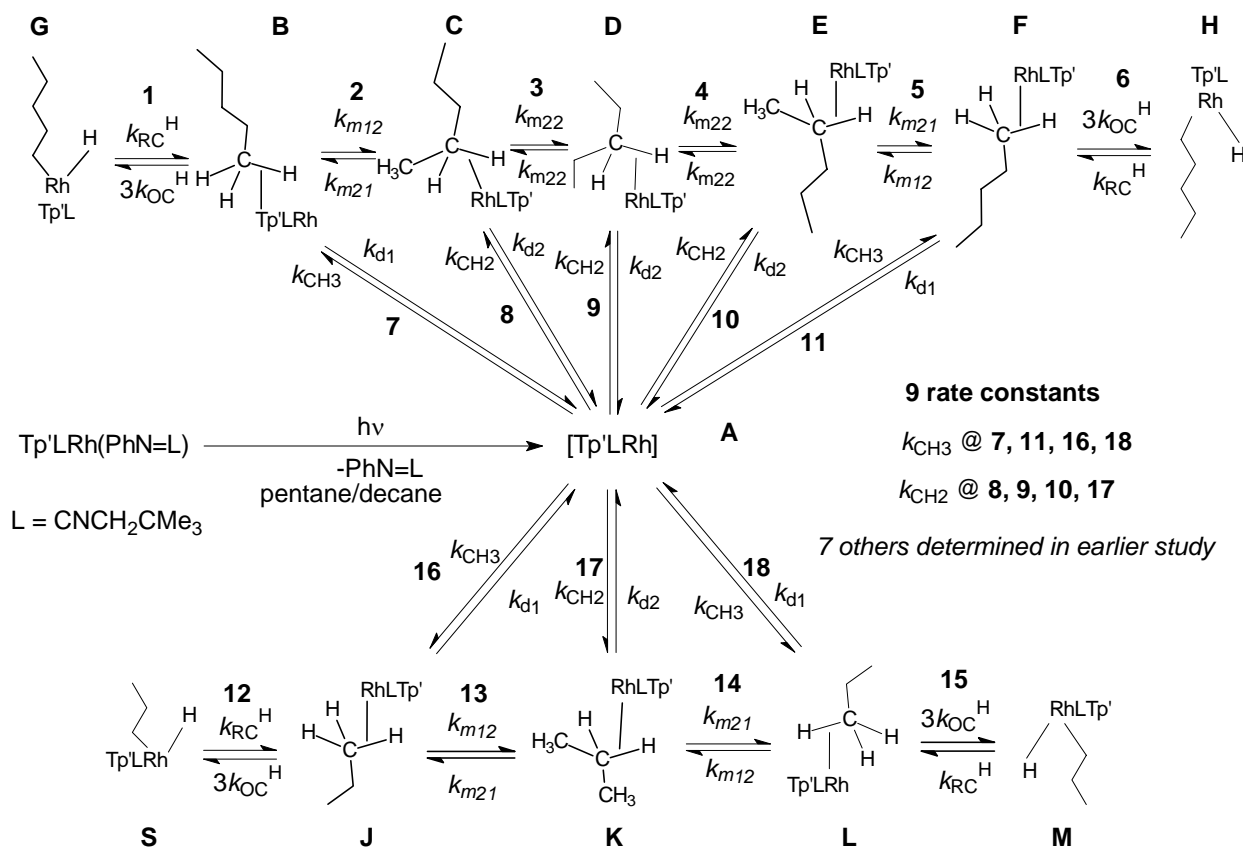


In the current project period, we established that (1) the TpRhL fragment coordinates to a linear alkane to give a σ -complex and that the coordination is favored at the methylene group over the methyl group by a ratio of 1.5:1. (2) a methyl group in pentane coordinates 1.2 times

faster than the more hindered methyl group of isobutane. (3) the oxidative cleavage of a methyl C-H bond (primary C-H) occurs $65K_{12}$ times faster than the C-H bond in a methylene group (secondary C-H), where K_{12} represents the equilibrium constant between primary and secondary alkane complexes. These conclusions were made building upon our earlier studies of the relative rates of oxidative cleavage, migration, and dissociation indicated in Scheme 1. The experimental evidence for these conclusions is given below.

The first new result is determination of the rate at which a reactive metal complex with a vacant site coordinates a methyl group (CH_3) vs a methylene group (CH_2). This was determined by looking at the product distribution in a competition experiment between pentane and propane. In this experiment, the metal intermediate would see an equal number of methyl groups in each substrate but differing numbers of methylenes (see Scheme 2). Note that in either case, only the terminal activation product would be seen since coordination to an internal methylene would lead to migration of the metal along the chain to the end, where oxidative cleavage would occur. If

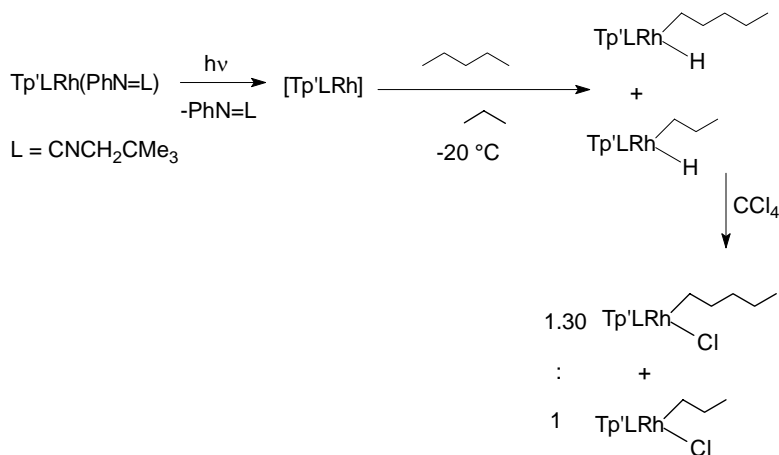
Scheme 2: Pathways for C-H coordination/activation in pentane-propane competition.



the reactive intermediate were to bind only to methyl groups C-H bonds, then a 1:1 product ratio would be expected. If the reactive intermediate were to bind only to methylene C-H bonds, then a product ratio favoring propane activation would be expected (corresponding to the increased number of methylene groups).

Scheme 2 shows all possible intermediates and pathways. It is rather complicated (!), but since the earlier studies established many of these relative rates, *only the rates of primary coordination (k_{CH3}) and secondary coordination (k_{CH2}) need to be determined*. In fact, we only want to know the ratio of these rates so that the ratio can be adjusted in a simulation to match the experimentally observed ratio of products. In the experiment, $Tp^*Rh(CNR)(\text{carbodiimide})$ was irradiated in a 1:1 mixture of pentane/propane. The alkyl hydride products were quenched with CCl_4 to give the stable chloro derivatives in a 1.3:1 ratio (Scheme 3). Consequently, the results are consistent with a slight preference for methylene group coordination, and the simulation indicates an actual preference of $k_{CH2}/k_{CH3} = 1.5:1$. As a test of this value, a competition was run between pentane and decane. A preference of 1.15:1 for decane was predicted from the simulation. When the experiment was run, a 1.15:1 ratio of products was seen, affording a high level of confidence in the relative binding abilities.

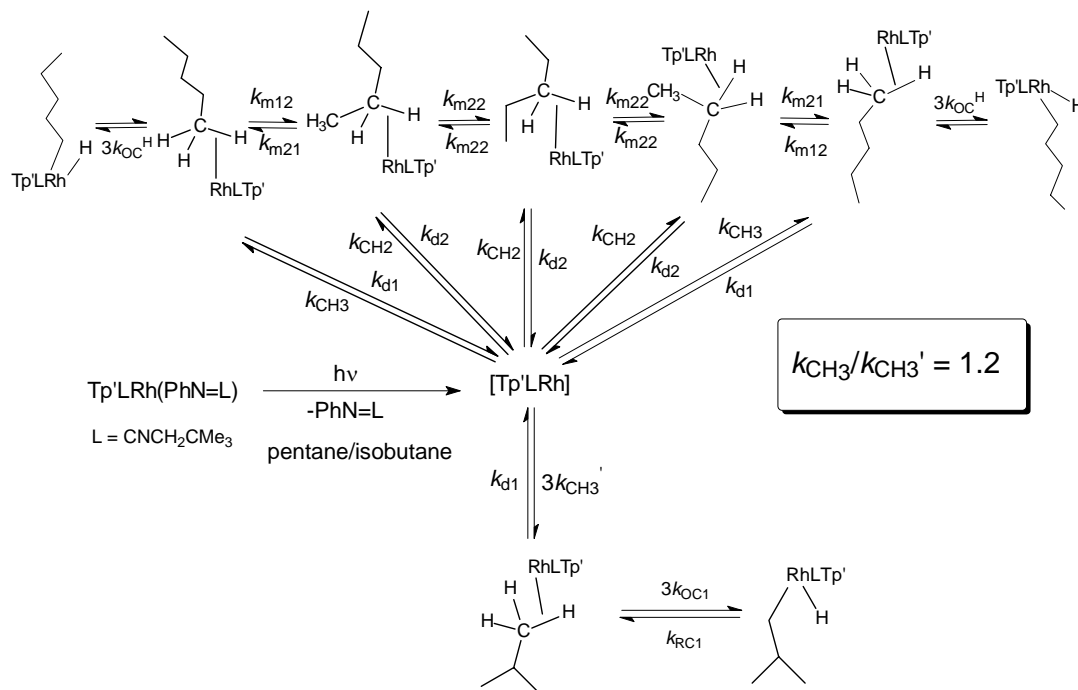
Scheme 3. Competition between pentane and propane.



Steric hinderence can interfere with the ability to coordinate to a methyl group C-H bond. This can be seen in a competition between pentane and isobutane. In this experiment, two methyl groups in a linear alkane compete with three methyl groups in a branched alkane. The

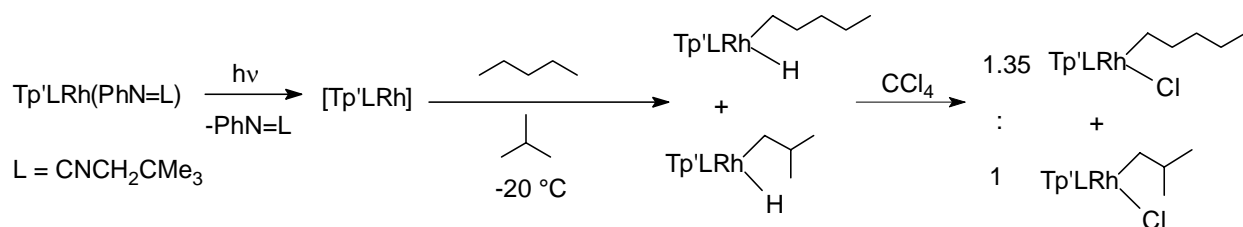
competitive reactions involved are shown in Scheme 4, with the two different rate constants for methyl group binding shown as k_{CH_3} and k_{CH_3}' .

Scheme 4. Pathways for C-H coordination/activation in pentane-isobutane competition.



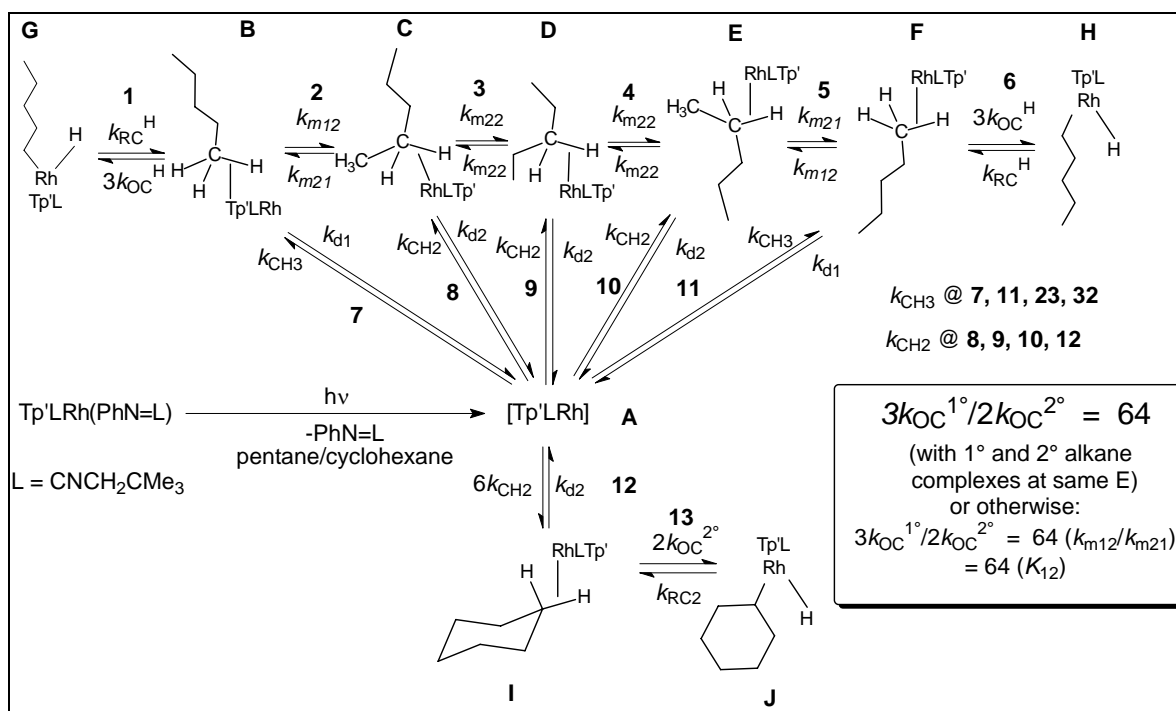
In the experiment, $\text{Tp}^*\text{Rh}(\text{CNR})(\text{carbodiimide})$ was irradiated in a 1:1 mixture of pentane/isobutane. The alkyl hydride products were quenched with CCl_4 to give the stable chloro derivatives in a 1.35:1 ratio (Scheme 5). Once again, simulation of the experiment while varying only the ratio $k_{\text{CH}_3}/k_{\text{CH}_3}'$ allows determination of the ratio as 1.2:1. Note that in this experiment, we assume that the rate of oxidative cleavage of the C-H bond in the two methyl complexes is the same. It is possible to interpret this experiment in terms of an *equal rate* of binding to the two types of methyl groups, but with a 1.2:1 ratio between the rate of the two oxidative cleavage rates.

Scheme 5. Competition between pentane and isobutane.



In the pentane/propane competition experiment, we learned about the relative rates of binding of unhindered CH_3 vs CH_2 . It would be reasonable to expect this rate ratio to apply in other competitions involving the binding of similar types of bonds. For example, the methylene C-H bonds in cyclohexane would be expected to bind to the $[\text{Tp}^*\text{RhL}]$ fragment with the same ease as those in pentane, since cyclohexane is an unstrained, 'natural' conformation similar to that in a linear alkane. Interestingly, cyclohexane does undergo activation of its C-H bonds by the $[\text{Tp}^*\text{RhL}]$ fragment because secondary C-H bonds are the only ones available. In a competition between pentane and cyclohexane, the metal fragment should bind to both alkanes in a predictable fashion since $k_{\text{CH}_3}/k_{\text{CH}_2}$ is known. From the ratio of products obtained, one should be able to determine the relative rates of oxidative cleavage of a secondary C-H bond ($k_{\text{OC}}^{2^\circ}$) vs a primary C-H bond ($k_{\text{OC}}^{1^\circ}$), provided the alkane σ -complexes are at the same energy. These pathways and the corresponding rate constants are shown in Scheme 6.

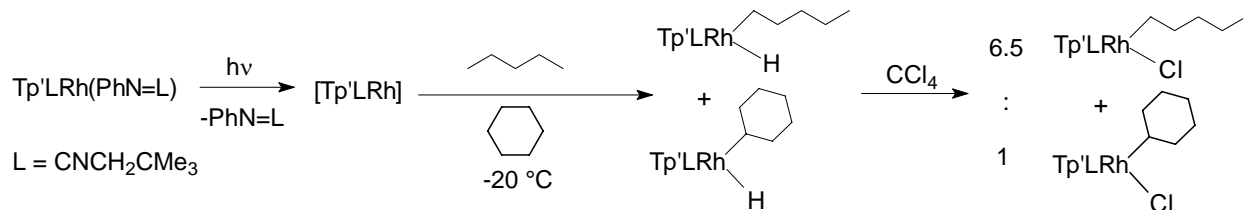
Scheme 6. Pathways for C-H coordination/activation in pentane-cyclohexane competition.



In the competition experiment, $\text{Tp}^*\text{Rh}(\text{L})(\text{carbodiimide})$ was irradiated in a 1:1 mixture of pentane/cyclohexane and quenched with CCl_4 . A 6.5:1 ratio of the n-pentyl and cyclohexyl chloride products was seen (Scheme 7). From the simulation, this corresponds to a 64:1 ratio for

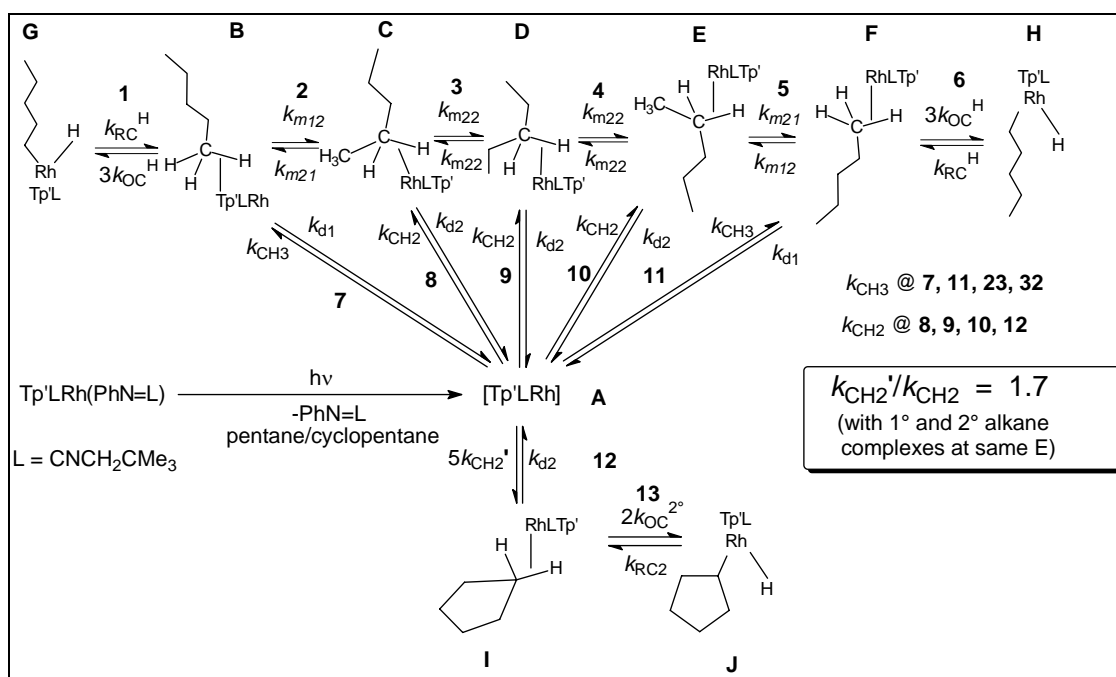
$k_{OC}^{1^\circ}/k_{OC}^{2^\circ}$, assuming the alkane σ -complexes are at the same energy. If they are at different energies, then a 'correction' must be applied corresponding to K_{eq} between the two σ -complexes.

Scheme 7. Competition between pentane and cyclohexane.



Finally, we have also looked at activation of cyclopentane vs pentane in a competition experiment. Here, due to the strain in the cyclopentane ring, it is *not* reasonable to assume that the rate of methylene coordination is the same as in a linear alkane. Consequently, the scheme for this experiment shows different rates for the two types of methylene coordination (Scheme 8), but the same rate of oxidative cleavage in the methylene-alkane complex.

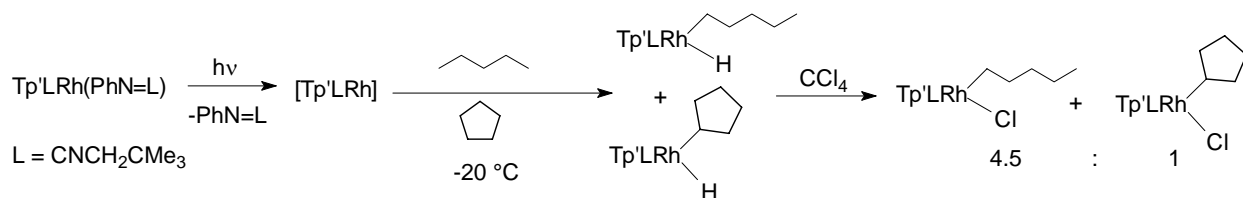
Scheme 8. Pathways for C-H coordination/activation in pentane-cyclopentane competition.



In the competition experiment, Tp^*RhL (carbodiimide) was irradiated in a 1:1 mixture of pentane and cyclopentane, and CCl_4 added to quench the products. A 4.5:1 ratio of n-pentyl to cyclopentyl products were seen (Scheme 9), showing that cyclopentane is slightly more reactive

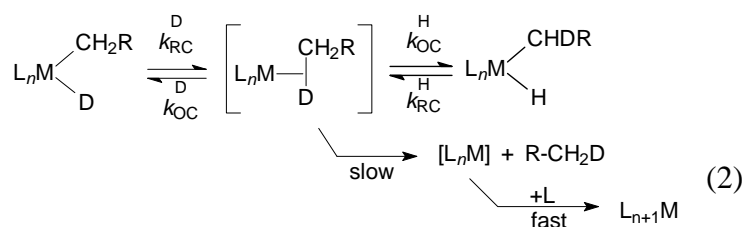
than cyclohexane, as anticipated. From the kinetic simulation of the competition, a ratio for $k_{\text{CH}_2'}/k_{\text{CH}_2}$ of 1.7 was obtained.

Scheme 9. Competition between pentane and cyclopentane.



As a check that this value represents the relative coordination abilities of cyclopentane vs cyclohexane, a competition experiment was run by irradiation of $\text{Tp}^*\text{RhL}(\text{carbodiimide})$ in a 1:1 mixture of cyclopentane/cyclohexane. A 1.9:1 ratio of cycloalkyl chloride products was observed. The excellent agreement between the competition ratio from these two independent experiments argues that the assumptions made in the simulations are reasonable.

One of the more interesting side-lights from these studies comes from the independent determination of isotope effects for both the 'oxidative cleavage' and the 'reductive coupling' steps of the C–H activation reaction indicated in equation 2. These isotope effects, both kinetic isotope effects on a fundamental reaction step, were found to be *normal* isotope effects. The overall effect on alkane reductive elimination, however, is to generate an *inverse* kinetic isotope. The initial equilibrium isotope effect between the alkyl hydride complex and the alkane sigma-complex is inverse, not because either of the individual rates are inverse, but because the *ratio* of these isotope effects is inverse. As this was the first known system where these effects had been completely sorted out, we published a more didactic article in *Accounts of Chemical Research* to shed light on the analysis of this controversial subject.

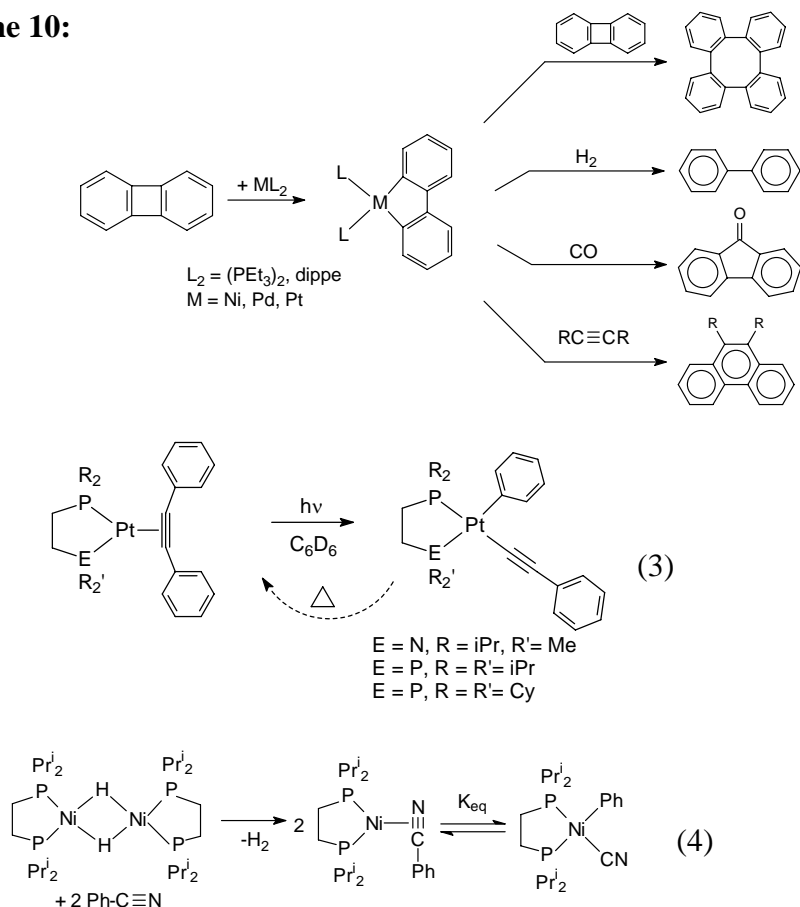


2. C-C Bond Cleavage Studies

Our DOE supported work showed that several types of C-C bonds can be cleaved. We have discovered 3 distinct classes of C-C bonds that can be cleaved: (1) strained rings such as

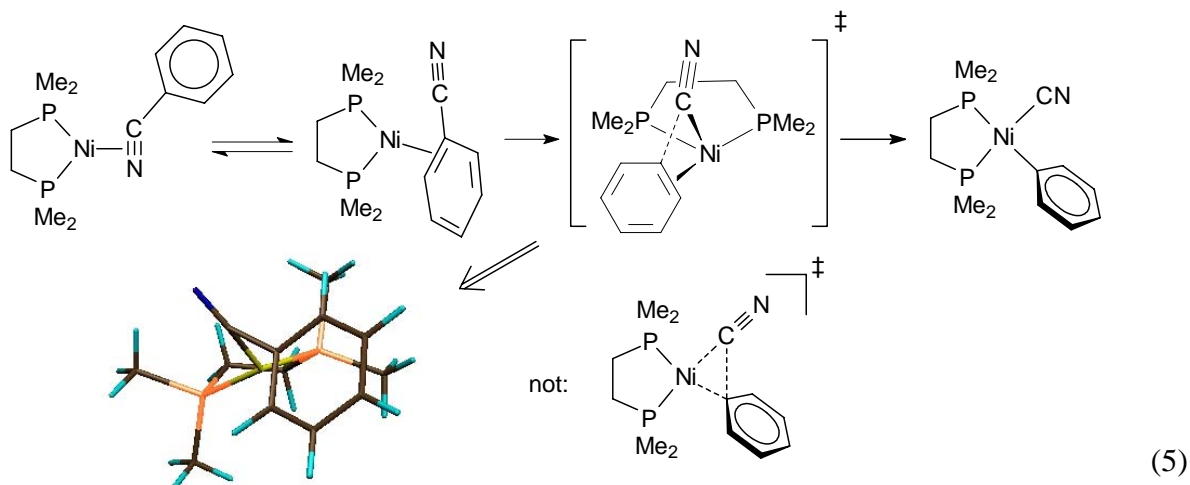
biphenylene undergo sp^2 - sp^2 C-C cleavage with a number of metal complexes to give a variety of products. (2) diphenylacetylene undergoes sp - sp^2 cleavage photochemically when attached to PtL_2 complexes. (3) aryl nitriles undergo sp^2 - sp C-CN cleavage when reacted with NiL_2 fragments, and η^2 -nitrile adducts can be observed as reaction intermediates. Examples of these discoveries are shown in Schemes 10, eq 3, and eq 4 below.

Scheme 10:



This latter reaction has been now investigated using DFT theoretical studies to examine the mechanism of reaction. The results are both surprising and unexpected. First, the product is found to have a large dipole moment (11.1 Debye) which means there is a large solvent effect upon the equilibrium. Second, while the η^2 -nitrile complex is found to be more stable than the oxidative addition product (in the gas phase), an η^2 -arene complex can be located that is intermediate in energy. Finally, we determined that this η^2 -arene complex is the precursor to the transition state for C-CN cleavage. The motion involved is a rotation about the nickel-olefin bond by approximately 110° , to place the olefin and nitrile carbon in a π -allyl arrangement perpendicular to the NiP_2 plane. From here, the C-C bond lengthens and is cleaved, relaxing to

the square planar Ni^{II} oxidative addition product as shown in equation 5. The expected transition state, an in-plane square-planar arrangement was found to lead back to the η^2 -arene complex.



The calculated energy profile for this reaction is summarized in Figure 2 below. In addition, calculations have been carried out on o-fluoro, m-fluoro, p-fluoro, and 2,6-difluorobenzonitrile derivatives. One can see the stabilizing effect of the fluorine on the oxidative addition product, and also some slight changes in the geometry of the transition state.

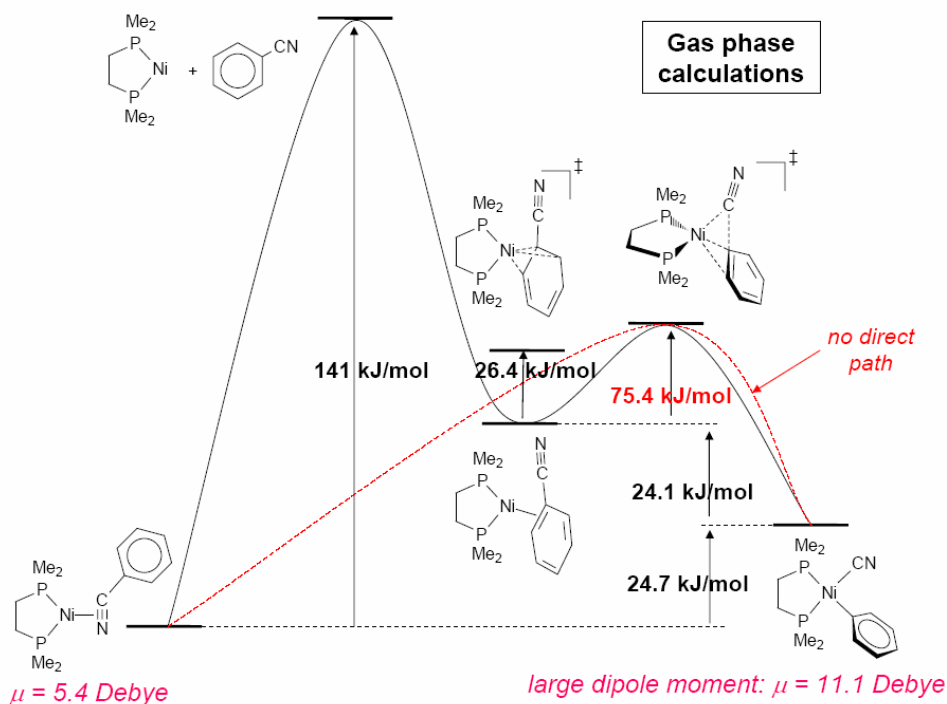
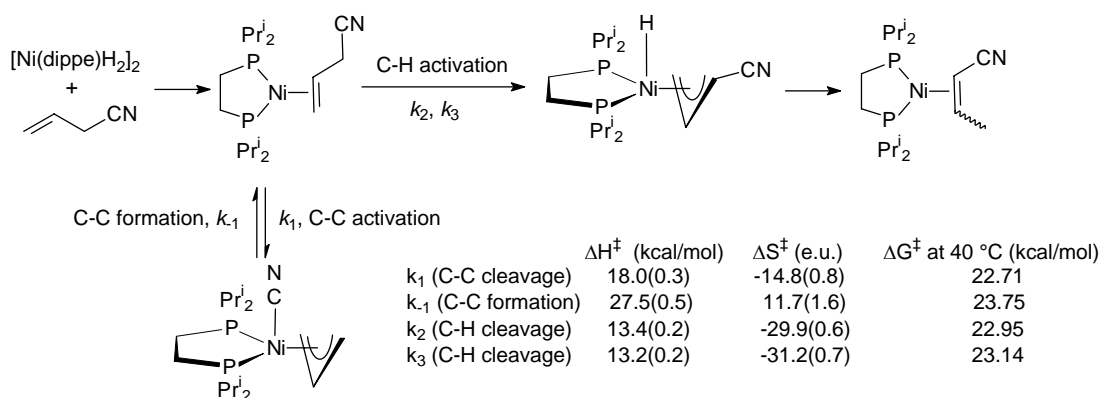


Figure 2. Energy diagram for the C-C cleavage in benzonitrile.

Recently, we have reported investigations of a new class of C-C cleavage, that of allyl-nitriles. At a metal center this cleavage reaction generates both a strong metal-cyanide bond and a π -allyl ligand, and hence has been found to be both facile and reversible. Indeed, at nickel(0), this reaction forms the basis of DuPont's synthesis of adiponitrile for the production of nylon via addition of HCN to butadiene, to the tune of over 400 thousand metric tons per year! This project continues through a collaboration with Professor Juventino Garcia at Universidad Nacional Autonomas de Mexico in Mexico City. The PIs share results, compounds, and methodology in this joint project.

We have discovered that the reactive hydride $[(\text{dippe})\text{NiH}]_2$, which serves as a room temperature source of $[\text{Ni}(\text{dippe})]$, reacts with allylcyanide to give initially a π -olefin complex (dippe = bis-(diisopropylphosphino)ethane). This species can be seen at low temperature by NMR spectroscopy, and upon warming to RT competitive C-H and C-CN cleavage takes place. C-H activation gives a π -allyl hydride complex that is not observed, because the hydride is transferred back to the opposite end of the allyl group to give a very stable crotononitrile complex (both cis and trans are formed). C-CN activation, however, leads to a metastable π -allyl cyanide complex that can be isolated and was structurally characterized. C-CN cleavage is reversible, so that ultimately, all nickel winds up as the crotononitrile complexes (Scheme 11).

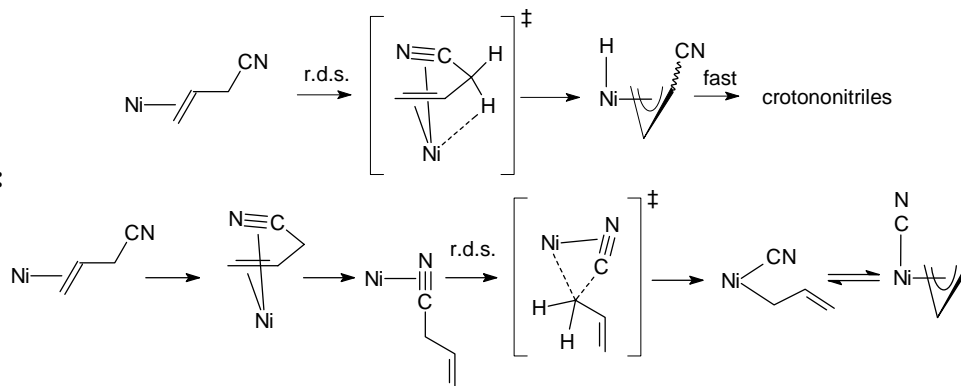
Scheme 11. C-C and C-H Bond Activation in allylcyanide.



By monitoring the distribution of species over time, we have been able to extract the rate constants for all of these species by kinetic simulation. In addition, by measuring the distribution of species as a function of temperature, we can obtain activation parameters for the various steps. The results are quite interesting, in that we find that while C-H activation and C-C activation have small temperature dependences, C-C cleavage has a large temperature

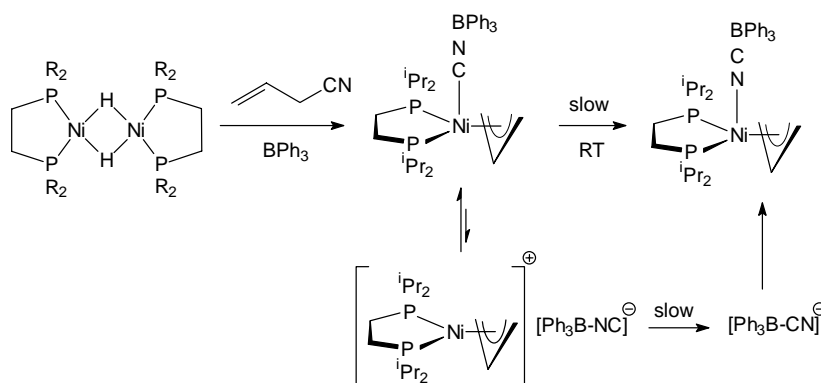
dependence. The result is that by raising the temperature, one can selectively drive the reaction in the direction of the less-favorable π -allyl cyanide complex. This is good news, since the DuPont catalysis requires that the C-C cleavage dominate the C-H cleavage. The activation parameters support the mechanism for C-H and C-C cleavage shown in Scheme 12.

Scheme 12:



We have also investigated the effect of the Lewis acid BPh_3 upon the isomerization reaction. Addition of BPh_3 to a cold solution of $(\text{dippe})\text{Ni}(\eta^2\text{-allylCN})$ leads to the immediate and quantitative formation of the BPh_3 adduct of the π -allyl cyanide adduct. Addition of a second equivalent of the Lewis acid leads to the removal of the cyanide ligand as the $[\text{Ph}_3\text{B-CN-BPh}_3]^-$ anion, leaving behind the $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+$ cation (Scheme 13). With only one equivalent of BPh_3 , there is evidence of linkage isomerism of the initial Ni-C-N-BPh_3 adduct to the Ni-N-C-BPh_3 adduct.

Scheme 13. Effect of Lewis acid on the C-C and C-H Bond Activation in allyl cyanide.

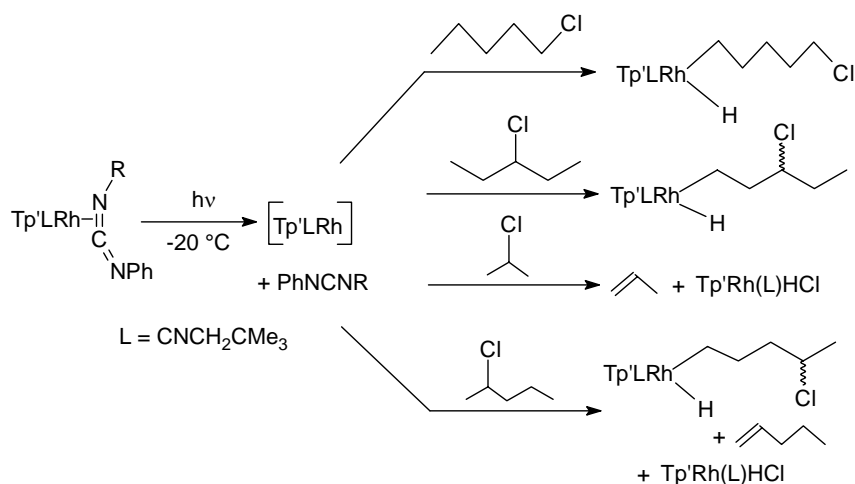


3. C-H Bond Activation and Functionalization Studies

We have conducted an extensive investigation of C-H activation in chloroalkanes using the reactive precursor $\text{Tp}^*\text{Rh}(\text{CNR})(\text{carbodiimide})$. Remarkably, the C-Cl bond does not undergo

oxidative addition. Rather, we find a strong selectivity for exclusive terminal methyl group C-H bond activation. Thus, 1-chloro alkane gives the 5-chloropentyl hydride as the only product. 3-chloropentane gives the 3-chloropentyl hydride product. In this case, however, two diastereomers are formed in a 1:1 ratio, since the metal is chiral and the 3-chloro substituent renders the ligand chiral. If a chlorine is present in a β -position, then β -chloride elimination occurs to give an olefin and the metal chloride. Therefore, 2-chloropropane gives only propene and the hydrido chloride $\text{Tp}^*\text{Rh}(\text{CNR})\text{HCl}$. 2-chloropentane gives a mixture of the C-H activation product 4-chloropentyl hydride, pentene, and the hydrido chloride. These reactions are summarized in Scheme 14.

Scheme 14. Reactions of Chloroalkanes with $[\text{Tp}^*\text{Rh}(\text{CNR})]$.



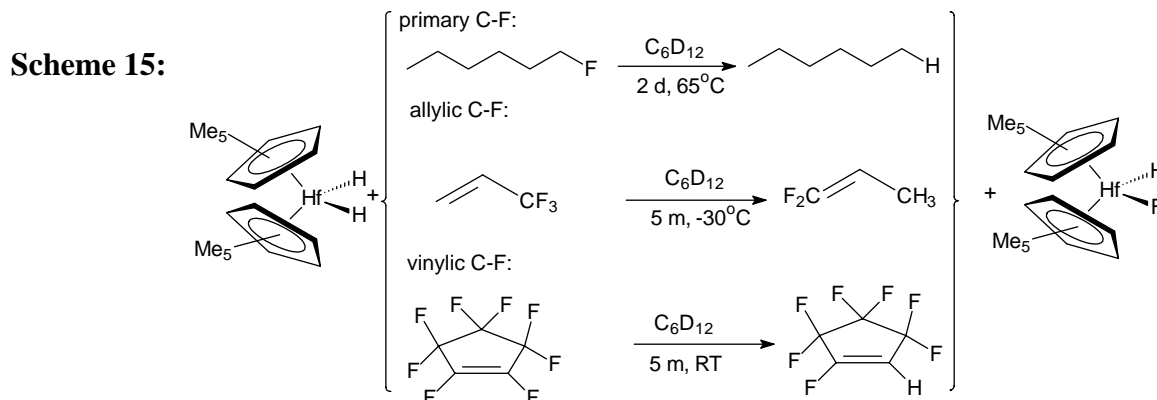
We have also begun to investigate aliphatic nitrile complexes. It appears that there is once again a selectivity for terminal methyl groups. With acetonitrile, the adduct $\text{Tp}^*\text{LRh}(\text{CH}_2\text{CN})\text{H}$ is formed, and is found to be stable for days at $60\text{ }^\circ\text{C}$! This is the most stable alkyl hydride in this series yet, and we may be able to do new functionalization chemistry with this derivative.

We have also found that aromatic C-H activation with $\text{Tp}^*\text{Rh}(\text{CNR})(\text{carbodiimide})$ in the presence of pinacol borane leads to the formation of arylboronates. These reactions are catalytic in rhodium and occur thermally under mild conditions. Further study of the intermediates in these reactions are underway.

4. C-F Bond Cleavage Studies

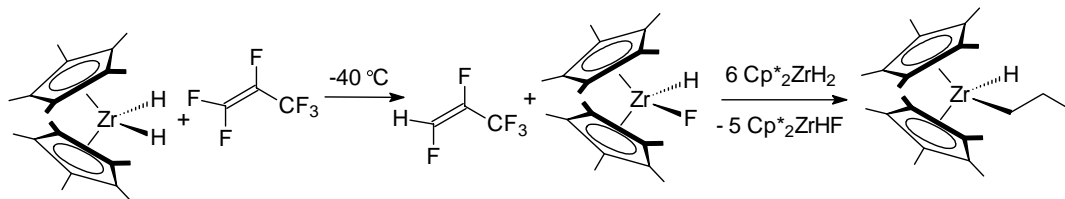
We have now nearly completed studies with the soluble, reactive $\text{Cp}^*_2\text{HfH}_2$ and found that this molecule cleaves a wide variety of aromatic, aliphatic, and vinylic C-F bonds, as did the

zirconium analog $\text{Cp}^*_2\text{ZrH}_2$. Systematic studies have shown that the reactivity of the hafnium derivative mimics that of the zirconium complex, although all reactions are slower (Scheme 15). The lower reactivity of the hafnium complex is attributed to its larger M-H bond strength.



We have now continued our investigation of the C-F cleavage in perfluoroolefins. These appear to be a special class of substrate, in that the mechanism of C-F cleavage may be different than that seen in our earlier studies with $\text{Cp}^*_2\text{ZrH}_2$. Reaction with perfluoropropene gives first the selective formation of *E*-CHF=CFCF₃. Further reaction with zirconium hydride leads to complete defluorination with no further intermediates being seen (Scheme 16).

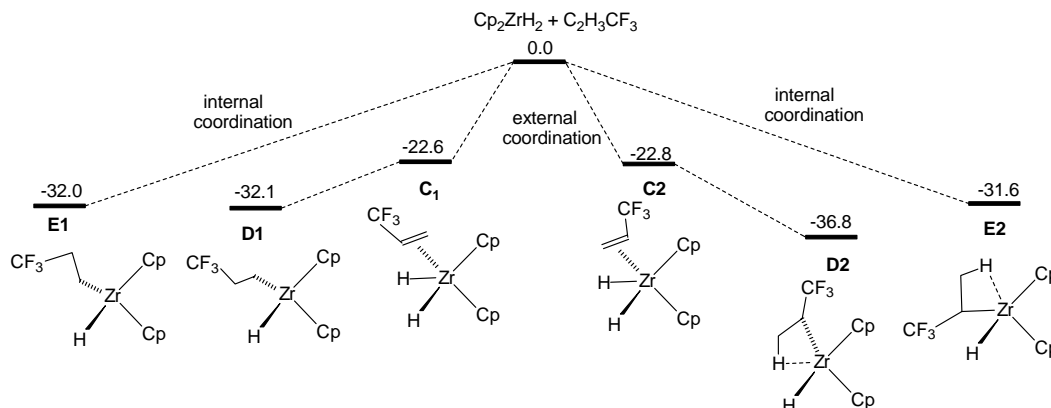
Scheme 16. Reaction of $\text{Cp}^*_2\text{ZrH}_2$ with perfluoropropene.



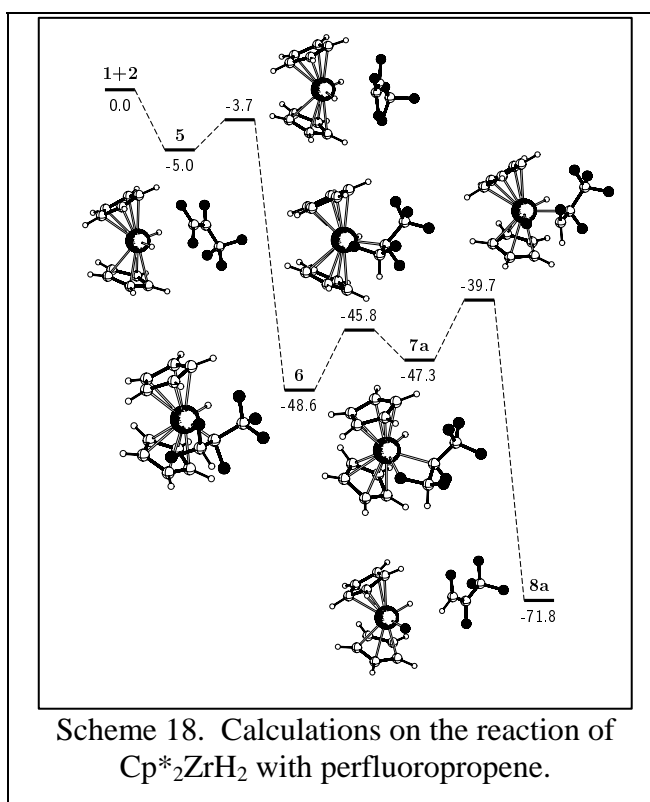
The mechanism for the reaction could involve hydridic attack on the olefin with H/F metathesis, or an insertion/elimination mechanism. The olefin could approach centrally, between the two hydrides, or laterally, with the two hydrides remaining cis to each other. In order to investigate these possibilities, we have a collaboration with a theory group in Montpellier. Odile Eisenstein and Eric Clot have provided high level calculations investigating these systems, and the work is providing guidance for the mechanism of reaction. Initial studies were done on the insertion reaction of ethylene with Cp_2ZrH_2 . We then progressed to trifluoropropene, which has been shown experimentally to undergo an insertion/ β -fluoride elimination pathway. The calculations done thus far are able to reproduce the selective internal

insertion product, and further work is underway to look at the β -fluoride elimination step (Scheme 17).

Scheme 17. Calculations on the reaction of $\text{Cp}^*_2\text{ZrH}_2$ with trifluoropropene.



Further calculations have been recently completed with Cp_2ZrH_2 reacting with perfluoropropene. The results show that interaction of the olefin internally with Cp_2ZrH_2 leads to olefin insertion followed by an external β -fluoride elimination. Other pathways were investigated but all were found to lie at higher energies (Scheme 18).



Scheme 18. Calculations on the reaction of $\text{Cp}^*_2\text{ZrH}_2$ with perfluoropropene.

**Publications during the current grant cycle acknowledging DOE support,
December 1, 2004 - November 30, 2005:**

Manuscripts in print:

1. "Kinetics, Thermodynamics and Effect of BPh₃ on Competitive C-C and C-H Bond Activation Reactions in the Interconversion of Allyl Cyanide by [Ni(dippe)]," Nicole M. Brunkan, Donna M. Brestensky, and William D. Jones, *J. Am. Chem. Soc.*, **2004**, *126*, 3627-3636.
2. "Cleavage of Carbon-Carbon bonds in Alkyl Nitriles Using Nickel(0)," Juventino J. García, Alma Arévalo, Nicole M. Brunkan, and William D. Jones," *Organometallics*, **2004**, *23*, 3997-4002.
3. "Defluorination of Perfluoropropene using Cp*₂ZrH₂ and Cp*₂ZrHF: A Mechanistic Investigation from a Joint Experimental-Theoretical Perspective," Eric Clot, Claire Megret, Bradley M. Kraft, Odile Eisenstein, and William D. Jones, *J. Am. Chem. Soc.*, **2004**, *126*, 5647-5653.
4. On the Nature of Carbon-Hydrogen Bond Activation at Rhodium and Related Reactions, William D. Jones, *Inorg. Chem.* **2005**, *44*, 4475-4484.
5. "Alkane Coordination Selectivity in Hydrocarbon Activation by [Tp'Rh(CNneopentyl)]: The Role of Alkane Complexes," Andrew J. Vetter, Christine Flaschenriem, and William D. Jones, *J. Am. Chem. Soc.* **2005**, ASAP 10-Aug-2005.

Manuscripts Submitted/in press:

6. "Kinetics and Mechanism of Dealkylation of Coordinated Isocyanide in Fe(PMe₃)₂(*t*-BuNC)₃," Christine L. Tennent and William D. Jones, *Can. J. Chem.* **2005**, in press.

Manuscripts in Preparation:

7. "Mechanistic Investigation of Vinylic Carbon-Fluorine Bond Activation of Perfluorinated Cycloalkenes using Cp*₂ZrH₂ and Cp*₂ZrHF," Eric Clot, Bradley M. Kraft, Odile Eisenstein, and William D. Jones, *J. Am. Chem. Soc.*, to be submitted.
8. "Bond Cleavage Reactions in Substituted Thiophenes by a Rhodium Complex," Tulay Atesin, Andrew W. Myers, Lingzhen Dong, and William D. Jones, to be submitted.
9. "The Activation of Alkyl Cyanides using a Trispyrazolylborate Rhodium Complex," Andrew J. Vetter, Christine Flaschenriem, and William D. Jones, to be submitted.
10. "The Functionalization of Hydrocarbons by Boranes using Trispyrazolylborate Complexes," Andrew J. Vetter and William D. Jones, to be submitted.
11. "The Synthesis and Structural Properties of [M(dippe)(η²-C₄H₄S)] Complexes of Ni, Pd, and Pt," Stephen S. Oster, Rene J. Lachicotte, and William D. Jones, to be submitted.

Recent Special Recognitions Received by the PI:

ACS Award in Organometallic Chemistry, 2003

Associate Editor, *J. Am. Chem. Soc.*, January 2003-

Chair of Organometallic Subdivision, Inorganic Division of the American Chemical Society, 2001.

Charles F. Houghton Professor of Chemistry, 2000-present

July 2000- 2003: Chairman, Department of Chemistry

Organometallic Gordon Conference, Chairman, Newport, RI, 2000.

Opening speaker at Inorganic Reaction Mechanisms Gordon Conference, Ventura, 2003.

Opening speaker at Organometallic Gordon Conference, Newport, 2003.

Speaker at Inorganic Gordon Conference, Newport, 2003.

Speaker at Isotope Effects Gordon Conference, Ventura, 2004.

Co-organizer of Symposium on Activation of Unreactive Bonds in Organic Synthesis (#147)
with Naoto Chatani and Victor Snieckus, for Pacifichem 2005

Additional Comments:

We anticipate using all allocated funds for the first year of this project.

We apologize for the length of this report.