

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

BY

Prof. William D. Jones  
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Department of Chemistry  
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FOR

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

William D. Jones, Principal Investigator  
Phone: 585-275-5493  
Grant No. DE-FG02-86ER13569

Current Project Period: December 1, 2005 - November 30, 2006 (year 2)

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

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

**Continuation Request Period: December 1, 2006 - November 30, 2007**

Continuation Request Amount (year 3): \$135,000

Unexpended Balance from Previous Year: \$0

## *Abstract of FY 2006 Research in the Chemical Sciences*

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

Grant# FG02-86ER13569

P.I.: William D. Jones, Department of Chemistry, University of Rochester, Rochester, NY 14627  
[jones@chem.rochester.edu](mailto:jones@chem.rochester.edu) 585-275-5493

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

Current Grant Period: 12/1/05-11/30/06, \$135,000 for year one

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

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**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 second 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, including chloroalkanes and (4) carbon-fluorine bond activation with hafnium. 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 cleaved C-C bonds in aryl-acetylenes, aryl-nitriles, and alkyl-nitriles, expanding tremendously the breadth of C-C cleavage; (2) we have investigated factors that affect the cleavage of 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; (3) we have measured C-H activation selectivities in a variety of chloroalkanes, showing a preference for activation of the terminal methyl groups and the facile  $\beta$ -chloride elimination reaction, (4) 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. The P.I. was a plenary lecturer at the 2006 International Conference on Organometallic Chemistry in Zaragoza, Spain. DOE funds have been used for the partial support of 4 graduate students (Ahmed Gunay, Brett Swartz, Ryan Reith, and Ting Li) during the current grant period, as well as several undergraduates (Bill Drelles, Suzanne Becker). 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.

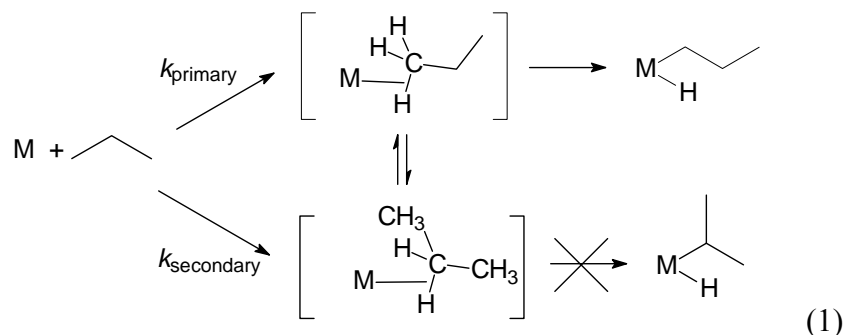
A detailed report follows, followed by a listing of the DOE supported publications.

## Detailed Progress Report for the Project Period Dec. 1, 2005- Nov. 30, 2006 (year 2).

This report summarizes research that has been completed during the second year of the current 3-year grant.

### 1. Tris-pyrazolylborate Rhodium Alkane Binding and Activation Studies.

Our rhodium-trispyrazolylborate 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  $\text{Tp}'\text{RhL}$ . In the prior 3-year project period, we established that the  $\text{Tp}'\text{RhL}$  fragment coordinates an alkane to give a  $\sigma$ -complex. A series of labelling studies allowed the determination of the relative rates of the processes available to the alkane  $\sigma$ -complex, specifically C-H activation (called oxidative cleavage), migration down the alkane chain, and simple dissociation. In the current grant project period, we completed and published studies that determine *which C-H bond of an alkane first binds to the  $\text{Tp}'\text{RhL}$  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 easily determine how the alkane initially bound if a single product is observed. However, using competitive activation studies (e.g. pentane vs. decane), we were able to sort out these differences in binding preference.

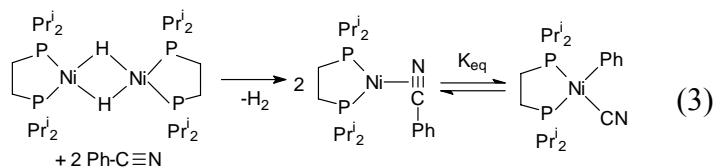
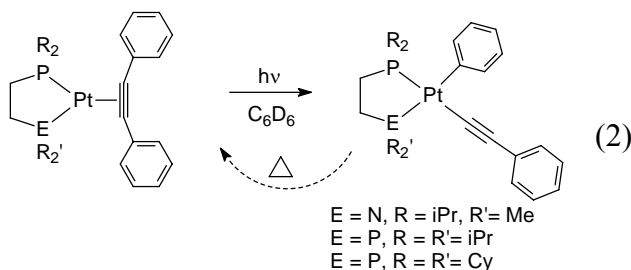
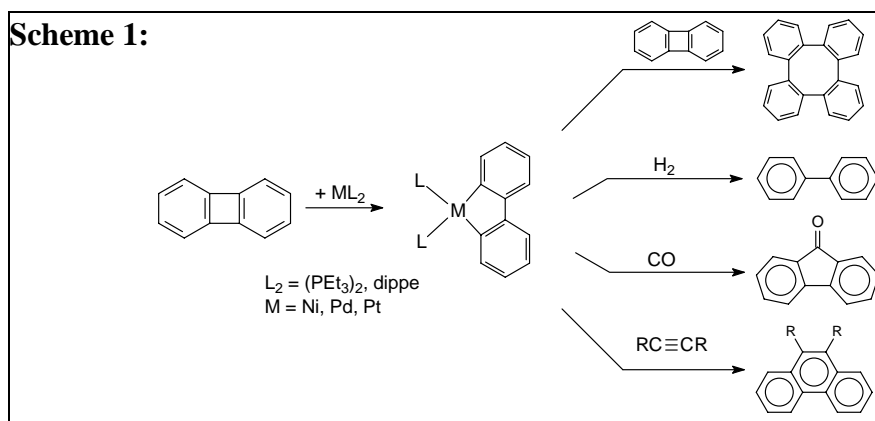


In the current project period, we established that (1) the  $\text{Tp}'\text{RhL}$  fragment coordinates to a linear alkane to give a  $\sigma$ -complex and that the coordination is favored at the methylene group over the methyl group by a ratio of 1.5:1. (2) a methyl group in pentane coordinates 1.2 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.

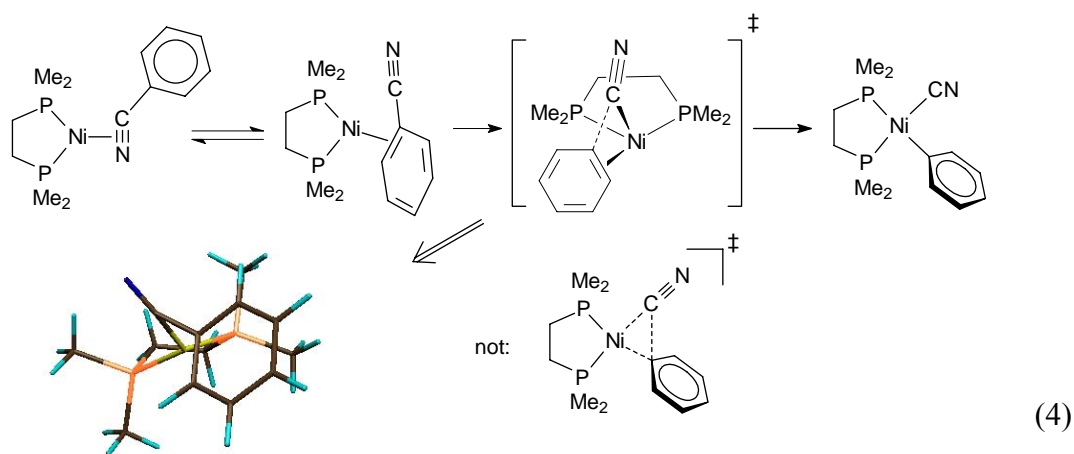
## 2. C-C Bond Cleavage Studies

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) diphenylacetylenes undergo  $sp$ - $sp^2$  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  $\eta^2$ -nitrile adducts can be observed as reaction intermediates. Examples of these discoveries are shown in Schemes 1, eq 2, and eq 3 below.



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  $\eta^2$ -nitrile complex is found to be more stable than the

oxidative addition product (in the gas phase), an  $\eta^2$ -arene complex can be located that is intermediate in energy. Finally, we determined that this  $\eta^2$ -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  $110^\circ$ , to place the olefin and nitrile carbon in a  $\pi$ -allyl arrangement perpendicular to the  $\text{NiP}_2$  plane. From here, the C-C bond lengthens and is cleaved, relaxing to the square planar  $\text{Ni}^{\text{II}}$  oxidative addition product as shown in equation 4. The expected transition state, an in-plane square-planar arrangement was found to lead back to the  $\eta^2$ -arene complex.

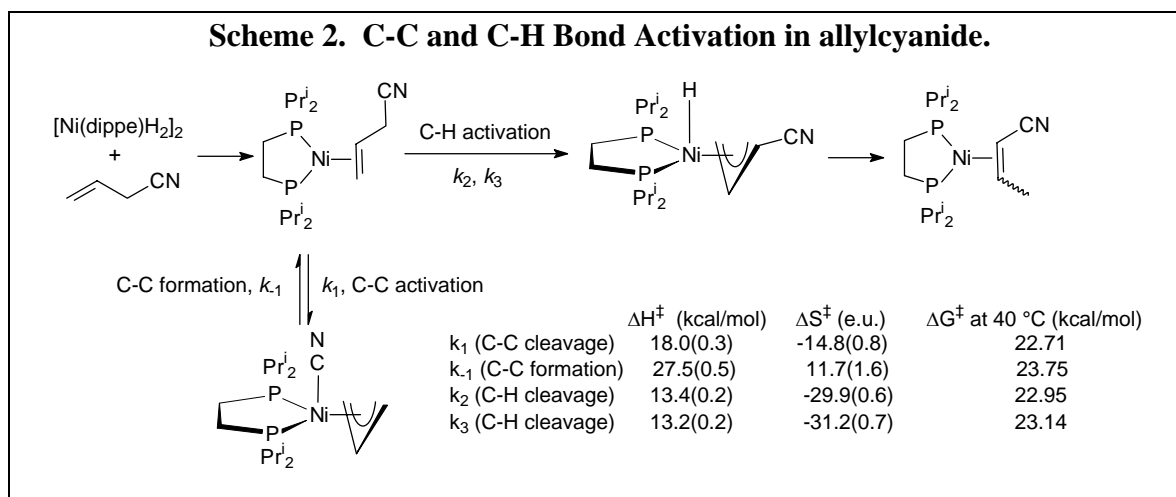


The calculated energy profile for this reaction is summarized in Figure 1 below. In

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Recently, we have reported investigations of a new class of C-C cleavage, that of allylnitriles. At a metal center this cleavage reaction generates both a strong metal-cyanide bond and a  $\pi$ -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 meet several times annually, either at international conferences or by visiting the home institutions. Recent publication of a new ferrocenyl phosphine catalyst for this reaction provides evidence for this collaboration.

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  $\pi$ -olefin complex ( $\text{dippe} = \text{bis}(\text{-diisopropylphosphino})\text{ethane}$ ). 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  $\pi$ -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  $\pi$ -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 2).



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

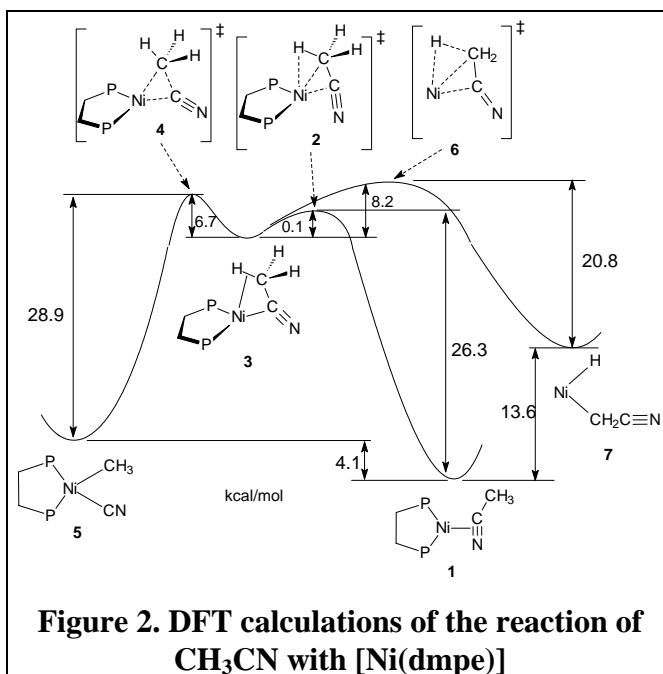
distribution of species as a function of temperature, we can obtain activation parameters for the various steps. The results are quite interesting, in that we find that while C-H activation and C-C activation have small temperature dependences, C-C cleavage has a large temperature dependence. The result is that by raising the temperature, one can selectively drive the reaction in the direction of the less-favorable  $\pi$ -allyl cyanide complex. This is good news, since the DuPont catalysis requires that the C-C cleavage dominate the C-H cleavage.

We have extended our studies with allyl cyanide to the industrially relevant nitrile, 2-methyl-3-butenitrile (2M3BN). This species undergoes two competitive processes as seen before with allyl cyanide: C-H activation leads to the formation of 2-methyl-2-butenitrile (cis

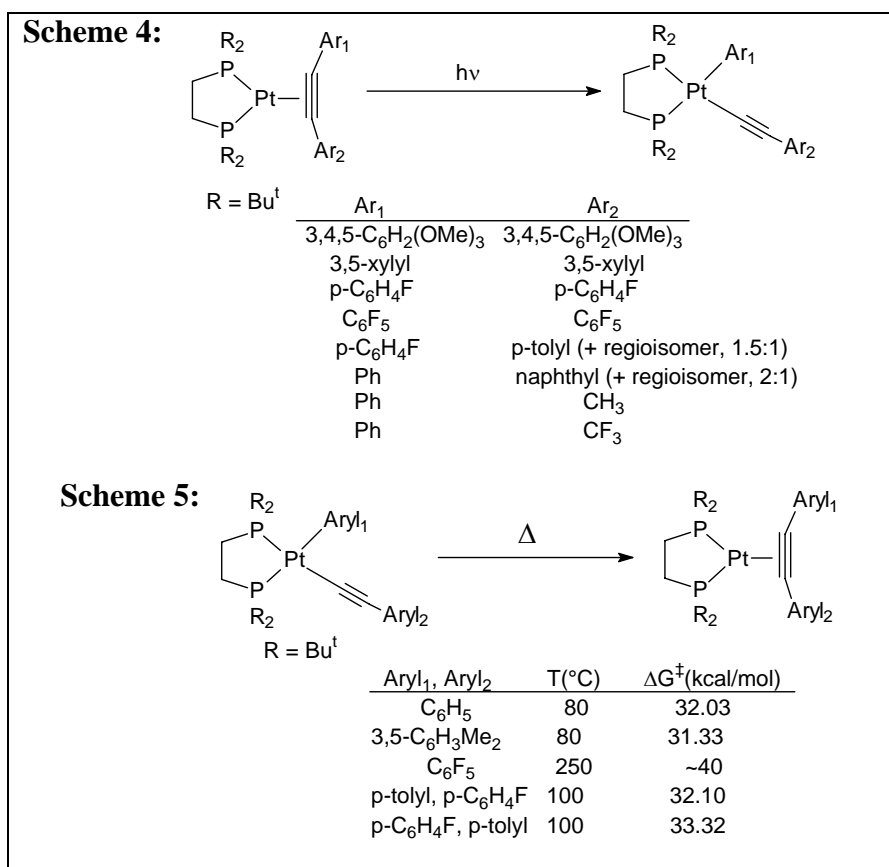
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Finally, we have also completed calculations on the simple acetonitrile C-CN activation using  $[\text{Ni}(\text{dmpe})\text{H}]_2$ . The results (gas phase) are shown in Figure 2 below, and show once again a transition state for C-C cleavage in which the C-C bond is inclined about  $30^\circ$  to the  $\text{NiP}_2$  plane. We also included the possibility of C-H activation, which is predicted to be thermodynamically quite unfavorable. We are making this species in the laboratory by the reaction of  $[\text{Ni}(\text{dippe})]$  with  $\text{ClCH}_2\text{CN}$  to give  $\text{Ni}(\text{dippe})(\text{CH}_2\text{CN})\text{Cl}$ , and then reducing this species to the hydride complex  $\text{Ni}(\text{dippe})(\text{CH}_2\text{CN})\text{H}$  using a reducing reagent such as  $\text{Cp}_2\text{ZrH}_2$ . We are also now including a solvation model in the calculations to account for the high dipole moment in the products and to give more realistic energies to the picture.



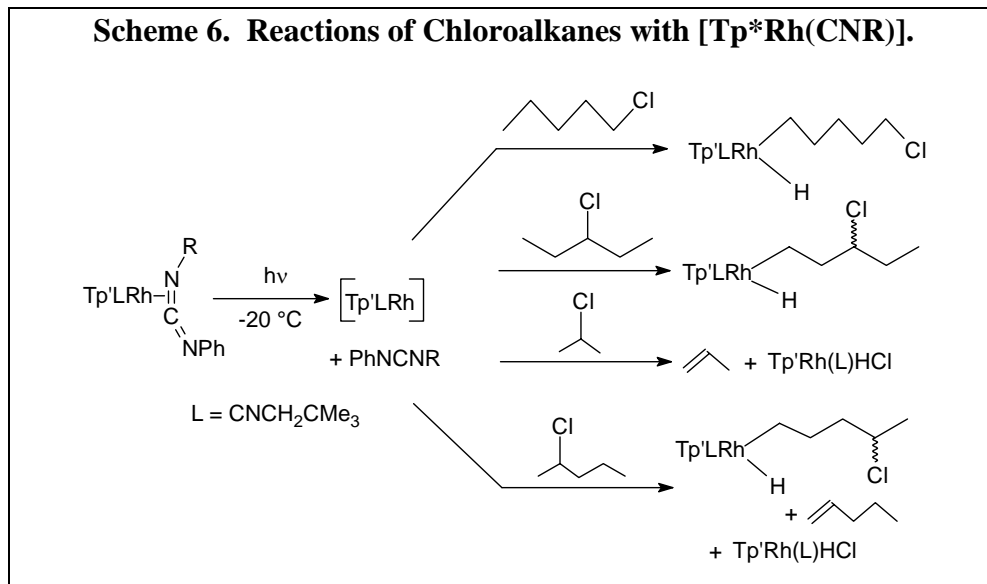
The C-C cleavage in aryl acetylenes has been accomplished photochemically using platinum complexes of the type Pt(dtbpe)( $\eta^2$ -acetylene) (Scheme 4). In all cases, C-C cleavage requires photolysis, and heating the product converts the Pt(II) oxidative addition product back to the  $\eta^2$ -acetylene complex. Only moderate selectivity is seen using hetero-substituted diarylacetylenes. The reductive elimination rates vary as a function of the aryl group on the acetylene, with barrier ranging from 31-40 kcal/mol (Scheme 5).



### 3. C-H Bond Activation and Functionalization Studies

We have conducted an extensive investigation of C-H activation in chloroalkanes using the reactive precursor Tp\*Rh(CNR)(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  $\beta$ -position, then  $\beta$ -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 6.

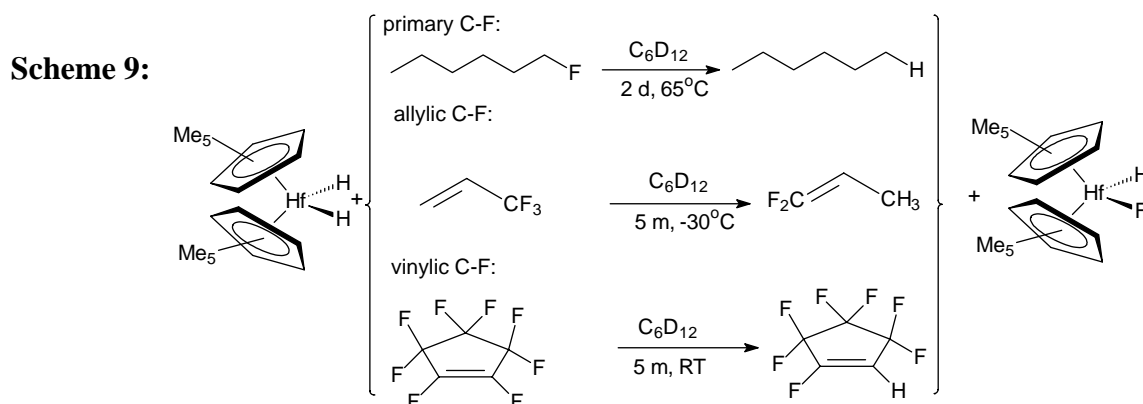


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#### 4. C-F Bond Cleavage Studies

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 9). The lower reactivity of the hafnium complex is attributed to its larger M-H bond strength.



We have now completed our investigation of the C-F cleavage in cyclic perfluoroolefins with  $\text{Cp}^*_2\text{ZrH}_2$ . 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  $\text{Cp}^*_2\text{ZrH}_2$ . Using DFT

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**Publications during the current grant cycle acknowledging DOE support,  
December 1, 2004 - November 30, 2006:**

**Manuscripts in print:**

1. *Activation and Functionalization of C-H Bonds*, K. I. Goldberg and A. S. Goldman, Eds., "Chapter 3. Alkane Complexes as Intermediates in C-H Bond Activation Reactions," William D. Jones, Andrew J. Vetter, Douglas D. Wick, Todd O. Northcutt, ACS Symposium Series 885, ACS, Washington, DC (2004).
2. "Carbon-hydrogen bond activation of chloroalkanes by a rhodium trispyrazolylborate complex," Andy J. Vetter and William D. Jones, *Polyhedron*, **2004**, *23*, 413-417.
3. "Kinetics, Thermodynamics and Effect of BPh<sub>3</sub> 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.
4. "Defluorination of Perfluoropropene using Cp\*<sub>2</sub>ZrH<sub>2</sub> and Cp\*<sub>2</sub>ZrHF: 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.
5. "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.
6. "Synthesis, Structure, and Reactivity of [Ir(dippe)(μ-Cl)]<sub>2</sub>, [Ir(dippe)<sub>2</sub>][Ir(dippe)Cl<sub>2</sub>], and [Ir(dippe)<sub>2</sub>]Cl," Stephen S. Oster and William D. Jones, *Polyhedron*, **2004**, *23*, 2959-2965.
7. "On the Nature of Carbon-Hydrogen Bond Activation at Rhodium and Related Reactions," William D. Jones, *Inorg. Chem.* **2005**, *44*, 4475-4484.
8. "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**, *127*, 12315-12322.
9. "Kinetics and Mechanism of Dealkylation of Coordinated Isocyanide in Fe(PMe<sub>3</sub>)<sub>2</sub>(*t*-BuNC)<sub>3</sub>," Christine L. Tennent and William D. Jones, *Can. J. Chem.* **2005**, *83*, 626-633.
10. "The Synthesis and Structural Properties of [M(dippe)(η<sup>2</sup>-C<sub>4</sub>H<sub>4</sub>S)] Complexes of Pd and Pt and Comparison with their Ni Analog," Tülay A. Ateşin, Stephen S. Oster, Karlyn Skugrud, William D. Jones, *Inorg. Chim. Acta*, **2006**, *359*, 2798-2805.
11. "Isomerization of 2-methyl-3-butenitrile with (bis-diphenylphosphinoferrocene)Nickel compounds. Catalytic and structural studies," Alberto Acosta-Ramírez, Miguel Muñoz-Hernández, William D. Jones, and Juventino J. García, *J. Organomet. Chem.* **2006**, *691*, 3895-3901.

**Manuscripts Submitted/in press:**

12.

**Manuscripts in Preparation:**

13. "Activation of Aromatic, Aliphatic, and Olefinic Carbon-Fluorine Bonds Using  $\text{Cp}^*_2\text{HfH}_2$ ," Ryan D. Rieth and William D. Jones, *European Journal of Inorganic Chemistry*, **2007**, in preparation.
14. "The Activation of Cyanoalkanes Using a Rhodiumtrispyrazolylborate Complex," Andrew J. Vetter, Ryan Reith, Christine Flaschenriem, and William D. Jones, *Proc. Nat. Acad. Sci.*, to be submitted in November 2006.
15. "The Activation of Chloroalkanes Using a Rhodiumtrispyrazolylborate Complex," Andrew J. Vetter, Ryan Reith, Christine Flaschenriem and William D. Jones, in preparation.
16. "Mechanistic Investigation of Vinylic Carbon-Fluorine Bond Activation of Perfluorinated Cycloalkenes using  $\text{Cp}^*_2\text{ZrH}_2$  and  $\text{Cp}^*_2\text{ZrHF}$ ," Eric Clot, Bradley M. Kraft, Odile Eisenstein, 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 Pacificchem 2005

Plenary Lecturer, International Conference on Organometallic Chemistry, Zaragoza, Spain, 2006.

**Additional Comments:**

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