

**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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Grant No. DE-FG02-86ER13569

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Total Award Amount (3 years): \$ 395,000

Continuation Request Period: December 1, 2002 - November 30, 2003
Continuation Request Amount (year 2): \$125,000
Unexpended Balance from Previous Year: \$0

Summaries of the FY 2002 Research in the Chemical Sciences

Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds

Grant FG02-86ER13569

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Total Grant Period: 12/1/01-11/30/04, \$395,000 for three years

Overview of Research Goals and Accomplishments for the Period 12/1/01-11/30/02:

This project has as its overall goal improvement in the intelligent use of our energy resources, specifically petroleum derived products. This goal requires the development of new routes for the manipulation of C-H and C-C bonds, with transfer of the new technology to industry. During the first year of the current 3 year project period, our research has focussed on the following specific goals: (1) discovery of new carbon-carbon bond cleavage reactions, (2) fundamental studies of C-H bond cleavage reactions of trispyrazolylboraterhodium complexes, (3) catalytic C-H and C-C bond functionalization, and (4) carbon-fluorine bond activation. We have made progress in each of these areas, as described in the following report, and will continue our studies in these areas.

The accomplishments of the current year include: (1) we have successfully measured and quantitatively modeled the processes available to metal alkyl hydride complexes in a trispyrazolylborate-rhodium complex; (2) we have *for the first time* determined the isotope effects on the specific fundamental steps involved in alkane oxidative addition and reductive elimination; (3) 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; (4) we have cleaved C-C bonds in biphenylene, aryl-nitriles, and aryl-acetylenes, expanding tremendously the breadth of C-C cleavage; (5) we have established 3 different mechanisms for C-F bond cleavage of fluorocarbons using $Cp^*_2ZrH_2$; (6) we have synthesized and studied several hemilabile P-N complexes of platinum and nickel, and demonstrated that the labile nitrogen give enhanced reactivity not observed with the well-known P-P chelate complexes; (7) we have discovered new C-H and C-C functionalizations that allow introduction of reactive boronate and olefin functional groups.

A wide variety of chemistry has been examined, resulting in *over a dozen manuscripts* that have appeared or been accepted for publication since the end of our last 3-year project period as a result of this DOE funded effort. 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, Brad Kraft, Steve Oster, Karlyn Skugrud) and 1 postdoc (Nicole Brunkan) during the current grant period, as well as several undergraduates (Jason Holt, Mike Evans, John Curley).

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.

Selected key references:

1. "Investigation of the Mechanism of Alkane Reductive Elimination and Skeletal Isomerization in $\text{Tp}'\text{Rh}(\text{CNneopentyl})(\text{R})\text{H}$ Complexes: The Role of Alkane Complexes," Todd O. Northcutt, Douglas D. Wick, Andrew J. Vetter, and William D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 7257-7270.
2. "Carbon-Carbon Bond Activation in $\text{Pt}(0)$ -Diphenylacetylene Complexes Bearing Chelating P,N- and P, P-Ligands, Christian Müller, Carl N. Iverson, Rene J. Lachicotte, and William D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 9718-9719.
3. "Cleavage of Carbon-Carbon Bonds in Aromatic Nitriles using Nickel(0)," Juventino J. Garcia, Nicole M. Brunkan, and William D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 9547-9555.

Detailed Progress Report for the Project Period Dec. 1, 2001- Nov. 30, 2002.

This report summarizes research that has been performed since our last submitted report in July of 2001, and covers work completed and published through July of 2002.

1. Tris-pyrazolylborate Rhodium C-H 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 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.

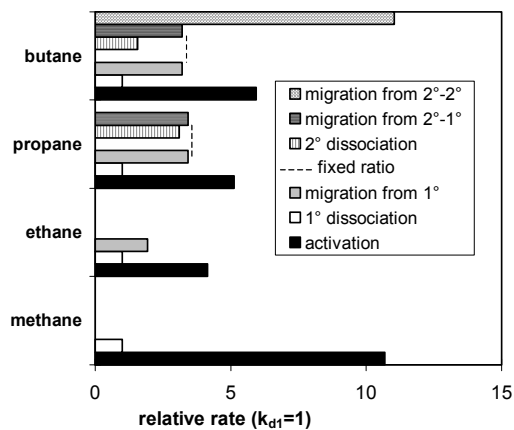
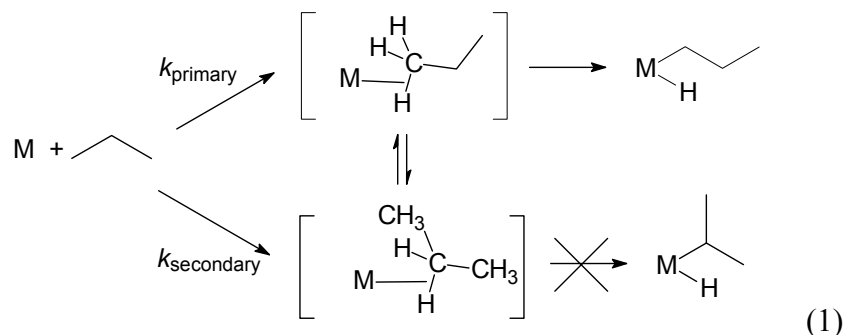
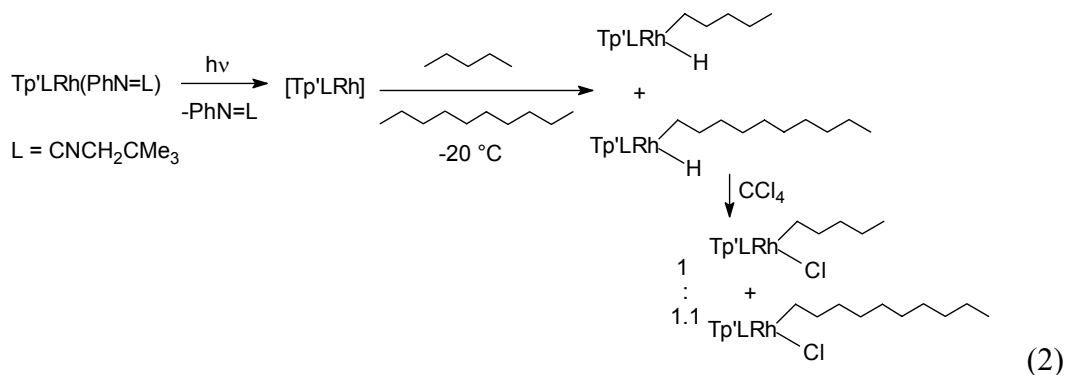


Figure 1. Relative rates of σ -alkane processes.

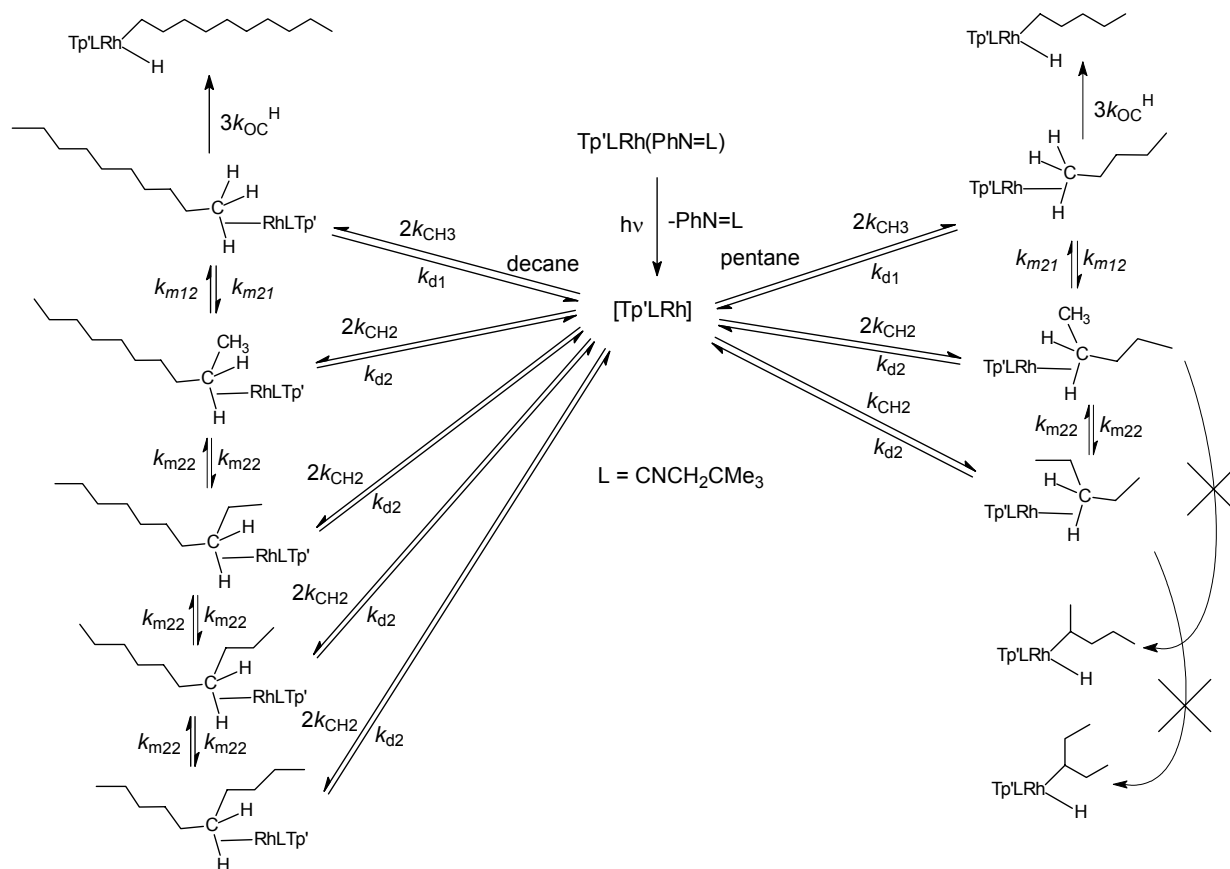
With the relative rates of all of these processes now known for any linear alkane, we have now initiated studies to determine which C-H bond of an alkane first binds to the Tp'RhL fragment. The execution of this experiment is not completely obvious, as reaction of the fragment with any linear hydrocarbon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



In order to circumvent this problem, we examined the competitive kinetic selectivity between two alkanes that differed only in the number of methylene groups, pentane and decane. In the limit that Tp'RhL binds only to methyl groups, one should observe a 1:1 ratio of the n-pentyl and n-decyl activation products. In the limit that Tp'RhL binds only to methylene groups, one should see a 3:8 ratio of products. In the competition experiment, a 1:1.1 ratio was seen (eq 2). Since the behavior of any of the possible σ -alkane complexes could be predicted from our earlier studies, the only unknown in the system was the relative binding abilities of the methyl and methylene groups, $k_{\text{CH}_3}/k_{\text{CH}_2}$. This rate ratio was then adjusted in the kinetic model (shown in full detail in Scheme 1) to give the appropriate 1:1.1 product ratio. The final conclusion was that *the methyl group binds 2.5 times faster than the methylene group*. Therefore the widespread preference for activation of primary C-H bonds is also due to the fact that they bind more rapidly than the other hydrocarbon groups, in addition to the kinetic factors outlined earlier.



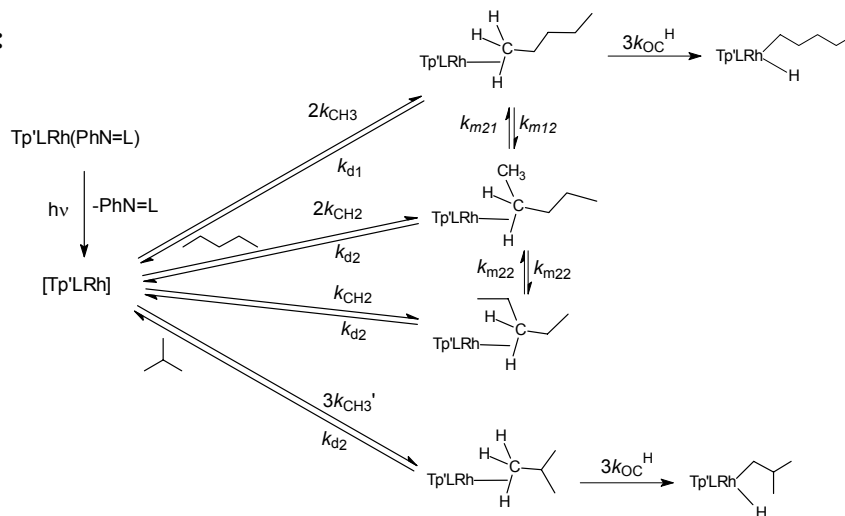
Scheme 1:



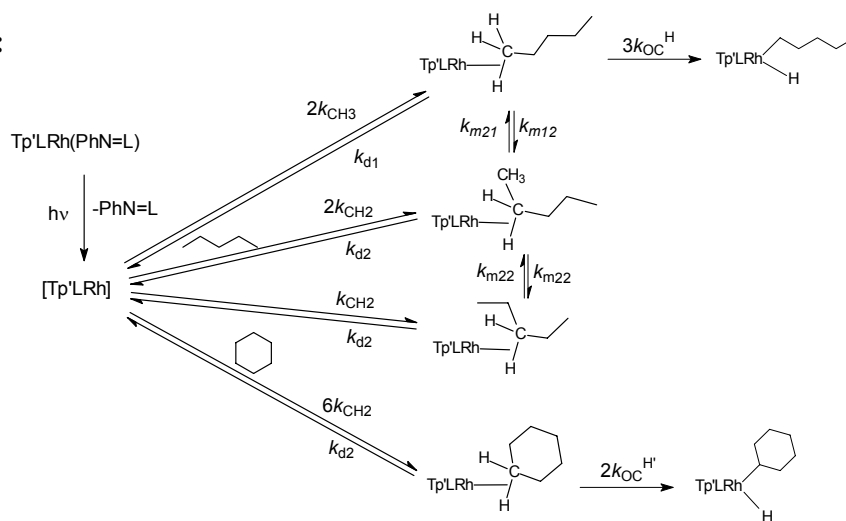
This study has been tremendously successful, and we are now in the process of examining competition reactions of one alkane vs another to determine several effects in alkane binding:

- (1) Competition of pentane vs isobutane will determine the effect that branching has on the C-H activation of methyl groups (Scheme 2).
- (2) Competition of cyclohexane vs pentane will allow the determination of the relative rate primary C-H activation vs secondary C-H activation. We expect that the metal will bind to methylenes of both of these alkanes at similar rates, so the only variable left is the relative C-H oxidative cleavage rates (Scheme 3).
- (3) Competition of cyclopentane vs pentane will allow determination of the relative rate of binding of an unstrained methylene vs a constrained methylene (Scheme 4).
- (4) Competition of cyclopentane vs cyclohexane will serve as a check of the above.

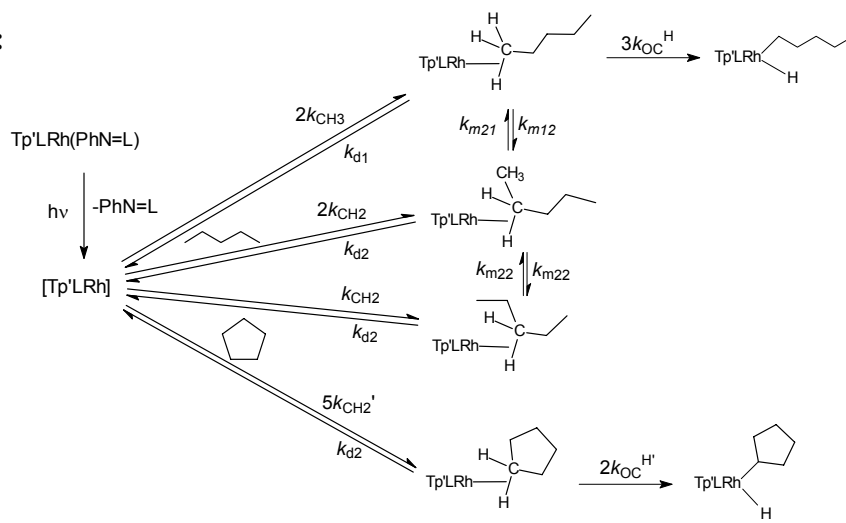
Scheme 2:



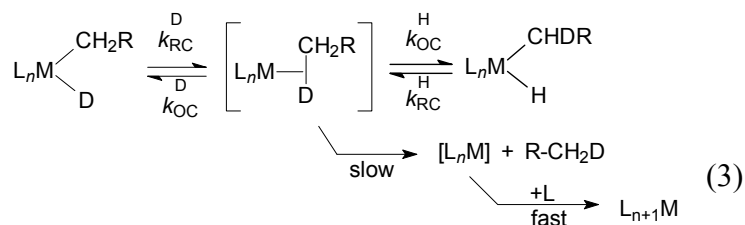
Scheme 3:



Scheme 4:



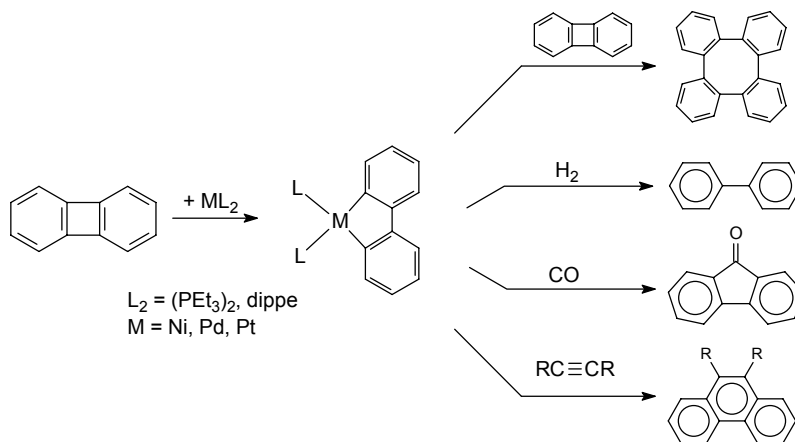
One of the more interesting side-lights from these studies comes from the independent determination of isotope effects for both the 'oxidative cleavage' and the 'reductive coupling' steps of the C–H activation reaction indicated in equation 3. These isotope effects, both kinetic isotope effects on a 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 effect as indicated in equation 3. 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 is the only known system where these effects have been completely sorted out, we are publishing 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

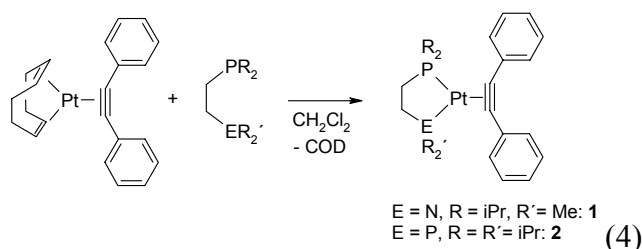
Earlier DOE supported work showed that the complexes $\text{Pt}(\text{PEt}_3)_3$, $\text{Pd}(\text{PEt}_3)_3$, and $[\text{Ni}(\text{dippe})\text{H}]_2$ cleave the C-C bond of biphenylene to give $(\text{PEt}_3)_2\text{Pt}(2,2'\text{-biphenyl})$, $(\text{PEt}_3)_2\text{Pd}(2,2'\text{-biphenyl})$, and $(\text{dippe})\text{Ni}(2,2'\text{-biphenyl})$, respectively. These complexes underwent catalytic chemistry to give functionalized products, such as tetraphenylene, biphenylene, fluorenone, or phenanthrenes (Scheme 5).

Scheme 5:



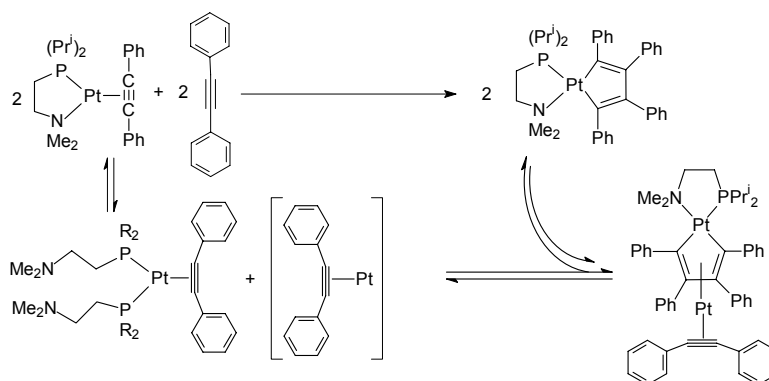
In the case of Ni(dippe), it was found that catalysis required the introduction of small amounts of oxygen, just enough to oxidize the phosphine to phosphine oxide. The remaining 'naked' metal was efficient at catalyzing the insertion of alkynes into biphenylene to give phenanthrenes. The requirement of a labile chelate led us to investigate the use of the hemi-labile ligand $\text{Pr}^i_2\text{PCH}_2\text{CH}_2\text{NMe}_2$ in these same metal systems.

The platinum complexes proved to be the easiest to synthesize and study, since the adducts are fairly stable. The strategy was to use a source of Pt(0) in the presence of the P-N chelate and an alkyne, to isolate the complex, and then to look at reactions of the complex. With diphenylacetylene, the preparation of the adduct was straightforward and allowed comparison of the P-P chelate with the P-N chelate (eq 4).

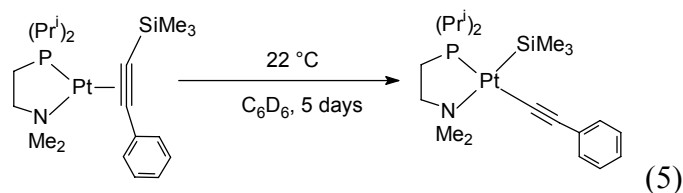


While the P-P chelated complex showed *no reactivity* with added diphenylacetylene even after heating, the P-N chelated complex reacted at room temperature to give a metallacyclopentadiene complex. Further studies of the system showed that the nitrogen of the chelate is quite labile, and that once it dissociates the phosphine ligands can then redistribute between metals to generate two observable intermediates (Scheme 6). Ultimately, however, thermodynamics takes over and one winds up with quantitative production of the metallacycle. Heating this sample results in the slow catalytic formation of hexaphenylbenzene.

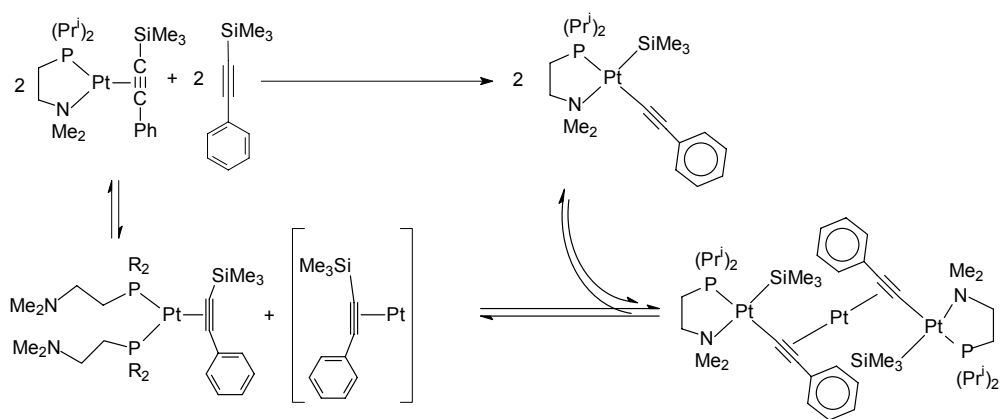
Scheme 6:



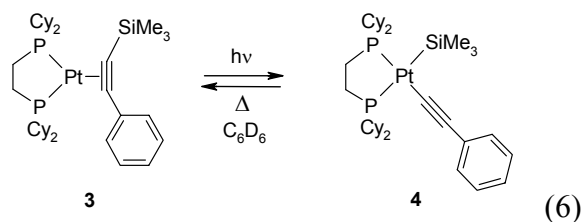
With trimethylsilylphenylacetylene, the preparation of the initial complex is similar but now the alkyne complex undergoes insertion into the C-Si bond at room temperature (eq 5). Once again, *no such reaction is seen for the complex with a bis-phosphine chelate*. Just as in the case of diphenylacetylene, ligand dissociation and redistribution is observed at intermediate times to give two observable intermediates (Scheme 7). Once again, thermodynamics takes over and only a single product, the C-Si insertion complex, is observed at longer reaction times.



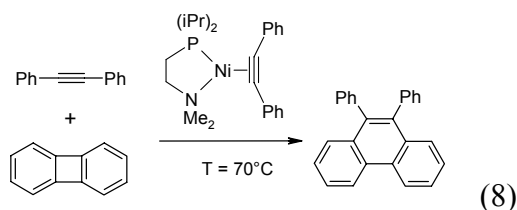
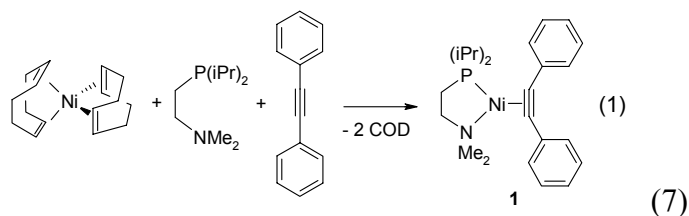
Scheme 7:



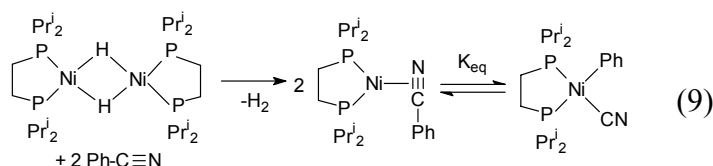
While the dippe P-P chelate complex is unreactive thermally, it does react photochemically to give a C-Si insertion product (eq 6). Remarkably, however, this complex reverts to the Pt(0) alkyne complex thermally! This observation leads to the important conclusion that *oxidative addition is favored thermodynamically by the presence of the P-N ligand, whereas reductive elimination is thermodynamically favored by the P-P ligand*. This conclusion implies that the study of a chelating, sterically hindered, bis-(dialkylamino)ethane ligand should give a metal fragment that will strongly favor C-C cleavage. This hypothesis will be tested in the next year.



In addition to the above work with platinum, we have also prepared the analogous nickel complex (eq 7). These complexes have proven to be efficient catalysts for the selective coupling of biphenylene and alkynes to give phenanthrenes (eq 8).



We have also discovered that the nickel complex $[\text{Ni}(\text{dippe})\text{H}]_2$ reacts with benzonitrile to give first an η^2 -nitrile complex, which then undergoes C-C cleavage of the carbon-CN bond (eq 9). Furthermore, the reaction does not go to completion but forms an equilibrium mixture of the η^2 -nitrile and C-CN oxidative addition product. We know of no such example of *reversible* C-C cleavage in the literature. Other examples of aryl C-CN cleavage are under investigation.



We have also looked at the effects of electron withdrawing and electron donating groups on the aryl cyanide. The results show that both the rate and equilibrium for C-CN cleavage is affected, as shown in the plots in Figure 1. For the equilibration, K_{eq} is found to have a ρ value of +6.1. This large and positive value for ρ indicates that negative charge is being stabilized on the ipso carbon of the substituted aryl group, consistent with the organometallic nature of this bond as possessing substantial $\text{Ni}^{\delta+}-\text{C}^{\delta-}$ character. Similarly, a plot of $\ln k_l$ vs. σ , also shown in Figure 1b, gives a ρ value of +1.3. While there is somewhat more scatter in this plot, the positive slope correlation is unmistakable and is consistent with the localization of charge density on the ipso carbon in the transition state for C-CN bond cleavage, although not so much as the Ni(II) product.

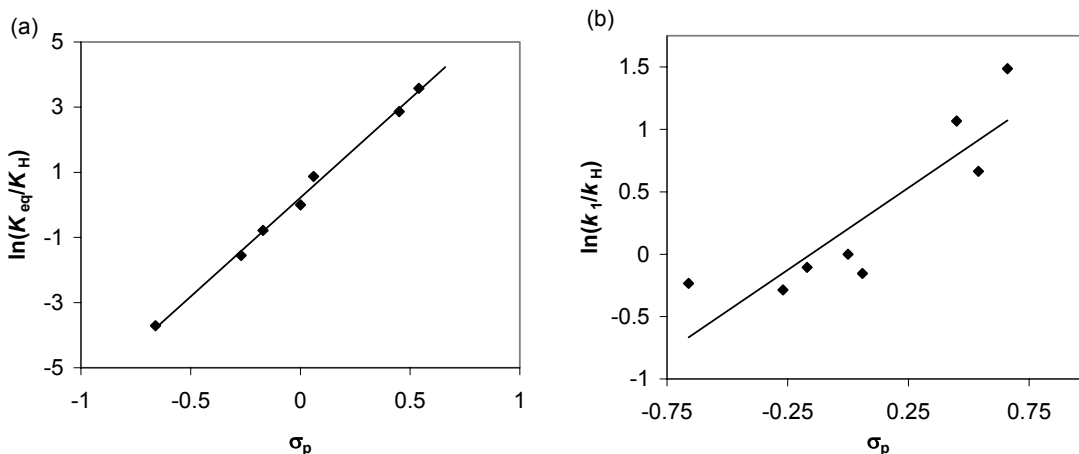
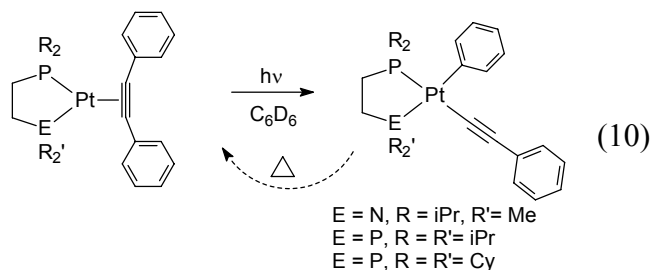


Figure 1. (a) Hammett plot for the equilibrium constants (K_{eq}) from equation 9 vs. σ_{p} at 54 °C. (X = CN omitted) (b) Hammett plot for the forward rate constants (k_{f}) from equation 29 vs. σ_{p} at 54 °C.

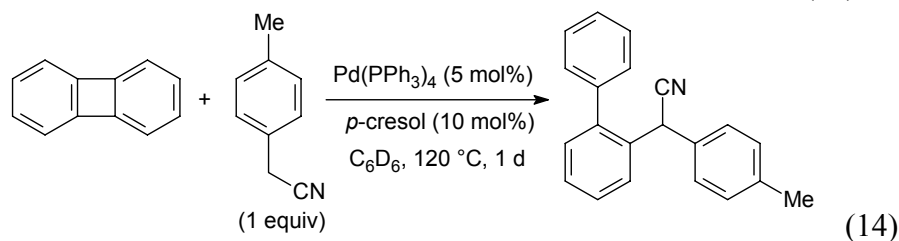
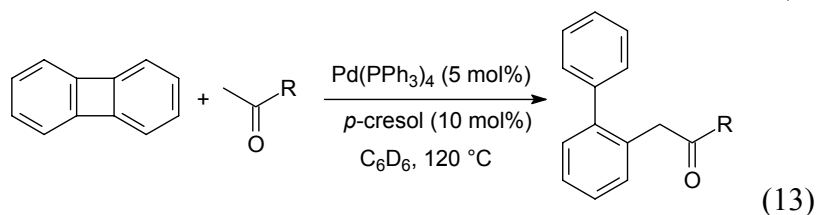
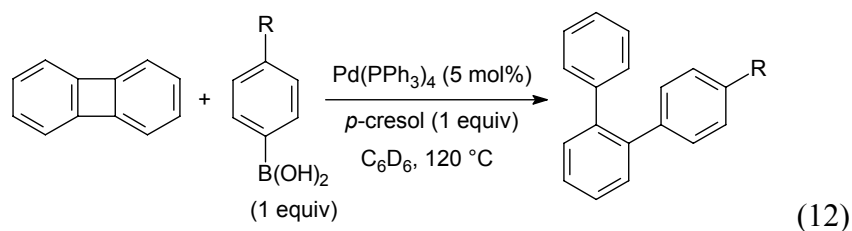
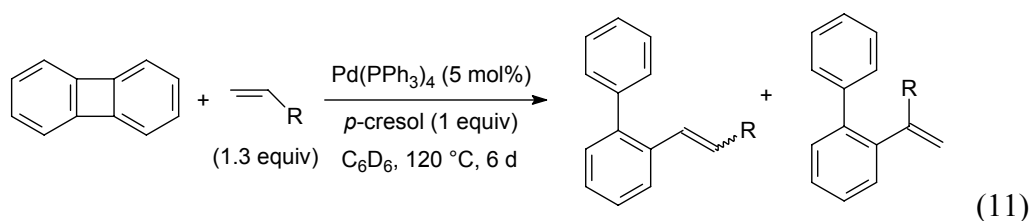
We have also discovered an important new type of C-C bond oxidative addition, cleavage of sp - sp^2 C-C bonds in aryl acetylenes. This is a *new class* of C-C bond cleavage, and offers many exciting possibilities. We have found that irradiation of either P-P or P-N chelate complexes of Pt-(diphenylacetylene) leads to the clean and quantitative formation of the oxidative addition product (eq 10). The reaction works for all complexes we have examined to date. Furthermore, the oxidative cleavage reaction is reversible, in that heating the Pt(II) complexes results in their reversion to the Pt(0)-alkyne complexes. Consequently, we now have methodology to break and make C-C \equiv C bonds, and further development of this reaction will be the subject of future studies.



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

We have also initiated investigations of the above systems for their ability to serve in further functionalization reactions. For example, we have found that C-C bonds can not only be cleaved, but functionalized using 'standard' organic reagents. A nice example of the application

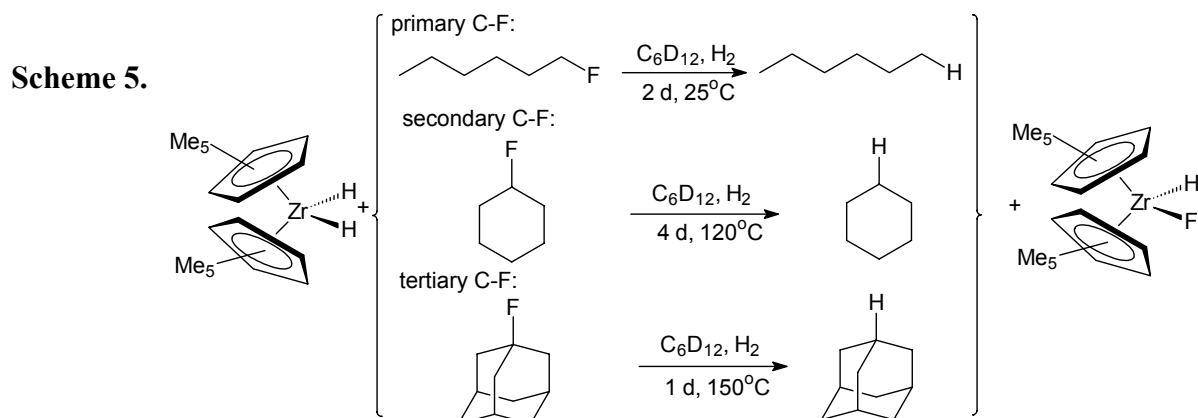
of this chemistry appears in our work with palladium catalyzed reactions of biphenylene. Using a Pd(0) precursor, we can activate the C-C bond of biphenylene and then protonate one of the Pd-C bonds using a weak acid of the appropriate pH. Next, one can perform Heck or Suzuki-type couplings using olefins or boronic acids to give functionalized products (eq 11, 12). Furthermore, other acidic C-H bonds can be added across the activated C-C bond using pH control. For example, α -keto C-H bonds or α -nitrile C-H bonds can add across biphenylene to give functionalized biaryls (eq 13, 14).



We have also made advances in functionalization of C-H bonds. We have discovered the $\text{Tp}^*\text{Rh}(\text{CO})_2$ is a catalyst for the activation of benzene in the presence of pinacol borane to give phenylpinacolborane in high yields and turnover numbers. Initial studies indicate that the catalyst is superior to either the Hartwig or Smith systems that have been published. Further development of this very recent result will be carried out in the year to come.

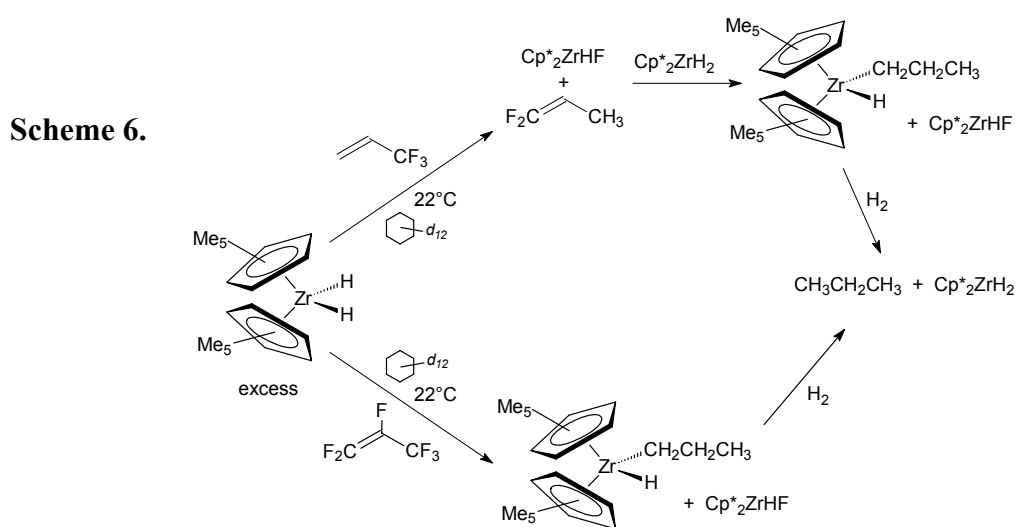
4. C-F Bond Cleavage Studies

We have now begun studies with the soluble, more reactive $\text{Cp}^*_2\text{ZrH}_2$ and found that this molecule cleaves a wide variety of aromatic and aliphatic C-F bonds. Systematic studies have shown that primary, secondary, and tertiary C-F bonds can all be cleaved with progressively greater difficulty (Scheme 5). In addition, di-fluorosubstituted carbons can be made to react with even more forcing conditions. Trifluoromethyl groups scarcely react at all even under extreme conditions.

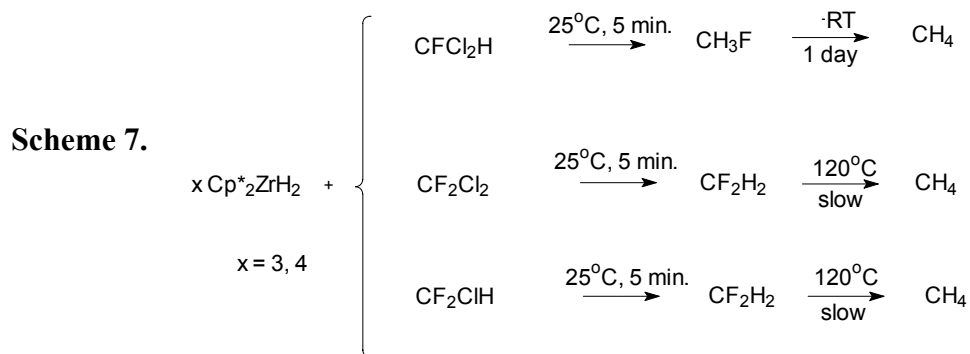


Most remarkable, however, even trifluoromethyl C-F bonds can be easily cleaved if they are adjacent to a double bond. 3,3,3-trifluoropropene is *completely defluorinated in 5 min at room temperature* to give the zirconium-n-propyl hydride complex (Scheme 6).

Perfluoropropene undergoes a similar reaction to give the same product. Details of the



mechanism are under further study. Defluorination reactions are also seen with nonafluorohexene, perfluorocyclobutene, perfluorocyclopentene, perfluorobenzene, trifluorotoluene, and related substrates. Chlorofluorocarbons (CFCs) react rapidly to give first fluorocarbons (HFCs), which then are converted to hydrocarbons (HCs) in accord with the above established reactivities (Scheme 7). Mechanistic investigations into the aliphatic fluorocarbons has revealed evidence for a radical chain mechanism. Further mechanistic work with the fluoroolefins is underway suggesting an insertion/ β -fluoride elimination pathway.



Research Plans for the Period December 1, 2002 - November 30, 2003 (year 2 of 3):

This coming year, our research will focus on the items presented in our proposal where we have had success. These include: (1) carbon-carbon bond cleavage reactions, (2) fundamental studies of C-H bond cleavage reactions of trispyrazolylboraterhodium complexes, (3) reactions of hemilabile ligands, and (4) carbon-fluorine bond activation. We have made progress in each of these areas over the past year, as described in our report, and will continue our studies in these areas.

Our work in carbon-carbon bond cleavage will examine several new types of C-C cleavage. There are very few such examples in organometallic chemistry, and this project will serve to expand the breadth of C-C cleavage reactions to include new classes of substrates. For example, we have discovered examples of C-CN cleavage in aromatic nitriles, and we will extend this work to other metal complexes and also to non-aromatic nitriles. Specifically, alkyl nitriles and allyl nitriles will be examined. The latter are of interest to the production of adiponitrile, and the ability to selectively cleave and rearrange allyl cyanides could lead to a single-step process to replace the existing 3-step technology. We will also examine C-C cleavage in *sp-sp*² bonds, such as aryl-alkyne bonds. Recent results show that these bonds can be photochemically activated by metal complexes, and we will determine if thermal activation is possible by employing electron withdrawing groups on the arene.

In the area of trispyrazolylborate chemistry, we will continue our ongoing study of alkane activation. Specifically, we will focus on determination of the relative binding abilities of methylene (CH₂) vs methyl (CH₃) vs methine (CH) groups. Our previous studies of alkyl hydride complexes allows us to predict the behavior of any alkyl hydride complex of this system, and we will take advantage of this knowledge to look at competitive selectivities with different hydrocarbons, both linear and branched, both cyclic and acyclic. The studies will allow us to determine the relative C-H oxidative cleavage rates of primary vs secondary C-H bonds as well. We will also continue to develop our C-H functionalization using Tp'Rh(CO)₂.

We have also made recent discoveries using hemilabile phosphorus-nitrogen chelate ligands to show that group 10 metal complexes containing these ligands are *much* more reactive than their bisphosphine counterparts. Furthermore, one of the studies suggests that bis-dialkylamino chelates should be even more reactive in a thermodynamic sense. We will test this hypothesis by synthesizing 1,2-bis-(diisopropylamino)ethane and studying reactions of metals to which it is attached.

Finally, we will continue to study the fruitful area of carbon-fluorine bond activation using zirconium hydride complexes. The cleavage of strong C-F bonds fits into our DOE supported program on cleavage of strong carbon-element bonds.

Publications appearing (or in press) since the last DOE report for prior support, acknowledging DOE support, Year 1: December 1, 2001 - November 30, 2002:

1. "Palladium-Catalyzed Coupling Reactions of Biphenylene with Olefins, Arylboronic Acids, and Ketones Involving C-C Bond Cleavage," Tetsuya Satoh and William D. Jones, *Organometallics* **2001**, *20*, 2916-2919.
2. "Investigation of the Mechanism of Alkane Reductive Elimination and Skeletal Isomerization in Tp'Rh(CNneopentyl)(R)H Complexes: The Role of Alkane Complexes," Todd O. Northcutt, Douglas D. Wick, Andrew J. Vetter, and William D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 7257-7270.
3. "Carbon-Carbon Bond Activation in Pt(0)-Diphenylacetylene Complexes Bearing Chelating P,N- and P, P-Ligands, Christian Müller, Carl N. Iverson, Rene J. Lachicotte, and William D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 9718-9719.
4. "Aliphatic and Aromatic Carbon-Fluorine Bond Activation Using Cp*₂ZrH₂: Mechanisms of Hydrodefluorination," Bradley M. Kraft, Rene J. Lachicotte, and William D. Jones, *J. Am. Chem. Soc.* **2001**, *123*, 10973-10979.
5. "Rhodium Catalyzed Activation and Functionalization of the C-C Bond of Biphenylene," Carl N. Iverson and William D. Jones, *Organometallics*, **2001**, *20*, 5745-5750.
6. "Perspectives: Synthetic Chemistry. The Key to Successful Organic Synthesis is...", William D. Jones, *Science*, **2002**, *295*, 289-290.
7. "Formation of Tetrafluorobenzynes by β -Fluoride Elimination In Zirconium-Perfluorophenyl Complexes," Bradley M. Kraft, Rene J. Lachicotte, and William D. Jones, *Organometallics*, **2002**, *21*, 727-731.
8. "Cleavage of the Carbon-Carbon Bond in Biphenylene using Transition Metals," Christophe Perthuisot, Brian L. Edelbach, Deanna L. Zubris, Nira Simhai, Carl N. Iverson, Christian Müller, Tetsuya Satoh, and William D. Jones, *J. Mol. Catal. A, Chemical*, **2002**, in press.
9. "Chelating P,N versus P,P Ligands: Differing Reactivity of Donor Stabilized Pt-(η^2 -PhC \equiv CPh) Complexes Towards Diphenylacetylene," Christian Müller, Rene J. Lachicotte, and William D. Jones, *Organometallics*, **2002**, *21*, 1118-1123.
10. "Thermal and Photolytical Silicon-Carbon Bond Activation in Donor Stabilized Pt(0)-Alkyne Complexes," Christian Müller, Rene J. Lachicotte, and William D. Jones, *Organometallics*, **2002**, *21*, 1190-1196.
11. "Catalytic C-C Bond Activation in Biphenylene and Cyclotrimerization of Alkynes: Reactivity of P,N versus P,P Substituted Nickel Complexes," Christian Müller, Rene J. Lachicotte, and William D. Jones, *Organometallics*, **2002**, *21*, 1975-1981.
12. "Mechanism of Vinylic and Allylic Carbon-Fluorine Bond Activation of Non-Perfluorinated Olefins using Cp*₂ZrH₂," Bradley M. Kraft, Rene J. Lachicotte, and William D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 8681-8689.

13. "Cleavage of Carbon-Carbon Bonds in Aromatic Nitriles using Nickel(0)," Juventino J. Garcia, Nicole M. Brunkan, and William D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 9547-9555.
14. "Carbon-Fluorine Bond Activation of Perfluorinated Arenes with Cp*₂ZrH₂," Bradley M. Kraft and William D. Jones, *J. Organomet. Chem.*, in press.

Manuscripts Submitted:

1. "η²- Coordination and C-H Activation of Electron-poor Arenes," Carl N. Iverson, Rene J. Lachicotte, Christian Müller and William D. Jones, *Organometallics*, accepted pending revision.
2. "Isotope Effects in C-H Bond Activation Reactions by Transition Metals," William D. Jones, *Acc. Chem. Res.*, submitted June 2002.

Manuscripts in Preparation:

1. "Mechanistic Investigation of Vinylic Carbon-Fluorine Bond Activation of Perfluorinated Alkenes using Cp*₂ZrH₂ and Cp*₂ZrHF," Bradley M. Kraft and William D. Jones, *J. Am. Chem. Soc.*, written-to be submitted.

Recent Special Recognitions Received by the PI:

ACS Award in Organometallic Chemistry, 2003

Appointed Associate Editor, *J. Am. Chem. Soc.*, beginning 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.

Additional Comments:

Our renewal budget for 2001-2004 was *less than our budget for the prior grant period*. On the basis of our success and productivity, as delineated by the DOE request for the specific information included in this progress report, it is not at all clear how funding relates to the objectives of this program. It is difficult to continue to operate a successful program under these conditions.