

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

BY

Prof. William D. Jones  
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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

Total Project Period: December 1, 2001 - November 30, 2004  
Total Award Amount (3 years): \$ 395,000

Continuation Request Period: December 1, 2003 - November 30, 2004  
Continuation Request Amount (year 3): \$125,000  
Unexpended Balance from Previous Year: \$0

## *Executive Summary of the FY 2003 Research in the Chemical Sciences*

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### **Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds**

Grant FG02-86ER13569

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Current Budget Period: 12/1/02-11/30/03, \$125,000 for one year

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

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### **Overview of Research Goals and Accomplishments for the Period 12/1/02-11/30/03:**

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 3 year project period, our research is 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. This year we have made progress in several of these areas, as described in the following report.

The accomplishments of the current year include: (1) we have examined the reactivity of group 10 Pt complexes toward C-H and C-C cleavage using a sterically unencumbered phosphine ligand. (2) we have determined and compared isotope effects in C-H activation reactions, showing that alkane complexes are involved. (3) we have completed experiments 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 allyl nitriles, leading to isomerization of the C-C skeleton. This reaction is critical to the DuPont synthesis of Nylon from butadiene. (5) we have measured C-H activation selectivities in chloroalkanes and alkylnitriles, showing a preference for activation of the terminal methyl groups and the facile  $\beta$ -chloride elimination reaction. (6)

A wide variety of chemistry has been examined, resulting in publication of a half-dozen manuscripts that have appeared or been accepted for publication during our last 1-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 (Brian Warsop, Susan Golisz).

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.

A detailed report follows, followed by future research plans, and recent special recognitions received by the PI.

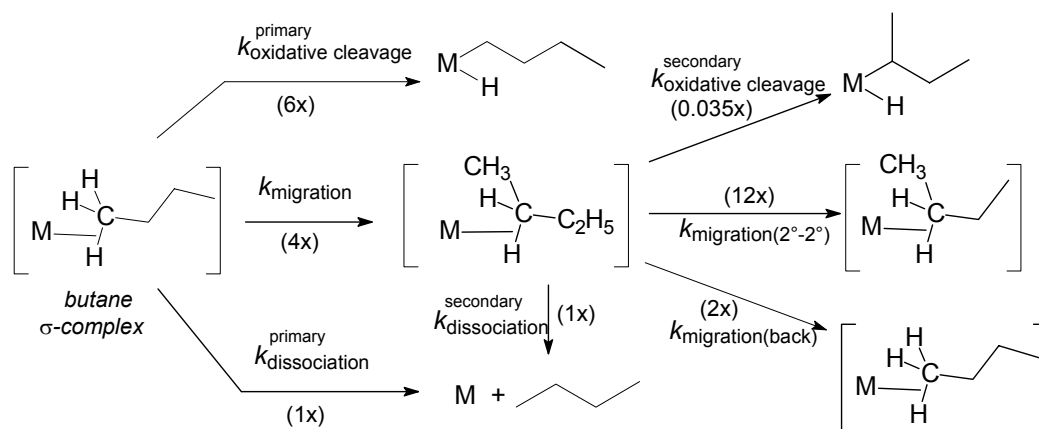
## Detailed Progress Report for the Project Period Dec. 1, 2002- Nov. 30, 2003.

This report summarizes research that has been performed since our last submitted report in August of 2002, and covers work completed and published through August of 2003.

### 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  $\text{Tp}^*\text{RhL}$ . 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 methyl group over the methylene group by a ratio of 2.5:1. (2) a methyl group in pentane coordinates 1.9 times faster than the more hindered methyl group of isobutane. (3) the oxidative cleavage of a methyl C-H bond (primary C-H) occurs 28.5 times faster than the C-H bond in a methylene group (secondary C-H). These conclusions were made building upon our earlier studies of the relative rates of oxidative cleavage, migration, and dissociation indicated in Scheme 1. As described below, the rate of secondary activation can now be included in this scheme.

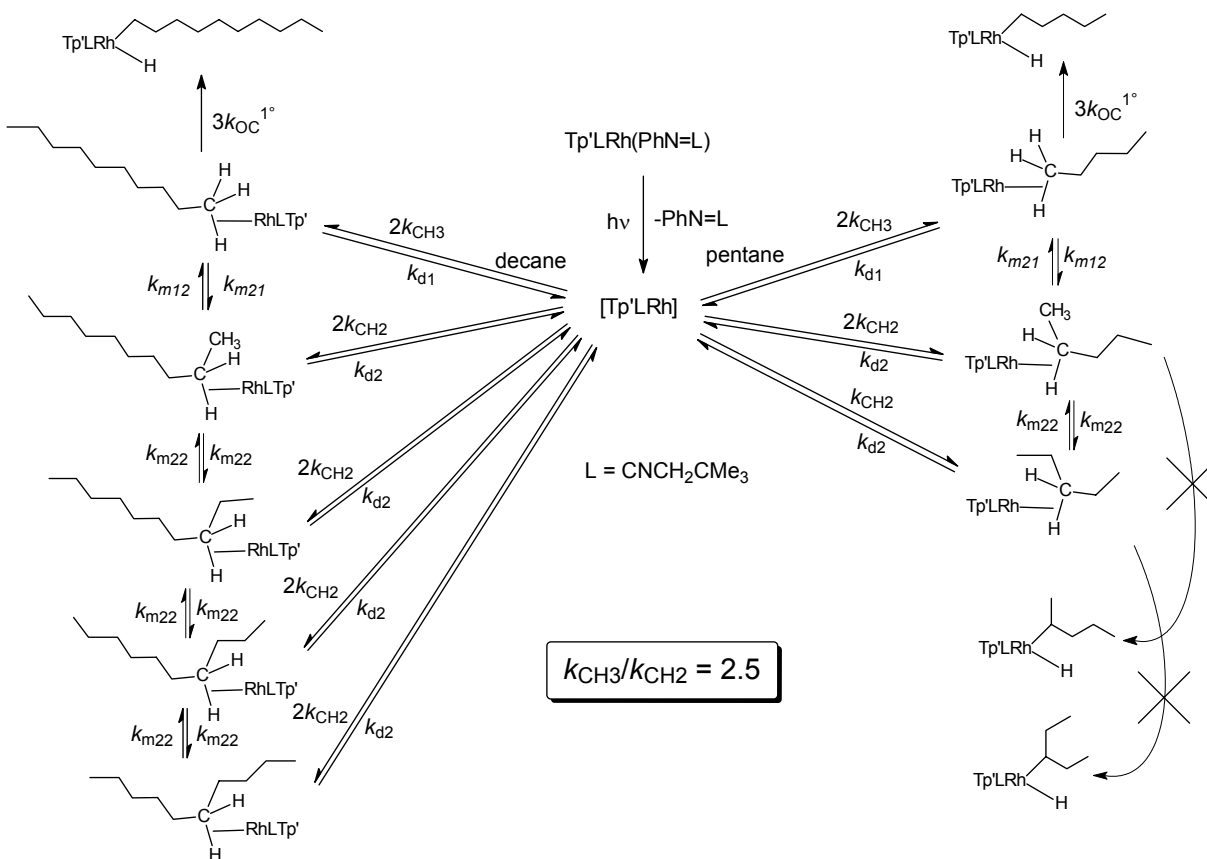
**Scheme 1. Relative rates of processes available in primary ( $1^\circ$ ) and secondary ( $2^\circ$ ) alkane complexes.**



The first new conclusion is the rate at which a reactive metal complex with a vacant site coordinates to a methyl group C-H vs a methylene C-H. This was determined by looking at the product distribution in a competition experiment between pentane and decane. In this experiment, the metal intermediate would see an equal number of methyl groups in each substrate but differing numbers of methylenes. 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 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 3:8 product ratio would be expected (corresponding to the 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.

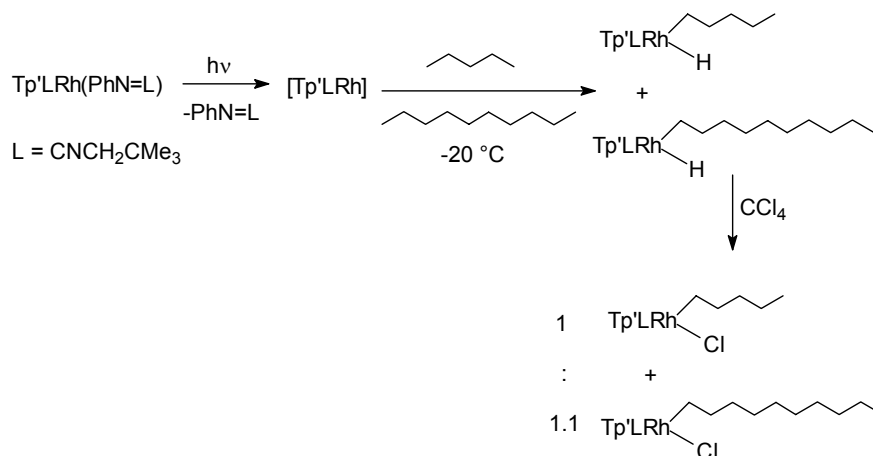
**Scheme 2. Pathways for C-H coordination/activation in pentane-decane competition.**



In the experiment,  $\text{Tp}^*\text{Rh}(\text{CNR})(\text{carbodiimide})$  was irradiated in a 1:1 mixture of pentane/decane. The alkyl hydride products were quenched with  $\text{CCl}_4$  to give the stable chloro derivatives in a 1.1:1 ratio (Scheme 3). Consequently, the results are consistent with a strong

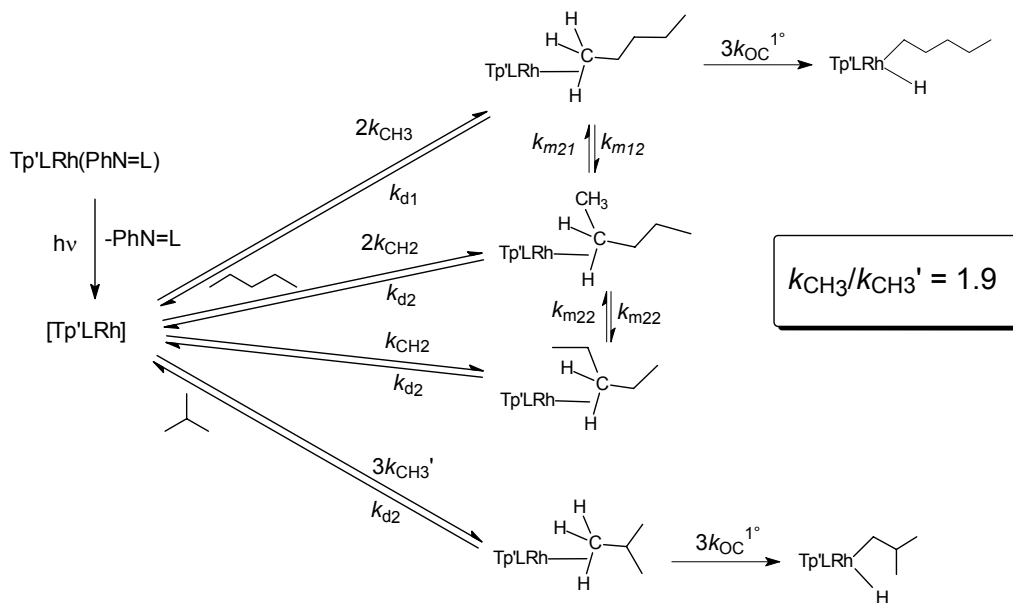
preference for methyl group coordination, and the simulation indicates an actual preference of  $k_{\text{CH}_3}/k_{\text{CH}_2} = 2.5:1$ .

### Scheme 3. Competition between pentane and decane.



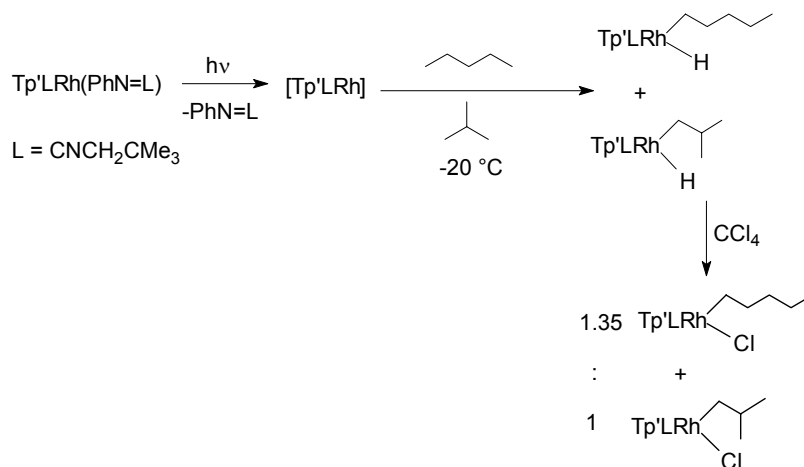
Steric hindrance can interfere with the ability to coordinate to a methyl group C-H bond. This can be seen in a competition between pentane and isobutane. In this experiment, two methyl groups in a linear alkane compete with three methyl groups in a branched alkane. The competitive reactions involved are shown in Scheme 4, with the two different rate constants for methyl group binding shown as  $k_{\text{CH}_3}$  and  $k_{\text{CH}_3}'$ .

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



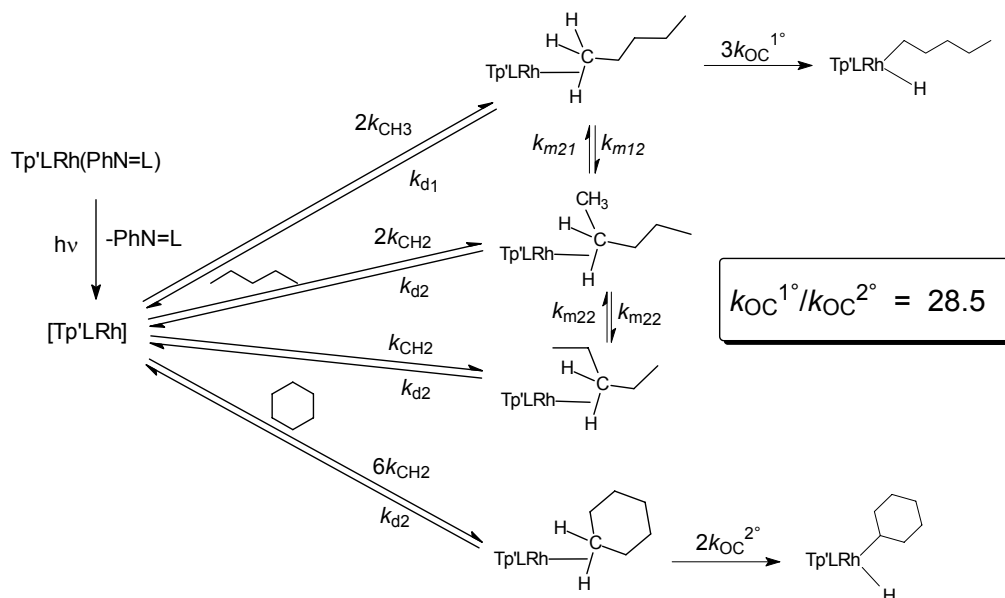
In the experiment,  $\text{Tp}^*\text{Rh}(\text{CNR})(\text{carbodiimide})$  was irradiated in a 1:1 mixture of pentane/isobutane. The alkyl hydride products were quenched with  $\text{CCl}_4$  to give the stable chloro derivatives in a 1.35:1 ratio (Scheme 5). Once again, simulation of the experiment while varying only the ratio  $k_{\text{CH}_3}/k_{\text{CH}_3'}$  allows determination of the ratio as 1.9:1. 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 1.9:1 ratio between the rate of the two oxidative cleavage rates.

**Scheme 5. Competition between pentane and isobutane.**



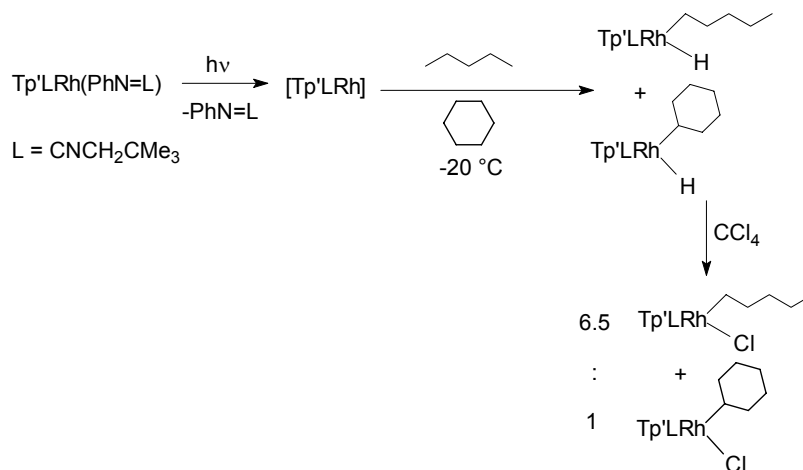
In the pentane/decane competition experiment, we learned about the relative rates of binding of unhindered  $\text{CH}_3$  vs  $\text{CH}_2$ . It would be reasonable to expect this rate ratio to apply in other competitions involving the binding of similar types of bonds. For example, the methylene C-H 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 ( $k_{\text{OC}}^{1^\circ}$ ). 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  $\text{CCl}_4$ . A 6.5:1 ratio of the n-pentyl and cyclohexyl chloride products was seen (Scheme 7).

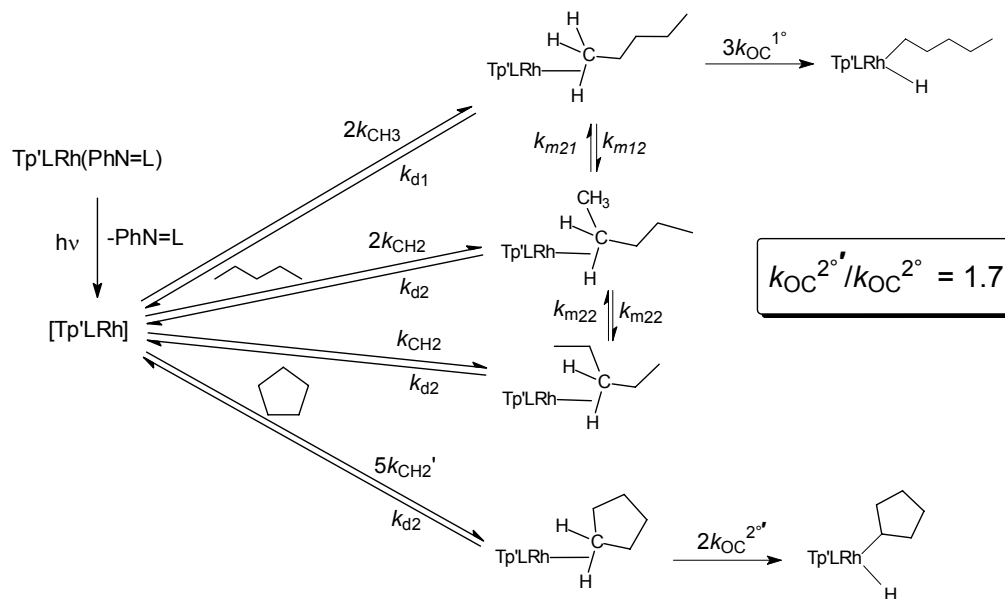
**Scheme 7. Competition between pentane and cyclohexane.**



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

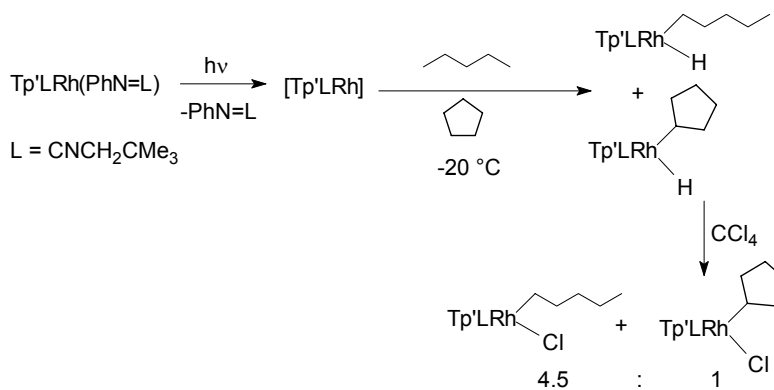
for this experiment shows different rates for the two types of methylene coordination (Scheme 8), but the same rate of oxidative cleavage in the methylene-alkane complex.

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



In the competition experiment,  $\text{Tp}^*\text{RhL}(\text{carbodiimide})$  was irradiated in a 1:1 mixture of pentane and cyclopentane, and  $\text{CCl}_4$  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  $k_{\text{OC}}^{2\circ'}/k_{\text{OC}}^{2\circ}$  of 1.7 was obtained.

**Scheme 9. Competition between pentane and cyclopentane.**

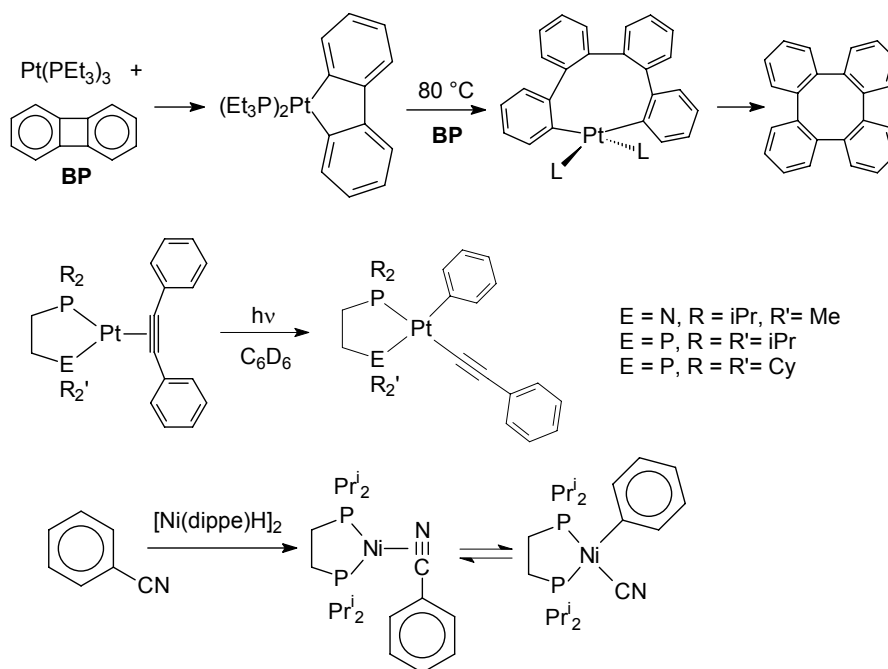


As a check that this value represents the relative coordination abilities of cyclopentane vs cyclohexane, a competition experiment was run by irradiation of  $\text{Tp}^*\text{RhL}(\text{carbodiimide})$  in a 1:1 mixture of cyclopentane/cyclohexane. A 1.9:1 ratio of cycloalkyl chloride products was observed.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

## 2. C-C Bond Cleavage Studies

Earlier 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  $\text{PtL}_2$  complexes. (3) aryl nitriles undergo  $sp^2-sp$  C-CN cleavage when reacted with  $\text{NiL}_2$  fragments, and  $\eta^2$ -nitrile adducts can be observed as reaction intermediates.

**Scheme 10. Examples of C-C Bond Activation Discovered by this DOE Project.**

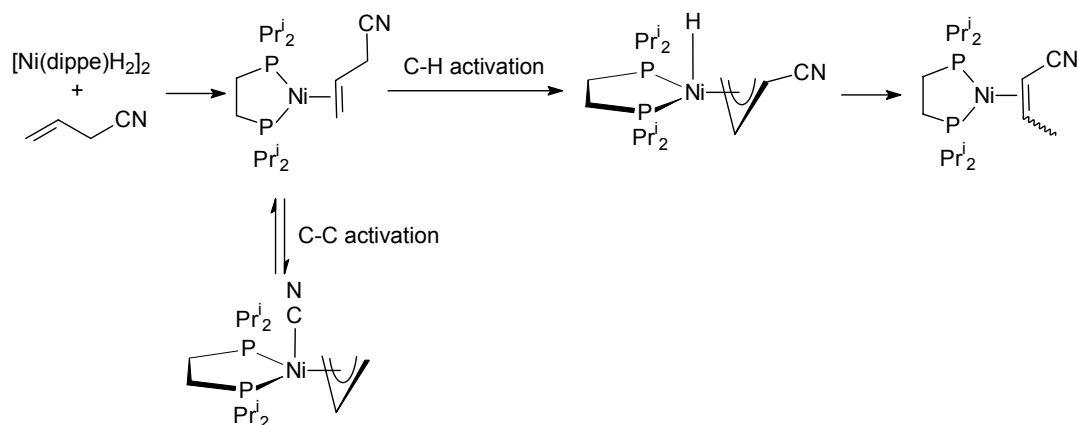


In the past year, we have initiated investigations of a new class of C-C cleavage, that of allyl-nitriles. At a metal center this cleavage reaction generates both a strong metal-cyanide bond and a  $\pi$ -allyl ligand, and hence has been found to be both facile and reversible. Indeed, at

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!

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 ( $\text{dippe}$  = 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  $\pi$ -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 11).

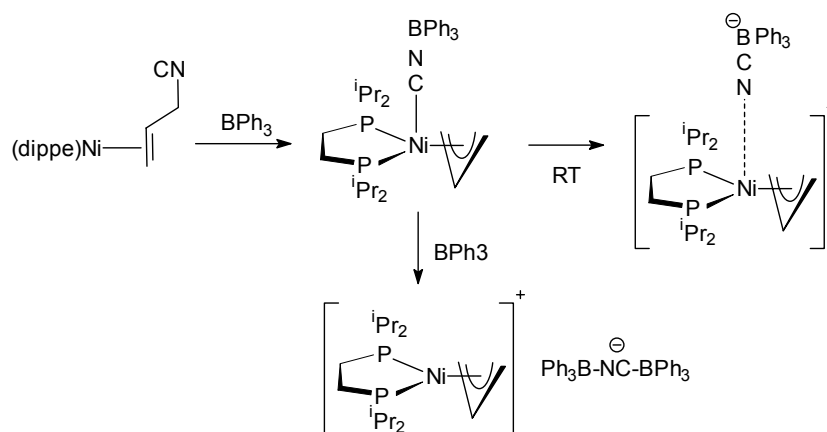
**Scheme 11. C-C and C-H Bond Activation in allylcyanide.**



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  $\pi$ -allyl cyanide complex. This is good news, since the DuPont catalysis requires that the C-C cleavage dominate the C-H cleavage.

We have also investigated the effect of the Lewis acid  $\text{BPh}_3$  upon the isomerization reaction. Addition of  $\text{BPh}_3$  to a cold solution of a solution of  $(\text{dippe})\text{Ni}(\eta^2\text{-allylCN})$  leads to the immediate and quantitative formation of the  $\text{BPh}_3$  adduct of the  $\pi$ -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 12). With only one equivalent of  $\text{BPh}_3$ , there is evidence of linkage isomerism of the initial  $\text{Ni-C-N-BPh}_3$  adduct to the  $\text{Ni-N-C-BPh}_3$  adduct.

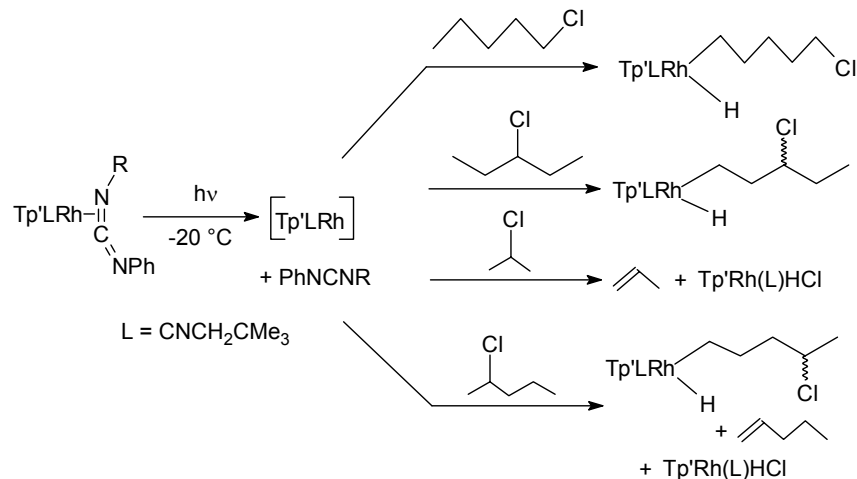
**Scheme 12. Effect of Lewis acid on the C-C and C-H Bond Activation in allylcyanide.**



### 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 of functionalized hydrocarbons. 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  $\beta$ -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 13.

**Scheme 13. Reactions of Chloroalkanes with [Tp\*Rh(CNR)].**

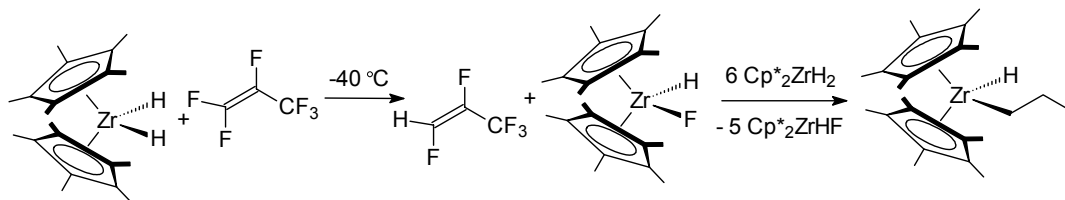


We have also begun to investigate aliphatic nitrile complexes. It appears that there is once again a selectivity for terminal methyl groups. With acetonitrile, the adduct Tp\*LRh(CH<sub>2</sub>CN)H is formed, and is found to be stable for days at 60 °C! This is the most stable alkyl hydride in this series yet, and we may be able to do new functionalization chemistry with this derivative.

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

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 Cp\*<sub>2</sub>ZrH<sub>2</sub>. Reaction with perfluoropropene gives first the selective formation of *E*-CHF=CFCF<sub>3</sub>. Further reaction with zirconium hydride leads to complete defluorination with no further intermediates being seen (Scheme 14).

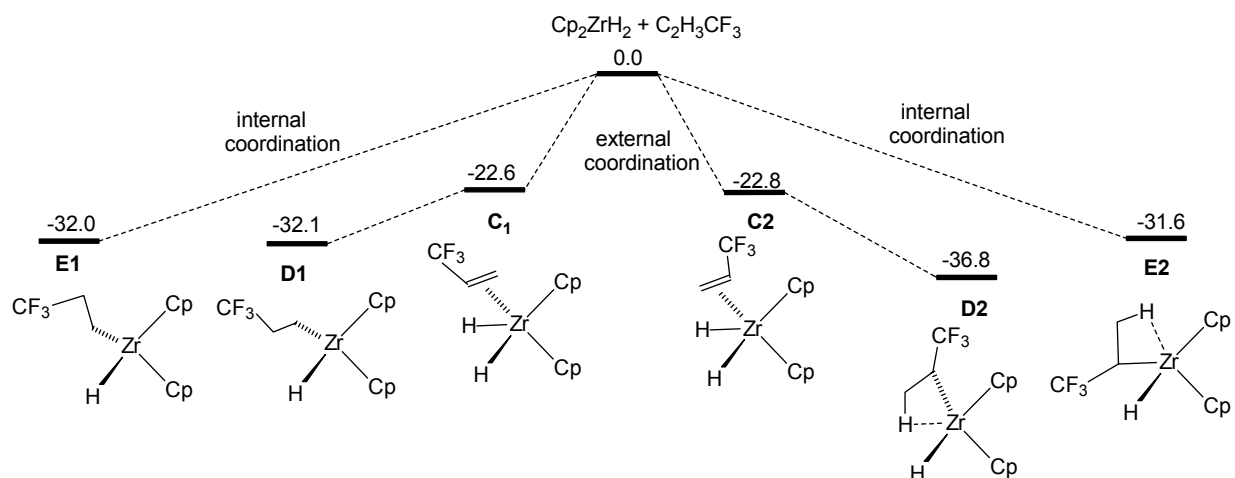
**Scheme 14. Reaction of Cp\*<sub>2</sub>ZrH<sub>2</sub> with perfluoropropene.**



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 initiated a collaboration with a theory group in Montpellier. Odile Eisenstein and Eric Clot have provided high level calculations investigating

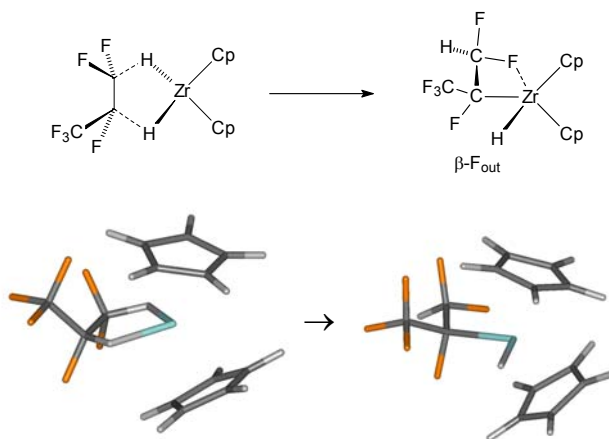
these systems, and the work is providing guidance for the mechanism of reaction. Initial studies were done on the insertion reaction of ethylene with  $\text{Cp}_2\text{ZrH}_2$ . We then progressed to trifluoropropene, which has been shown experimentally to undergo an insertion/ $\beta$ -fluoride elimination pathway. The calculations done thus far are able to reproduce the selective internal insertion product, and further work is underway to look at the  $\beta$ -fluoride elimination step (Scheme 15).

**Scheme 15. Calculations on the reaction of  $\text{Cp}^*_2\text{ZrH}_2$  with trifluoropropene.**



Further calculations are underway with  $\text{Cp}_2\text{ZrH}_2$  reacting with perfluoropropene. The initial results show that interaction of the olefin internally with  $\text{Cp}_2\text{ZrH}_2$  collapses to an adduct that can be seen to be the one responsible for the initial olefin product in Scheme 14 (Scheme 16).

**Scheme 16. Calculations on the reaction of  $\text{Cp}^*_2\text{ZrH}_2$  with perfluoropropene.**



**Research Plans for the Period December 1, 2003 - November 30, 2004 (year 3 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 2 years, as described in our reports, 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. We will continue to look at C-C cleavage in allylic nitriles, extending our fundamental studies to the butyronitrile system that is involved in DuPont's adiponitrile synthesis. The latter is of interest, in that 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*<sup>2</sup> 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 in functionalized hydrocarbons, as the reactivity appears to be surprising. Specifically, we will focus on activation of alkylnitriles and dinitriles. The stronger Rh-C adducts might allow us to look at new functionalizations such as olefin and alkyne insertion reactions.

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. This year's work will focus on the calculational treatment of the perfluoroolefin systems. 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 2: December 1, 2002 - November 30, 2003:**

**Manuscripts in print:**

1. “ $\eta^2$ - Coordination and C–H Activation of Electron-poor Arenes,” Carl N. Iverson, Rene J. Lachicotte, Christian Müller and William D. Jones, *Organometallics*, **2002**, *21*, 5320-5333.
2. “Isotope Effects in C-H Bond Activation Reactions by Transition Metals,” William D. Jones, *Acc. Chem. Res.* **2003**, *36*, 140-146.

**Manuscripts Submitted or in press:**

1. “Preparation, Structure, and Dynamics of a Nickel  $\pi$ -Allyl Cyanide Complex,” Nicole M. Brunkan and William D. Jones, *J. Organomet. Chem.* **2003**, in press.
2. “Activation of C-F Bonds using  $\text{Cp}^*_2\text{ZrH}_2$ : A Diversity of Mechanisms,” William D. Jones, *J. Chem. Soc., Dalton Trans.* **2003**, in press.
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, accepted pending revision.
4. “Carbon-hydrogen bond activation of chloroalkanes by a rhodium trispyrazolylborate complex,” Andy J. Vetter and William D. Jones, *Polyhedron*, accepted pending revision.
5. “C-CN Activation and Cleavage in Nickel(0) Allylcyanide Reactions,” Nicole M. Brunkan and William D. Jones, *J. Am. Chem. Soc.*, accepted pending revision.

**Manuscripts in Preparation:**

1. “Mechanistic Investigation of Vinylic Carbon-Fluorine Bond Activation of Perfluorinated Alkenes using  $\text{Cp}^*_2\text{ZrH}_2$  and  $\text{Cp}^*_2\text{ZrHF}$ ,” Bradley M. Kraft and William D. Jones, *J. Am. Chem. Soc.*, written-to be submitted.
2. “Bond Cleavage Reactions in Substituted Thiophenes by a Rhodium Complex,” Andrew W. Myers, Lingzhen Dong, and William D. Jones, written-to be submitted.
3. “Alkane Coordination Selectivity in Hydrocarbon Activation by  $[\text{Tp}'\text{Rh}(\text{CNneopentyl})]$ : The Role of Alkane Complexes,” Andrew J. Vetter, and William D. Jones, *J. Am. Chem. Soc.* **2003**, 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.

**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, we will difficulty performing the planned chemistry. It is imperative that the grant be increased so that 2.5 people can work on the projects. Our current stipend for a good student is \$22K/year, and the current budget is supporting only about 80% of these costs. We usually obtain several undergraduate workers for 'free' (i.e., paid by the University), but supply and instrument usage costs still need to be paid.