

**FINAL REPORT  
SUBMITTED TO  
THE DEPARTMENT OF ENERGY**

BY

University of Rochester  
River Campus  
Rochester, New York 14627

FOR

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

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Unexpended Balance at End of Grant Period: \$0

**Overview of Research Accomplishments for the Period Dec. 1, 1998-Nov. 30, 2001:**

These past 3 years, our research has focussed 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) 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.

Our carbon-carbon bond cleavage study is based upon the notion that metal-phenyl bonds are the strongest metal-carbon bonds. Cleavage of the C-C bonds in biaryl systems will therefore give two very strong metal-aryl bonds, and consequently offers the most thermodynamically preferred situation for observing C-C cleavage. We have had extensive success in C-C cleavage with biphenylene, a molecule with a weaker C-C bond than biphenyl. The success includes not only several new nickel, palladium, and platinum based metal systems of the type [M(chelating phosphine)] but also related rhodium systems for C-C cleavage. In addition, cyclobutanones have also been found to undergo ring-opening decarbonylation involving C-C cleavage. A new system has been investigated using a nickel-bisphosphine complex in which C-CN bonds can be *reversibly* cleaved. This chemistry appears to be extensive, and will continue to be investigated in coming years.

Another area that we are investigating involves a continuation of our studies with the trispyrazolylborate fragment [Tp'Rh(CNCH<sub>2</sub>CMe<sub>3</sub>)] and the examination of new derivatives of the type [Tp'Rh(L)]. We have completed our detailed studies and kinetic analysis of the selectivities available to the intermediate alkane complexes, specifically, C-H insertion vs. dissociation vs. migration down the alkyl chain. By using deuterium labeling, we have been able to monitor the isomeric species involved and provide for the first time kinetic information about the dynamics of these intermediates. The work requires sophisticated kinetic modeling, and the results have been very well received at recent lectures. In the future we will extend these studies to branched hydrocarbons.

Catalytic activation of the C-C bond of biphenylene has been coupled with hydrogenation, olefin insertion, alkyne insertion, and C-H addition reactions. The chemistry appears to be quite broad and general. Trimethylsilyl groups appear to readily undergo migration in these reactions, leading to fluorene derivatives.

The fourth area we have been active in is C-F bond activation of fluoroalkanes. We have discovered that Cp\*<sub>2</sub>ZrH<sub>2</sub> is capable of cleaving a wide variety of aliphatic C-F bonds, generating Cp\*<sub>2</sub>ZrHF and the reduced hydrocarbon. No other transition metal based system has shown this type of reactivity. For example, 1-fluorohexane is reduced to hexane and perfluoropropene is completely reduced to propane. CFCs are also very reactive, first producing HFCs via C-Cl reduction and eventually HCs via C-F reduction. We will extend this work to

other early metal compounds during the coming years to compare and contrast the different reactivities of these reactants.

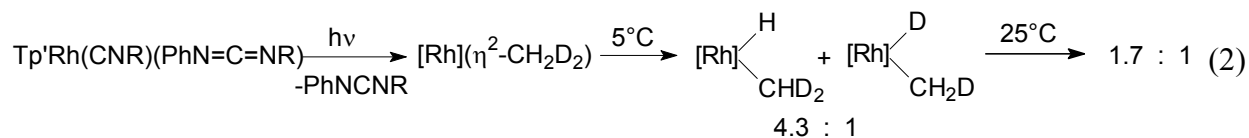
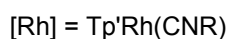
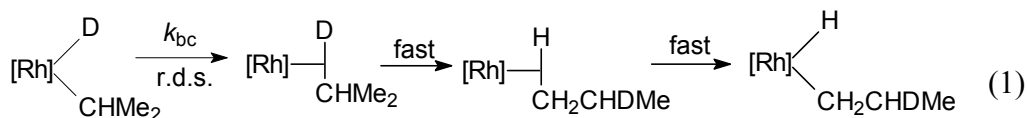
A variety of other chemistry has been examined, but is too extensive to give a full report here. The bibliography for this report contains references to the 22 manuscripts that will appear during the current grant period as a result of this DOE funded effort. Examination of the titles will provide an assessment of the variety of topics investigated.

DOE funds have been used for the support of 6 graduate students and 1 postdoc during the current grant period, as well as several undergraduates.

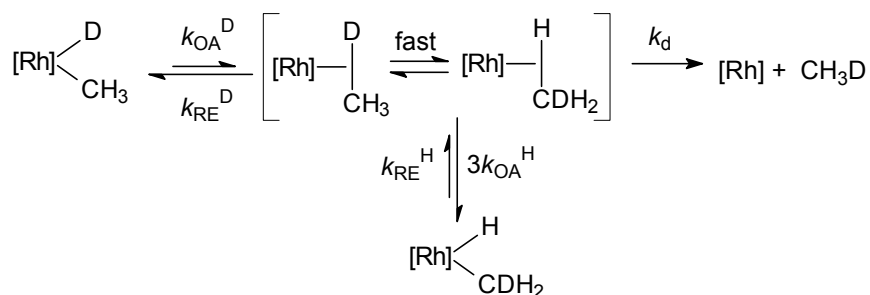
**Progress Report for the Period December 1, 1998- November 30, 2001.****1. Tris-pyrazolylborate Rhodium C-H Activation Studies.**

We have made many advances in our studies of rhodium tris-pyrazolylborate complexes for C-H bond activation with regard to alkane complex intermediates. Generation of the 16-electron fragment  $\{[\text{HB}(3,5\text{-dimethylpyrazolyl})_3]\text{Rh}(\text{CNCH}_2\text{CMe}_3)\}$  ( $\text{Tp}'\text{RhL}$ ) coordinated to an alkane allows the determination of the relative rates of the processes available to the alkane  $\sigma$ -complex, such as C-H activation, migration down the alkane chain, or simple dissociation. Several experiments have been performed that provide indirect evidence for the involvement of alkane  $\sigma$ -complexes in oxidative addition/reductive elimination reactions of  $\text{Tp}'\text{Rh}(\text{L})(\text{R})\text{H}$  complexes ( $\text{Tp}' = \text{tris-3,5-dimethylpyrazolylborate}$ ,  $\text{L} = \text{CNCH}_2\text{CMe}_3$ ). First, the methyl deuteride complex  $\text{Tp}'\text{Rh}(\text{L})(\text{CH}_3)\text{D}$  was observed to rearrange to  $\text{Tp}'\text{Rh}(\text{L})(\text{CH}_2\text{D})\text{H}$  prior to loss of  $\text{CH}_3\text{D}$ . Similarly,  $\text{Tp}'\text{Rh}(\text{L})(\text{CD}_3)\text{H}$  rearranges to  $\text{Tp}'\text{Rh}(\text{L})(\text{CD}_2\text{H})\text{D}$  prior to loss of  $\text{CD}_3\text{H}$ . Furthermore, there is a solvent isotope effect on the rate of methane loss ( $\text{C}_6\text{H}_6$  vs.  $\text{C}_6\text{D}_6$ ). These observations are consistent with the loss of methane in the  $\sigma$ -complex via an associative substitution pathway involving the solvent.<sup>9</sup>

Both of the H/D scrambling reactions described above occur via an intermediate methane  $\sigma$ -complex, and to simulate the kinetics for the interconversion isotope effects on both reductive elimination and oxidative addition were determined. The 'reductive bond formation' isotope effect was determined by comparing the rate of disappearance of the secondary isopropyl deuteride complex  $\text{Tp}'\text{Rh}(\text{L})(\text{CHMe}_2)\text{D}$  with the isopropyl hydride complex  $\text{Tp}'\text{Rh}(\text{L})(\text{CHMe}_2)\text{H}$ . The rate determining step in each of these reactions involves formation of the secondary propane  $\sigma$ -complex, so that  $k_{\text{H}}/k_{\text{D}}$  for this fundamental step could be determined ( $k_{\text{bc}}$  in eq 1). The 'oxidative bond cleavage' isotope effect for the reverse reaction was determined by examining the kinetic products in the activation of  $\text{CH}_2\text{D}_2$  (eq 2). Over time, the kinetic distribution adjusted to give a thermodynamic distribution favoring deuterium on carbon by a factor of  $\sim 2$ . Using these isotope effects, the simulation of the scrambling of  $\text{Tp}'\text{Rh}(\text{L})(\text{CH}_3)\text{D}$  could be successfully modeled as indicated in Scheme 1, and the relative rate constants for a methane  $\sigma$ -complex determined. Remarkably, the methane complex undergoes C-H oxidative addition 11x faster than it undergoes dissociation.<sup>19</sup>

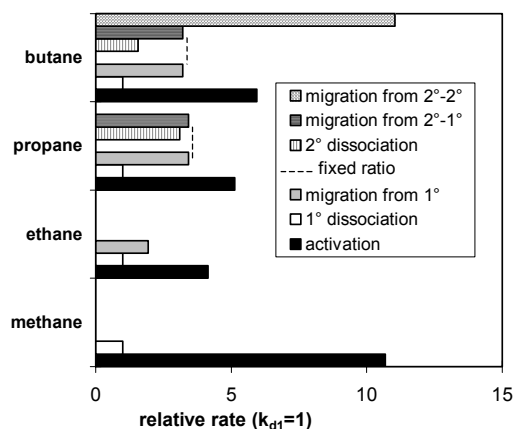


### Scheme 1:



Similar rearrangement studies were carried out using  $\text{Tp}'\text{Rh}(\text{L})(\text{R})\text{D}$  where  $\text{R} = \text{ethyl, propyl, butyl, pentyl, and hexyl}$ . As the chains become longer, new rate constants are necessary to include migration up and down the chain and dissociation from primary vs. secondary carbons. These simulations proved to be possible, allowing the determination of the relative rates for the processes available to any given alkane complex. However, once the chain length reached 4 carbons ( $\text{C}_4$ ), no new rate constants are needed to simulate the behavior of the system so that the pentyl and hexyl hydrides could be simulated using the previously determined rate constants.<sup>19</sup>

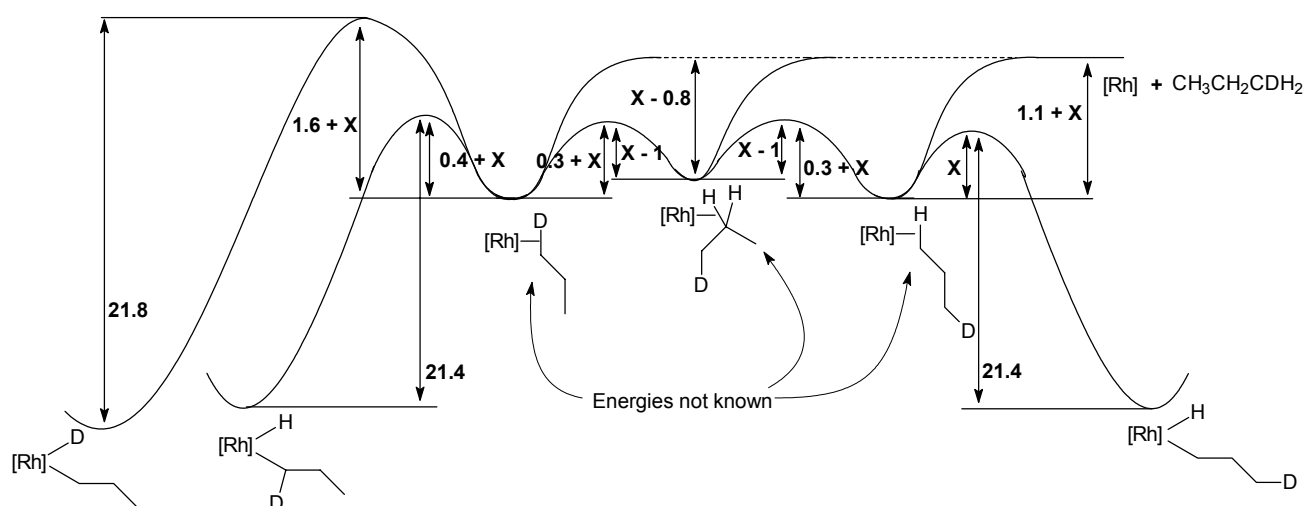
The conclusions of this study are summarized in the bar chart shown in Fig.1 below. For methane, C-H activation is strongly preferred over dissociation, whereas for ethane, the rates of these two processes are closer. End-to-end migration in ethane is intermediate. For propane, terminal C-H activation 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  $\sigma$ -alkane processes.

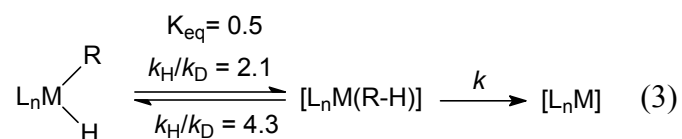
One interesting point learned in these modeling studies is that one cannot obtain absolute rates for these processes, but only relative rates. Furthermore, one cannot compare the rates of processes for different alkanes or even for different alkane complexes within the same alkane. The reason for this is seen by examination of the free energy picture for the scrambling in propyl deuteride complex (Fig.2). We do not know the absolute energies of the alkane  $\sigma$ -complexes, and therefore cannot obtain an absolute rate for any single process involving these complexes. We can, however, learn about the differences in barrier heights for the reactions open to any one of these complexes.

**Figure 2.**



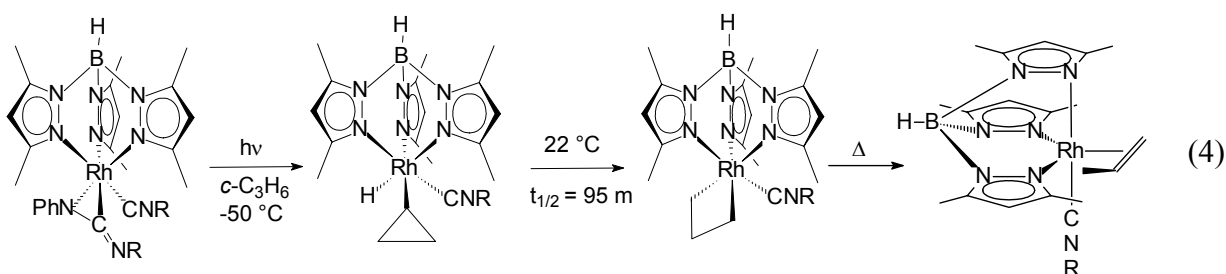
One of the more interesting side-lights from this study comes from the independent determination of isotope effects for both the 'oxidative bond cleavage' and the 'reductive bond formation' steps of the C-H activation reaction indicated in equations 1 and 2. These isotope

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 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.

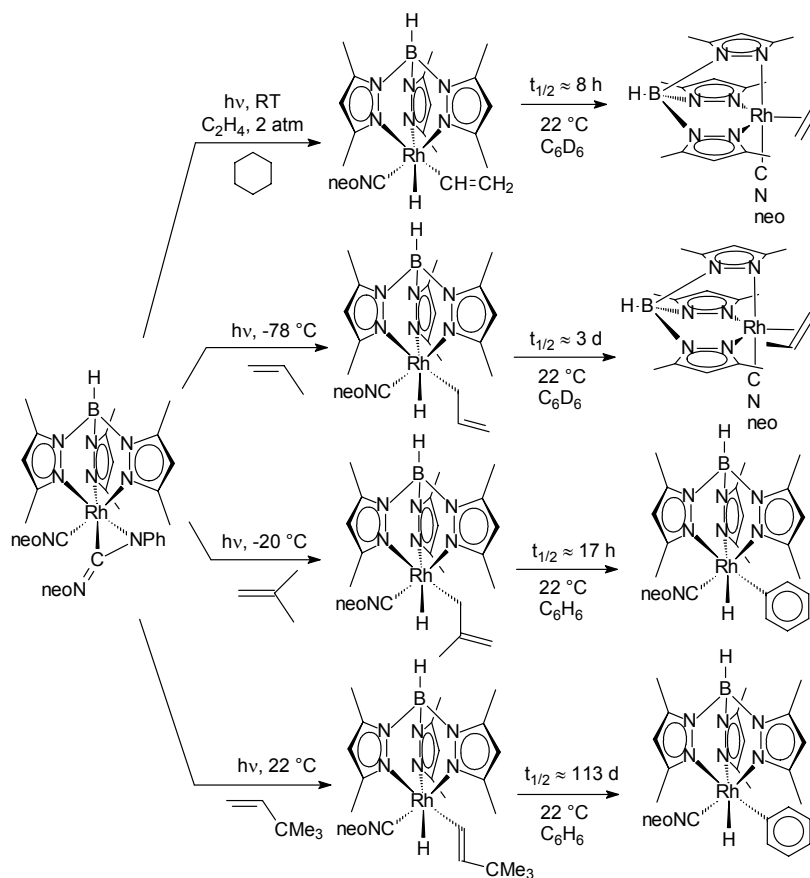


In addition to these studies, we also completed investigation of the reaction of [Tp'Rh(CNR)] with cyclopropane.<sup>2</sup> The first product is a C-H insertion adduct, which then rearranges to give a metallocyclobutane complex. Further heating leads to the conversion into an  $\eta^2$ -propene complex (eq 4). We also looked at examples of vinyl and allylic C-H activation using ethylene, propene, isobutene, and t-butylethylene as substrates (Scheme 2).<sup>6</sup> For ethylene and t-butylethylene, vinylic C-H activation was observed. The vinyl hydride rearranges to the  $\eta^2$ -ethylene complex, but the t-butylethylene complex is unstable and olefin is lost. The olefins with allylic C-H bonds show exclusive activation of these bonds. The  $\sigma$ -allyl hydride then rearranges to give the olefin complex (with propylene), or dissociated olefin (with isobutylene). These results show that C-H activation precedes olefin coordination, and that bulky olefins do not coordinate but rather directly reductively eliminate from the allyl/vinyl hydride complexes.

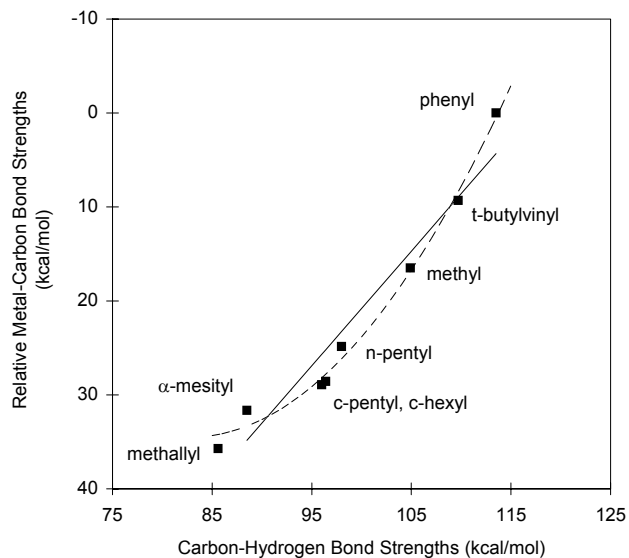
We have used these experiments to establish a trend in relative metal-carbon bond strengths vs. carbon-hydrogen bond strengths. As shown in Figure 3, the relationship between these values is parabolic, but a linear approximation shows a slope of 1.22, providing a rationale for the preference for the cleavage of stronger C-H bonds over weaker ones... the metal-carbon bond is  $\sim 1.2x$  stronger, in a relative sense.<sup>6</sup>



Scheme 2:

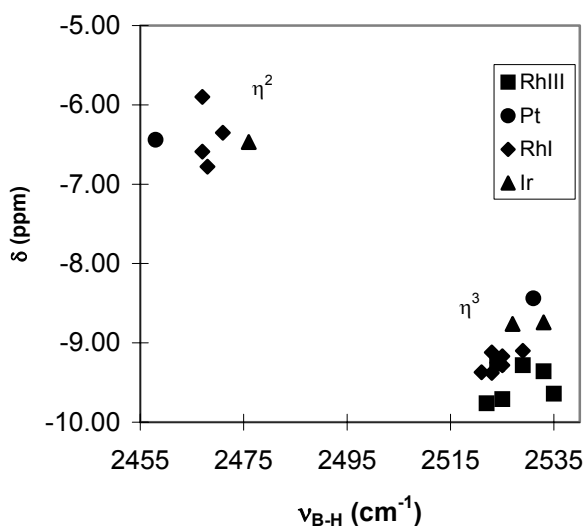


**Figure 3.** Plot of relative rhodium-carbon bond strengths vs. carbon-hydrogen bond strengths for hydrocarbon substrates. Slope of best line = 1.22. Dotted line is a least squares parabolic fit.



We have also discovered a new method for determination of the hapticity of the Tp' ligand in solution. A major advance was made in assigning hapticity recently by Akita et al., when they found that the B-H stretching frequency correlates with the hapticity of the tris-pyrazolylborate ligand in several complexes. In general, if  $\nu_{\text{B-H}} < 2500 \text{ cm}^{-1}$ , then the hapticity is  $\eta^2$ . If  $\nu_{\text{B-H}} > 2500 \text{ cm}^{-1}$ , then the hapticity is  $\eta^3$ . Of the 24 examples cited, there were one or two exceptions to this trend that were believed to be due to the different substituents on the pyrazole ring.

We have discovered what appears to be a simpler method for assigning hapticity in solution. The chemical shift of the boron in the  $^{11}\text{B}$  NMR spectrum appears to correlate well with hapticity in known complexes. These spectra can be acquired quickly and easily in solution, and while the resonances are broad due to quadrupolar relaxation, the chemical shifts fall into the range  $\delta$  -6 for  $\eta^2$  complexes and  $\delta$  -9 for  $\eta^3$  complexes. A plot of  $^{11}\text{B}$  chemical shifts vs.  $\nu_{\text{B-H}}$  dramatically shows how good this correlation is (Figure 4).<sup>4</sup>

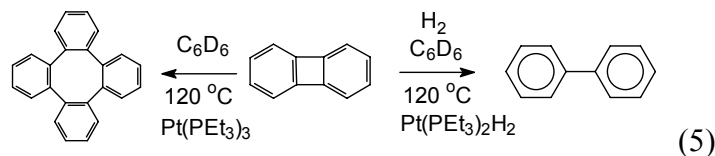


**Figure 4.** Correlation of  $^{11}\text{B}$  NMR chemical shifts and  $\nu_{\text{B-H}}$  stretching frequencies.

## 2. C-C Bond Cleavage Studies

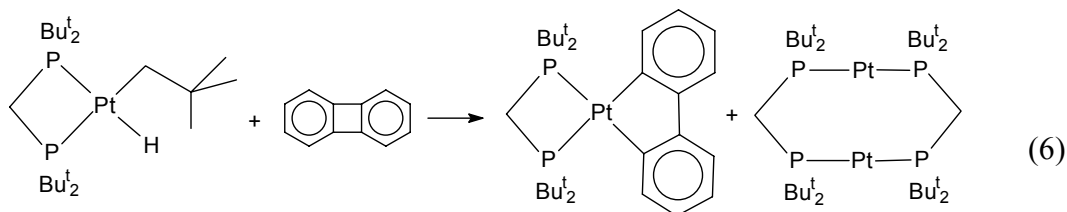
The complexes  $\text{Pt}(\text{PEt}_3)_3$  and  $\text{Pd}(\text{PEt}_3)_3$  cleave the C-C bond of biphenylene to give  $(\text{PEt}_3)_2\text{Pt}(2,2'\text{-biphenyl})$  and  $(\text{PEt}_3)_2\text{Pd}(2,2'\text{-biphenyl})$ , respectively. Heating  $(\text{PEt}_3)_2\text{Pt}(2,2'\text{-biphenyl})$  in the presence of biphenylene leads to C-C cleavage of a second biphenylene to give  $(\text{PEt}_3)_2\text{Pt}(2,2'\text{-tetraphenyl})$ , via a Pt(IV) intermediate, which in turn reductively eliminates

tetraphenylene at 115 °C. At 120 °C the reaction is catalytic, converting biphenylene to tetraphenylene (eq 5). In the presence of hydrogen, however, the initial C-C cleavage intermediate can be intercepted and hydrogenolysis occurs exclusively.<sup>3</sup>

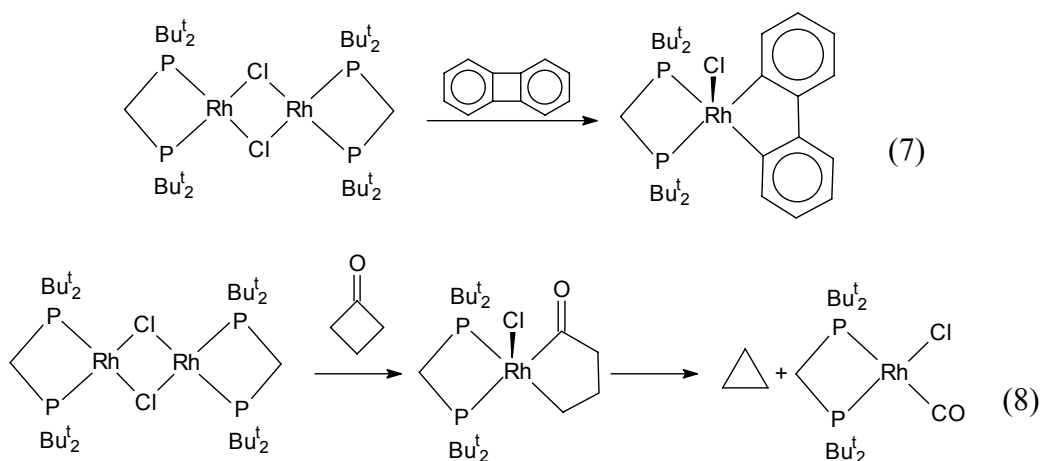


The nickel alkyne complexes (dippe)Ni(RC≡CR), (R = Ph, Me, CO<sub>2</sub>Me, or CH<sub>2</sub>OCH<sub>3</sub>) were found to be catalysts for the conversion of biphenylene and excess alkyne into the corresponding 9,10-disubstituted phenanthrenes. Trimethylsilylacetylenes gave both phenanthrenes and carbosilation addition products. Fluorenone was catalytically produced by heating (dippe)Ni(CO)<sub>2</sub>, biphenylene and CO. Catalytic insertion of 2,6-xylylisocyanide into the strained C-C bond of biphenylene was also achieved by heating (dippe)Ni(2,6-xylylisocyanide)<sub>2</sub>, excess biphenylene and 2,6-xylylisocyanide.<sup>12,13</sup>

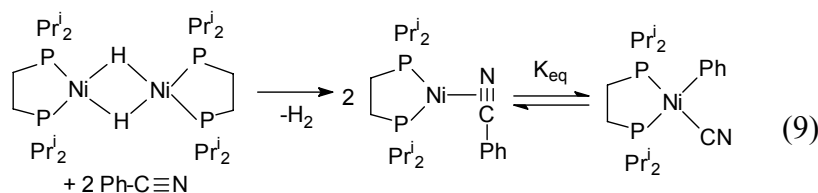
We have extended this chemistry to include the smaller chelate ligand, Bu<sup>t</sup><sub>2</sub>PCH<sub>2</sub>PBu<sup>t</sup><sub>2</sub> (dtbpm). We had anticipated that this ligand might permit the activation of less sterically accessible C-C bonds. While the platinum dtbpm complex does activate biphenylene more easily than the dippe complex, there is a competing side reaction involving ligand dissociation to create a dimer that renders these compounds unsuccessful for the desired chemistry (eq 6).<sup>20</sup>



We have also been successful in generating the 16-electron rhodium analog of this compound. Now, biphenylene can be activated cleanly and insertion reactions with substrates such as alkynes and CO can be carried out catalytically (eq 7). Furthermore, we have discovered that cyclobutanones undergo C-C cleavage and CO deinsertion to give the rhodium carbonyl complex and cyclopropane (eq 8). The reaction is *catalytic* at elevated temperatures.



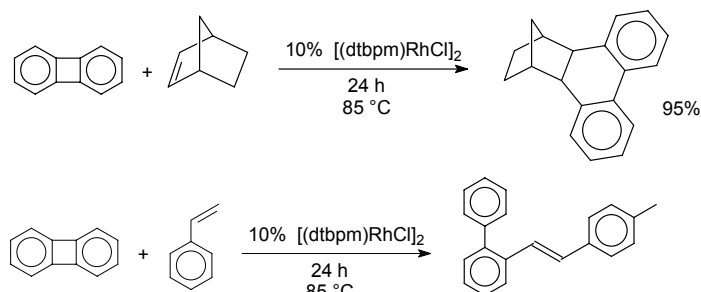
We have also discovered that the nickel complex  $[\text{Ni}(\text{dippe})\text{H}]_2$  reacts with benzonitrile to give first an  $\eta^2$ -nitrile complex, which then undergoes C-C cleavage of the carbon-CN bond (eq 9). Furthermore, the reaction does not go to completion but forms an equilibrium mixture of the  $\eta^2$ -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. <sup>18</sup>



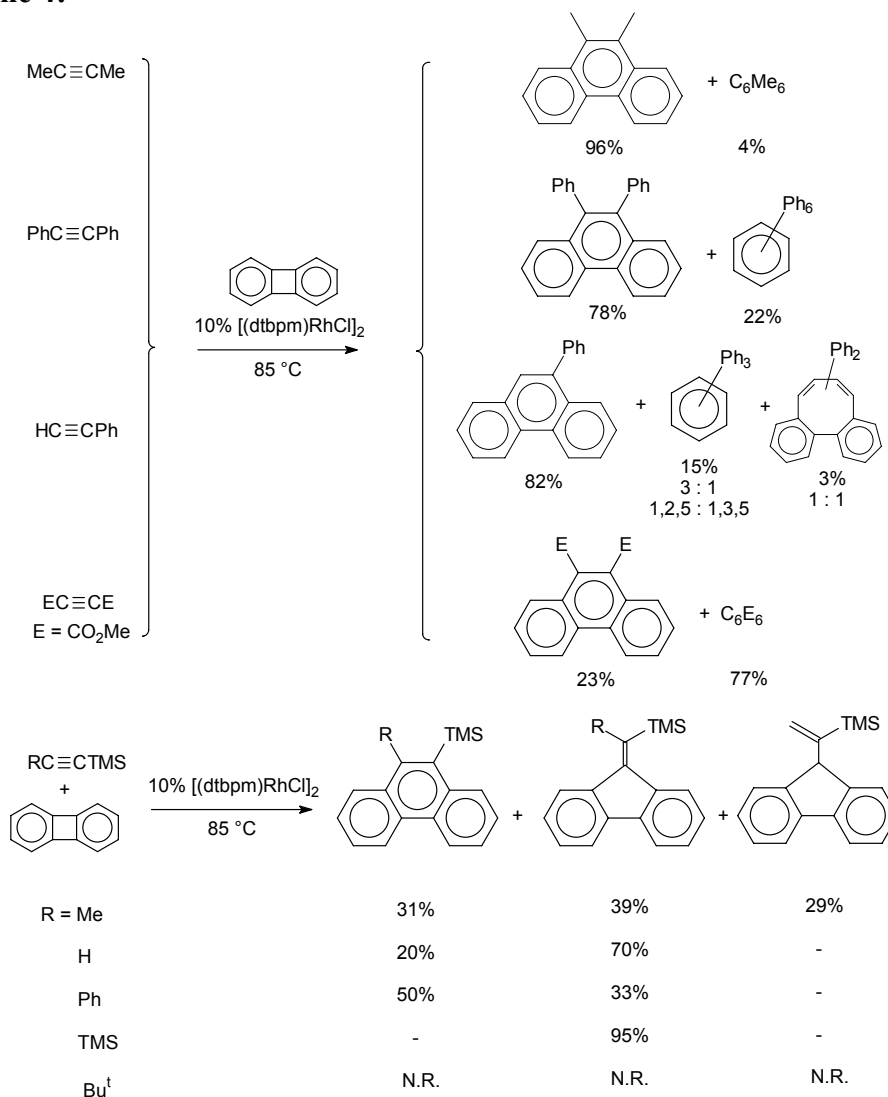
### 3. C-H and C-C Bond Functionalization Studies

We have also initiated investigations of the above systems for their ability to serve in further functionalization reactions. For example, the rhodium system reacts with biphenylene to give a C-C insertion adduct that can then be reacted with  $\text{H}_2$  to catalytically produce biphenyl. Preliminary studies indicate that olefins react with biphenylene in the presence of catalytic amounts of the rhodium complex to give insertion products or vinylic C-H addition products (Scheme 3).

**Scheme 3:**



In addition, catalytic reactions of biphenylene with acetylenes lead to phenanthrenes and/or 1,1-addition products involving what appears to be silicon migration from one carbon to another (Scheme 4).

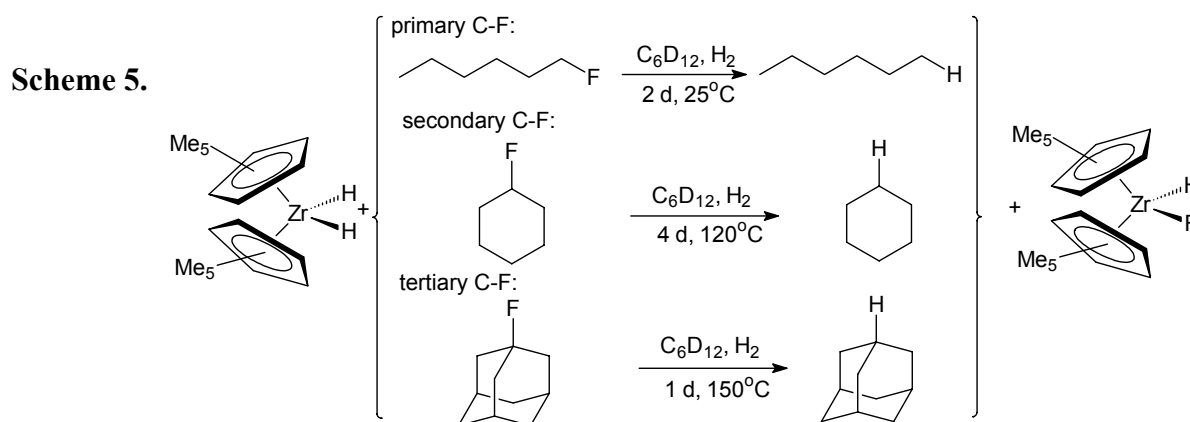
**Scheme 4:**

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

We have reported that the zirconium hydride dimer [Cp<sub>2</sub>ZrH<sub>2</sub>]<sub>2</sub> reacts with C<sub>6</sub>F<sub>6</sub> at ambient temperature to give Cp<sub>2</sub>Zr(C<sub>6</sub>F<sub>5</sub>)F as the major product along with Cp<sub>2</sub>ZrF<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>H and H<sub>2</sub>.<sup>11</sup> This reaction is difficult to study in that the starting complex, [Cp<sub>2</sub>ZrH<sub>2</sub>]<sub>2</sub>, is insoluble in most solvents. We also discovered a reaction of Cp<sub>2</sub>Zr(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> that appears to produce

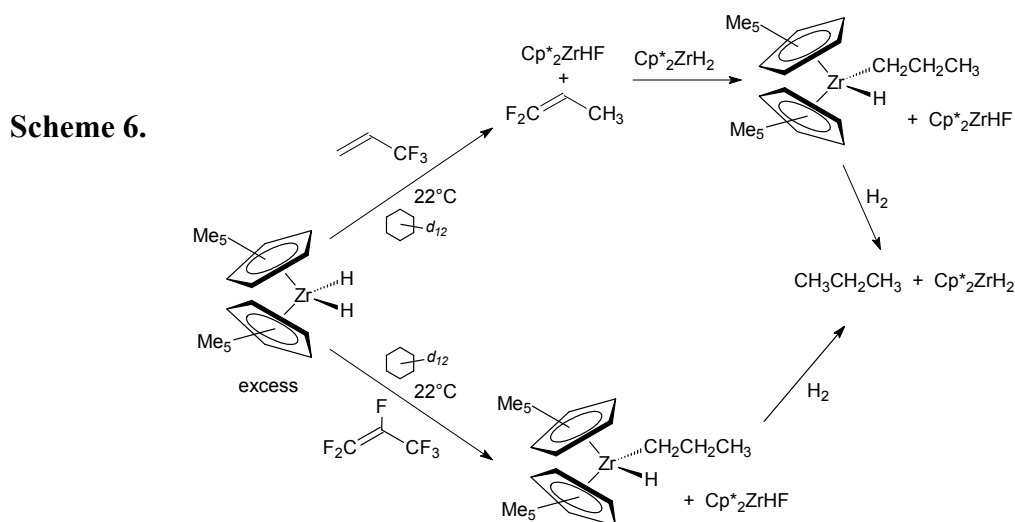
tetrafluorobenzene. A competing radical chain process leads to the formation of perfluoropolyphenylene oligomers ( $n \sim 20$ ).<sup>14</sup>

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.<sup>17</sup>



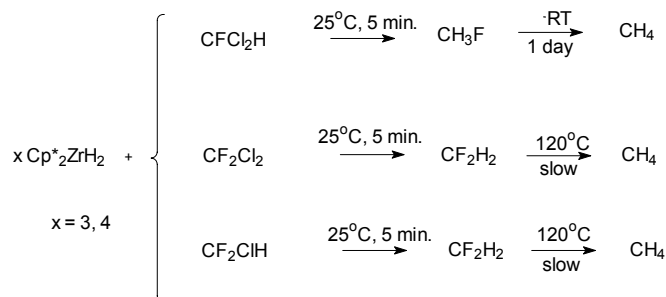
Most remarkable, however, even trifluoromethyl C-F bonds can be easily cleaved if they are adjacent to a double bond. 3,3,3-trifluoropropene is *completely defluorinated in 5 min at room temperature* to give the zirconium-*n*-propyl hydride complex (Scheme 6).

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.<sup>22</sup> Further mechanistic work with the fluoroolefins is underway suggesting an insertion/ $\beta$ -fluoride elimination pathway.

Scheme 7.



\* In all cases, the zirconium products were mixtures containing Cp\*<sub>2</sub>ZrHF, Cp\*<sub>2</sub>ZrF<sub>2</sub>, Cp\*<sub>2</sub>ZrHCl, Cp\*<sub>2</sub>ZrCl<sub>2</sub>, and Cp\*<sub>2</sub>ZrClF.

### **Publications appearing during the current grant period,**

#### **December 1, 1998 - November 30, 2001, resulting from DOE support:**

1. "Facile C-N Bond Cleavage Mediated by Electron-Rich Cyclopentadienyl Cobalt(I) Complexes," Helmut Werner, Gerhard Hörlin, and William D. Jones, *J. Organomet. Chem.* **1998**, 562, 45-51.
2. "Carbon-Hydrogen and Carbon-Carbon Bond Activation of Cyclopropane by a Hydridotrispyrazolylborate Rhodium Complex," Douglas D. Wick, Todd O. Northcutt, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1998**, 17, 4484-4492.
3. "Catalytic Hydrogenolysis of Biphenylene with Platinum, Palladium, and Nickel Phosphine Complexes," Brian L. Edelbach, David A. Vicic, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1998**, 17, 4784-4794.
4. "<sup>11</sup>B NMR: A New Tool for the Determination of Hapticity of Trispyrazolylborate Ligands," Todd O. Northcutt, Rene J. Lachicotte and William D. Jones, *Organometallics* **1998**, 14, 5148-5152.
5. "Insertion of Elemental Sulfur and SO<sub>2</sub> into the Metal-Hydride and Metal-Carbon Bonds of Platinum Compounds," Michael S. Morton, Rene J. Lachicotte, David Vicic, and William D. Jones, *Organometallics*, **1999**, 18, 227-234.
6. "Energetics of Homogeneous Intermolecular Vinyl and Allyl Carbon-Hydrogen Bond Activation by the 16 Electron Coordinatively Unsaturated Organometallic Fragment [Tp'Rh(CNCH<sub>2</sub>CMe<sub>3</sub>)]," William D. Jones and Douglas D. Wick, *Organometallics* **1999**, 18, 495-505.
7. "Topics in Organometallic Chemistry. Activation of Unreactive Bonds and Organic Synthesis," Chapter 2, *Activation of C-H Bonds. Stoichiometric Reactions*, William D. Jones, Springer-Verlag, 1999, Berlin.

8. "Photochemical C-H Activation and Ligand Exchange Reactions of  $\text{CpReH}_2(\text{PPh}_3)_2$ . Phosphine Dissociation is Not Involved," William D. Jones\*, Glen P. Rosini, and John A. Maguire, *Organometallics*, **1999**, *18*, 1754-1760.
9. "Evidence for Methane Sigma-Complexes in Reductive Elimination Reactions from  $\text{Tp}'\text{Rh}(\text{L})(\text{CH}_3)\text{H}$ ," Douglas D. Wick, Kelly A. Reynolds, and William D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 3974-3983.
10. "A new synthetic route to ligands of the general composition  $\text{R}_2\text{PCH}_2\text{ER}'_2$  (E = P, As) and some rhodium complexes derived thereof," Justin Wolf, Matthias Manger, Ulrich Schmidt, Guido Fries, Dietmar Barth, Birgit Weberndörfer, David A. Vicic, William D. Jones, Helmut Werner, *J. Chem. Soc., Dalton Trans.* **1999**, 1867-1876.
11. "Carbon-Fluorine Bond Cleavage by Zirconium Metal Hydride Complexes," Brian L. Edelbach, A. K. Fazlur Rahman, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1999**, *18*, 3170-3177
12. "Catalytic Carbon-Carbon Bond Activation and Functionalization by Nickel Complexes," Brian L. Edelbach, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1999**, *18*, 4040-4049.
13. "Catalytic Carbon-Carbon and Carbon-Silicon Bond Activation and Functionalization by Nickel Complexes," Brian L. Edelbach, Rene J. Lachicotte, and William D. Jones, *Organometallics* **1999**, *18*, 4660-4668.
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