

PROJECT SUMMARY REPORT

submitted to

THE U.S. DEPARTMENT OF ENERGY

for

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

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Total Project Period: December 1, 2004 - November 30, 2007
Total Award Amount (3 years): \$ 398,000

Unexpended Balance from Previous Year: \$0

Executive Summary of FY 2004-7 Research in the Chemical Sciences

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

Grant# FG02-86ER13569

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

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.

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 this 3 year project period, our research has focussed on the following general goals: (1) fundamental studies of C-H bond cleavage reactions of trispyrazolyl-boraterhodium complexes, including binding and activation, (2) C-H bond activation reactions in functionalized substrates, including alkylnitriles and (3) C-C bond activation in aryl-alkynes, aryl-nitriles, and allyl-nitriles, (4) carbon-fluorine bond activation with hafnium. We have made progress in each of these areas, as described in the following report.

The specific accomplishments of the current grant period include:

(1) we have successfully measured and quantitatively modeled the processes available to metal alkyl hydride complexes in a trispyrazolylborate-rhodium complex, including both linear and cyclic hydrocarbons;

(2) we have measured *for the first time* the selectivity for a metal fragment binding to methyl vs methylene groups in a linear hydrocarbon;

(3) we have measured C-H activation selectivities in aliphatic nitriles, showing a kinetic preference for activation of the terminal methyl groups;

(4) we have measured C-H activation selectivities in 1-, 2-, and 3-chloropentane, showing a preference for activation of the terminal methyl groups and facile β -chloride elimination;

(5) we have cleaved C-C bonds in aryl-acetylenes, aryl-nitriles, and alkyl-nitriles, expanding substantially the breadth of C-C cleavage;

(6) we have investigated factors that affect the cleavage of C-C bonds in allyl nitriles, leading to isomerization of the C-C skeleton. Solvent effects are incredibly large. This reaction is critical to the DuPont synthesis of Nylon from butadiene;

(7) we have discovered new C-H and C-C functionalizations that allow introduction of reactive boronate and olefin functional groups;

(8) we have established that Cp^*HfH_2 can effect C-F bond cleavage of fluorocarbons;

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 more detailed report follows, followed by a listing of the DOE supported publications and recent special recognitions received by the PI.

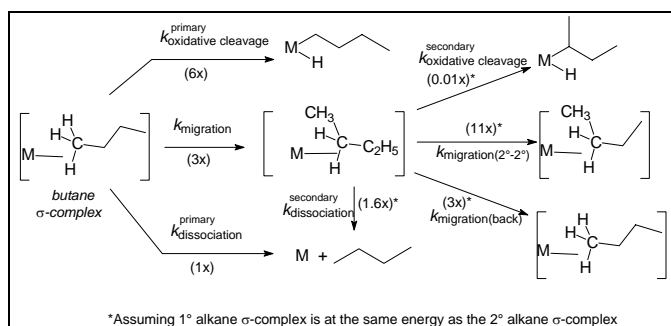
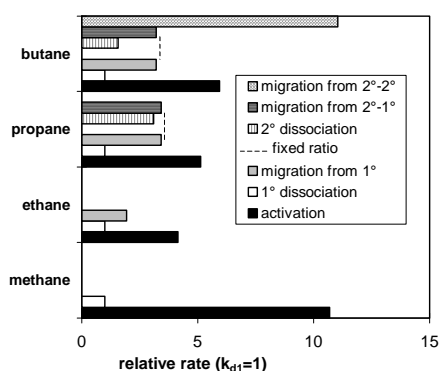
Progress Report for the Project Period Dec. 1, 2004- Nov. 30, 2007.

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

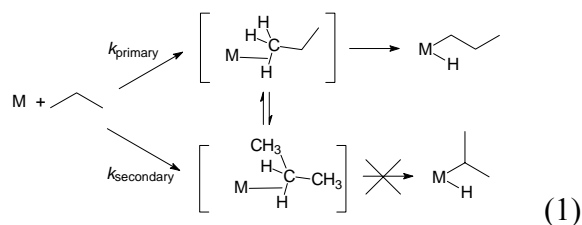
1. Tris-pyrazolylborate Rhodium C-H Activation Studies-Alkane σ -Complexes.

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 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. Figure 1 shows the relative rates of these processes for methyl, ethyl, n-propyl, and n-butyl derivatives, indicating that C-H activation is strongly preferred over dissociation, with migration from methyl to methylene or methylen to methyl lying inbetween. Interestingly, migration down the interior of an alkane chain (secondary to secondary) is the fastest process, accounting for the observed kinetic preference for terminal C-H activation. These conclusions can be expressed in a schematic fashion as shown in Scheme 1.

Figure 1. Relative rates of σ -alkane processes. **Scheme 1.** Relative rates in primary (1°) and secondary (2°) alkane complexes.

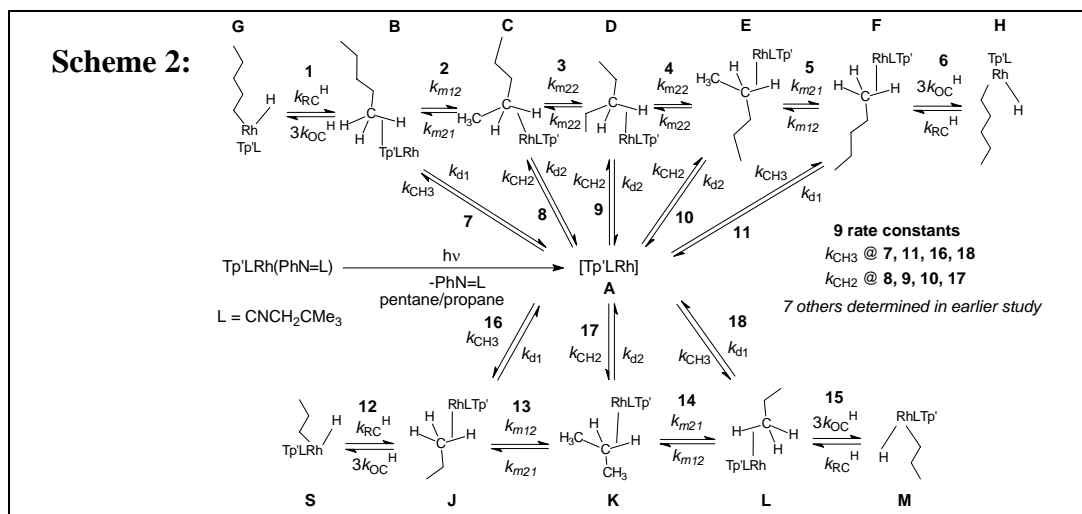


With the relative rates of all of these internal processes now known for any linear alkane, we have completed studies to determine *which C-H bond of an alkane first binds to the $\text{Tp}'\text{RhL}$ fragment*. The execution of this experiment is not completely obvious, as reaction of the fragment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



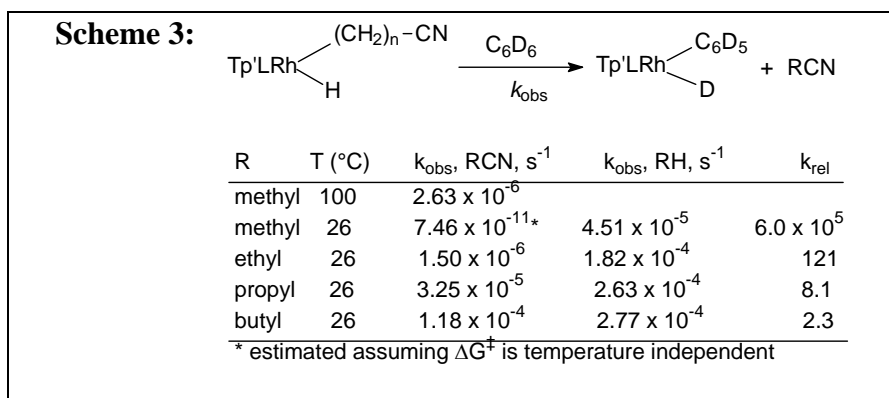
- In the current project period, we were able to use competition experiments to establish that:
- (1) in a linear alkane, the Tp'RhL fragment coordinates to a methylene group 1.5× faster than to a methyl group.
 - (2) the oxidative cleavage of a methyl C-H bond (primary C-H) occurs 65 K_{12} times faster 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.
 - (3) a methyl group in pentane coordinates 1.9 times faster than the more hindered methyl group of isobutane. Cyclopentane was found to bind 1.7 times faster than cyclohexane.

These conclusions were made building upon our earlier studies of the relative rates of oxidative cleavage, migration, and dissociation indicated in Scheme 1. Competition studies allowed determination of the relative binding rates for methylene (k_{CH_2}) vs. methyl (k_{CH_3}) C-H groups. As an example, Scheme 2 shows all possible intermediates and pathways for the competition between propane and pentane. In the experiment, Tp'Rh(CNR)(carbodiimide) was irradiated in a 1:1 mixture of pentane/propane. The alkyl hydride products were quenched with CCl_4 to give the stable chloro derivatives. A simulation in which the relative binding rates were varied to match the observed product ratio showed a slight preference for methylene group coordination, with $k_{CH_2}/k_{CH_3} = 1.5:1$.

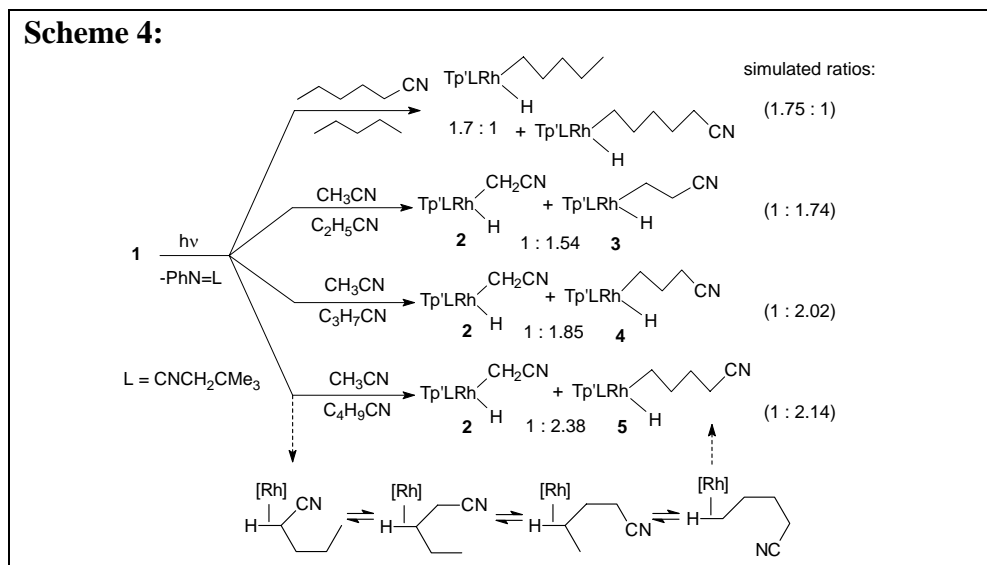


2. Tris-pyrazolylborate Rhodium C-H Activation Studies-Alkyl nitrile Activation.

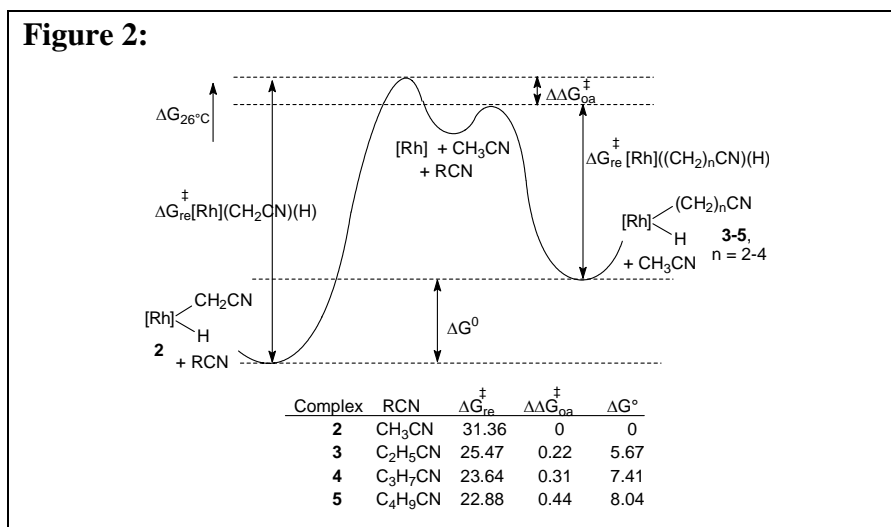
We have conducted an extensive investigation of C-H activation of aliphatic nitriles. It appears that there is once again selectivity for terminal methyl groups. With acetonitrile, the adduct $\text{Tp'LRh}(\text{CH}_2\text{CN})\text{H}$ is the only product formed, and is found to be stable at 60 °C for days! This is the most stable alkyl hydride in this series yet, indicating that an α -cyano group significantly strengthens the Rh-C bond. The activation of longer chain alkyl nitriles (C_2 - C_4) shows in each case terminal methyl C-H activation as the dominant process (>90%). In addition, the stability of each adduct was seen to depend on the number of methylenes separating the metal and the cyano substituent, with the effect being measurable up to 4 carbons away from the metal center (Scheme 3). This series provides evidence for a very strong inductive effect on the metal-carbon bond strength. In addition, traces of products attributed to C-H activation α - to the nitrile were seen (3-5%), and these adducts had the expected high stabilities. Despite their high thermodynamic stabilities, however, they are kinetically very slow to form. Consequently only traces are observed in the reaction.



Competition studies between pentane and hexanenitrile showed a preference for activation of pentane of 1.7:1, despite the presence of a similar number of C-H bonds. Competition reactions between acetonitrile and a second alkyl nitrile showed a kinetic preference for the alkyl nitrile, with the preference being greater as the length of the chain increased (Scheme 4). These observations were interpreted in terms of rate-determining binding to a C-H bond followed by migration down the chain to the terminal methyl group, where irreversible C-H activation occurred. A simulation of these competitions using the same rate constants as determined above for linear alkanes gave remarkably good agreement with the experimentally observed product ratios.



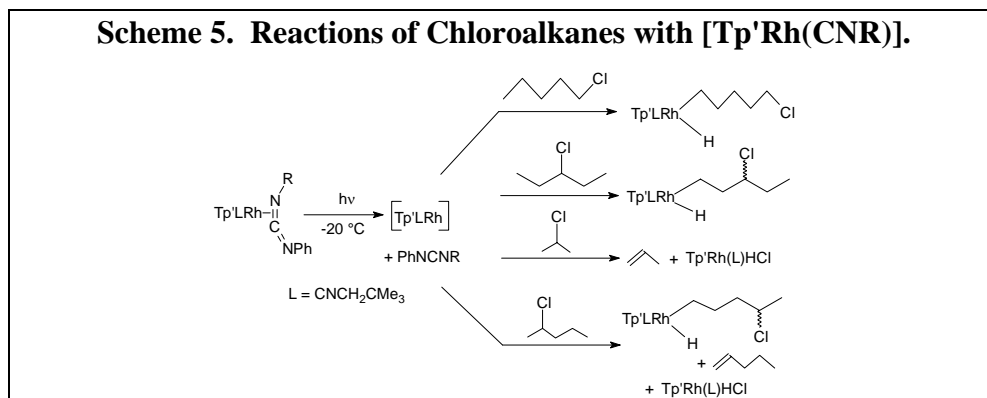
These competitions and the kinetic studies described above allow a quantitative evaluation of the effect of the cyano group on the metal-carbon bond strength. As shown in Figure 2, a free energy analysis of the competition ratios ($\Delta\Delta G_{\text{oa}}^\ddagger$) vs the rate of reductive elimination ($\Delta G_{\text{re}}^\ddagger$) of each nitrile allows determination of ΔG° for the pair of substrates. As the chain lengthens to 4 carbons, the free energy difference levels off at about 8 kcal/mol, which represents the increase in bond strength due to the α -cyano group.



3. Tris-pyrazolylborate Rhodium C-H Activation Studies-Chloroalkane Activation.

We have also conducted an initial 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 (Scheme 5). Thus, 1-chloropentane gives the 5-chloropentyl hydride as the only product. 3-chloropentane gives the 3-chloropentyl hydride product. If a chlorine is present in a β -position, then β -chloride elimination occurs to give an olefin and the metal chloride. Therefore, 2-chloropropane gives only propene and the hydrido chloride $\text{Tp}'\text{Rh}(\text{CNR})\text{HCl}$. 2-chloropentane gives a mixture of the C-H activation product 4-chloropentyl hydride, pentene, and the hydrido chloride.

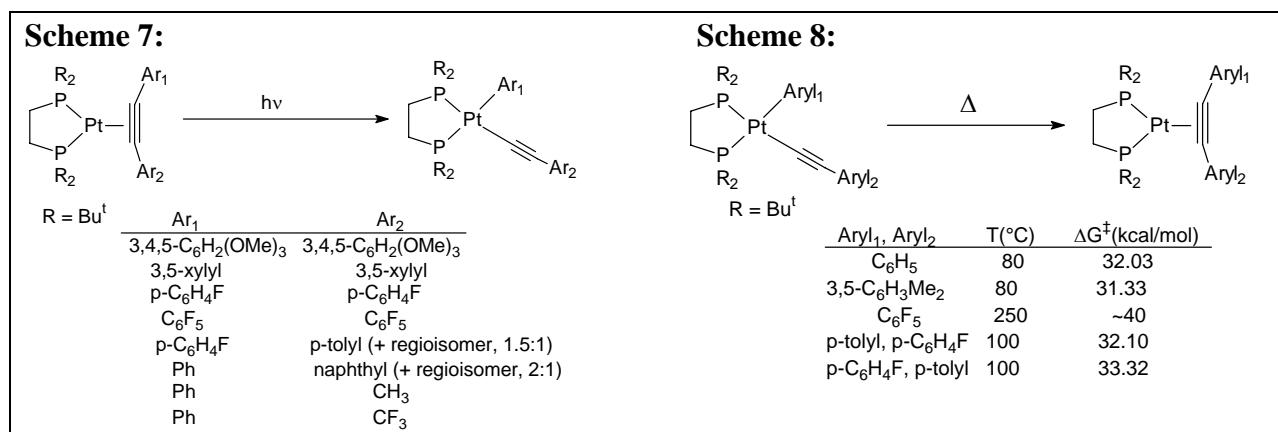


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4. C-C Bond Cleavage Studies - sp - sp^2 bonds in Acetylenes.

Our DOE supported work showed several types of C-C bond activation. We have found 3 distinct types 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 η^2 -nitrile adducts can be observed as reaction intermediates. The latter two categories were investigated during the current grant period, and are described in more detail below.

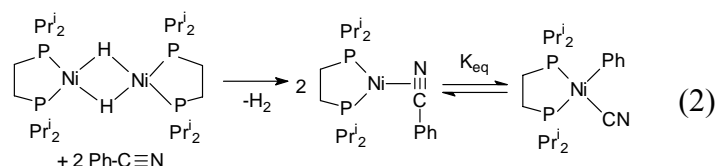
We have uncovered an important new type of C-C bond oxidative addition, cleavage of sp - sp^2 C-C bonds in aryl acetylenes. This is a *new class* of C-C bond cleavage, and offers many exciting possibilities. The reaction is quite general, proceeding with either P-P (dippe, dcpe, dtbpe) or P-N chelate complexes of Pt-(diphenylacetylene), leading to the clean and quantitative formation of the oxidative addition product (Scheme 7). In all cases, C-C cleavage requires photolysis, and heating the product converts the Pt(II) oxidative addition product back to the η^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 barriers ranging from 31-40 kcal/mol (Scheme 8).



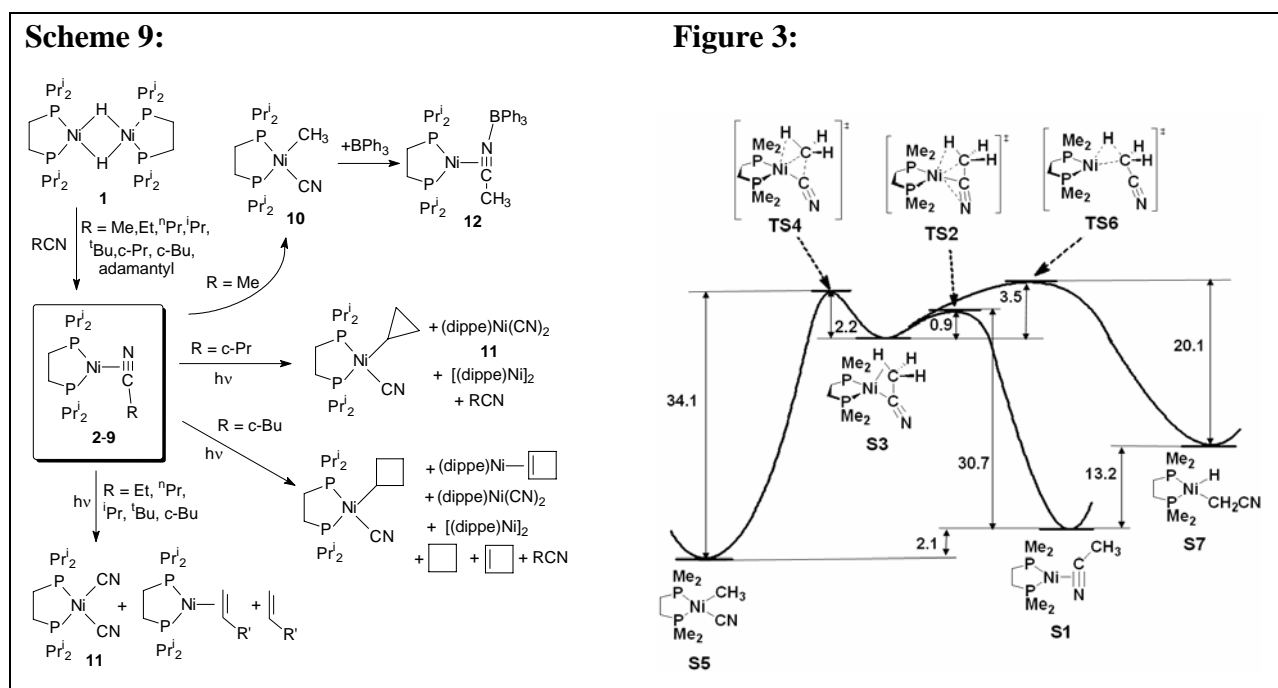
A tremendous stabilizing effect is seen with pentafluoro substitution, attributable to a much stronger platinum-aryl bond in the product. This increase in bond strength is likely due to the presence of two ortho-fluorines, which are known to have a profound effect on D_{M-C} . Despite the stronger M-C bond, however, the reaction to cleave the C-C bond is still uphill thermodynamically.

5. C-C Bond Cleavage Studies - $sp-sp^3$ bonds in Alkyl nitriles and $sp-sp^2$ bonds in PhCN.

We 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 2). The reaction does not go to completion but forms an equilibrium mixture of the η^2 -nitrile and C-CN oxidative addition product. We have also found that electron withdrawing and electron donating groups on the aryl cyanide have a profound effect upon both the equilibrium and the rate of C-CN cleavage.



We have extended this C-CN cleavage chemistry to alkyl nitriles. The cleavage reactions proceed upon heating, and with longer chain nitriles, β -hydrogen elimination occurs to give the corresponding olefin and $(\text{dippe})\text{Ni}(\text{CN})\text{H}$ (Scheme 9). We have investigated the reaction with acetonitrile in considerable detail, using DFT theory to model the system and examine the transition state for C-C cleavage. In addition, we have examined the corresponding C-H activation product $(\text{dippe})\text{Ni}(\text{CH}_2\text{CN})\text{H}$ which is not observed during the reaction. A summary of the free energy picture is shown in Figure 3. The diagram shows several interesting



features regarding the C-CN activation process. First, there is a stable high-energy intermediate that interconnects the η^2 -nitrile complex, the C-CN cleavage product, and the C-H cleavage product. Second, if we use the Polarized Continuum Model (PCM) to apply a solvation correlation, the reaction is exothermic. In the gas phase, the C-C cleavage is substantially endothermic, indicating that it is critical to include solvent effects on the C-CN cleavage reaction since a very polar M-CN bond is being formed. Third, the C-H activation product is very high in energy (too high to be observed) and kinetically disfavored.

We have experimental confirmation of this energy picture. Reaction of $[\text{Ni}(\text{dippe})\text{H}]_2$ with ClCH_2CN gives $\text{Ni}(\text{dippe})(\text{CH}_2\text{CN})\text{Cl}$, which can be reduced with LiHBEt_3 at low temperature to give $\text{Ni}(\text{dippe})(\text{CH}_2\text{CN})\text{H}$. This material is very unstable, decomposing to the η^2 -nitrile complex above -40°C . Consequently, we have found that DFT/B3LYP theory with PCM correction gives good agreement with experiment. We have examined 6 additional basis sets for comparison, but B3LYP gives the best results in comparison to known structures.

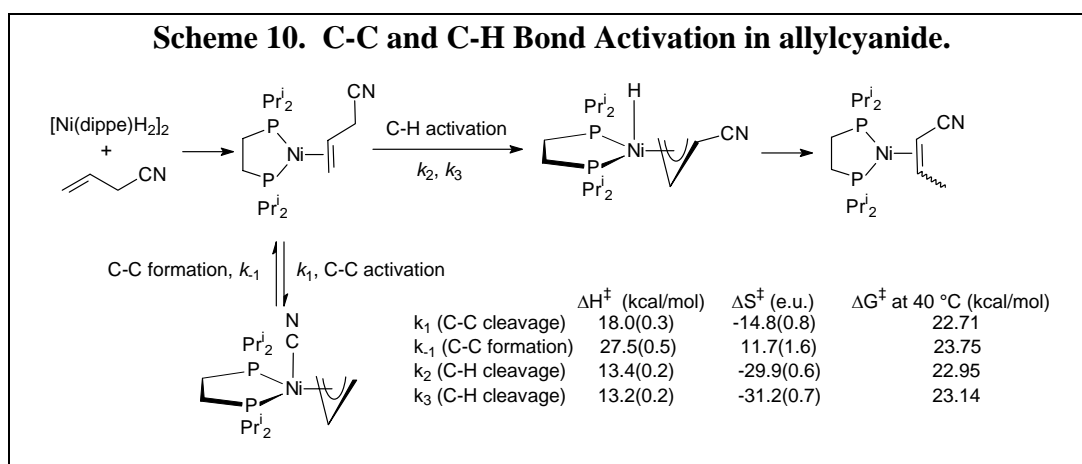
The transition state for C-CN cleavage is most interesting, arising from the intermediate labeled **S3** in Figure 3. In **S3**, the acetonitrile is bound through the nitrile and an agostic C-H interaction with the metal. The nitrile is perpendicular to the NiP_2 plane. In the transition state for C-CN cleavage, there is a rotation so that the agostic nitrile is at an angle of $\sim 40^\circ$ to the NiP_2 plane. The Ni-CN and Ni-CH₃ bonds are virtually formed with only slight C-C cleavage. Consequently, the transition state can be viewed as inbetween a d^{10} tetrahedral adduct of an intact CH_3CN and a d^8 square planar oxidative addition product.

We have now begun to investigate the cleavage of the benzonitrile system using DFT calculations. While these studies are not complete, we find amazing similarities to the acetonitrile results. The transition state places the C-C bond at an angle to the NiP_2 plane ($\sim 30^\circ$), and there is an intermediate prior to C-CN cleavage. In this case, however, the intermediate is the η^2 -C,C adduct of benzonitrile with the metal attached to the double bond adjacent to the nitrile. To get to the transition state, this intermediate must rotate to place the nitrile group perpendicular to the NiP_2 plane, and Ni-CN and Ni-aryl bond formation occurs prior to rupture of the C-CN bond.

6. C-C Bond Cleavage Studies - sp - sp^3 bonds in Allylnitriles.

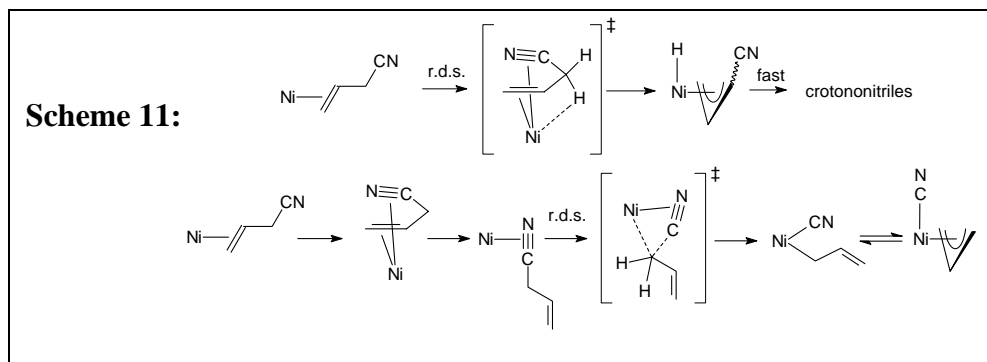
We have also investigated C-CN cleavage in allyl-nitriles. At a metal center this cleavage reaction generates both a strong metal-cyanide bond and a π -allyl ligand, and hence has been found to be both facile and reversible. Indeed, at nickel(0), this reaction forms the basis of DuPont's synthesis of adiponitrile for the production of nylon via addition of HCN to butadiene, to the tune of over 400 thousand metric tons per year!

We have discovered that the reactive hydride $[(\text{dippe})\text{NiH}]_2$, which serves as a room temperature source of $[\text{Ni}(\text{dippe})]$, reacts with allylcyanide to give initially a π -olefin complex. This species can be seen at low temperature by NMR spectroscopy, and upon warming to RT competitive C-H and C-CN cleavage takes place. C-H activation gives a π -allyl hydride complex that is not observed, because the hydride is transferred back to the opposite end of the allyl group to give a very stable crotononitrile complex (both cis and trans are formed). C-CN activation, however, leads to a metastable π -allyl cyanide complex that can be isolated and structurally characterized. C-CN cleavage is reversible, so that ultimately, all nickel winds up as the crotononitrile complexes (Scheme 10).



By monitoring the distribution of species over time, we have been able to extract the rate constants for all of these species by kinetic simulation. In addition, by measuring the distribution of species as a function of temperature, we can obtain activation parameters for the various steps. The results are quite interesting, in that we find that while C-H activation and C-C activation have small temperature dependences, C-C cleavage has a large temperature dependence. The result is that by raising the temperature, one can selectively drive the reaction in the direction of the less-favorable π -allyl cyanide complex. This is good news, since the

DuPont catalysis requires that the C-C cleavage dominate over the C-H cleavage. The activation parameters support the mechanism for C-H and C-C cleavage shown in Scheme 11.



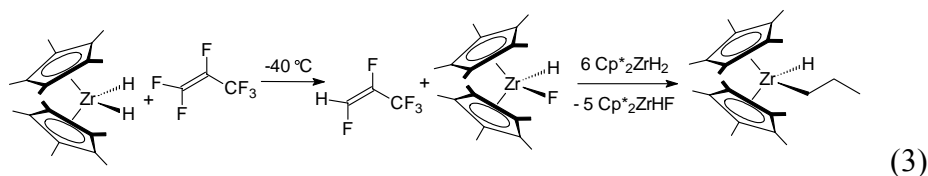
We have extended our studies with allyl cyanide to the industrially relevant nitrile, 2-methyl-3-butenitrile (2M3BN). This species undergoes two competitive processes as seen

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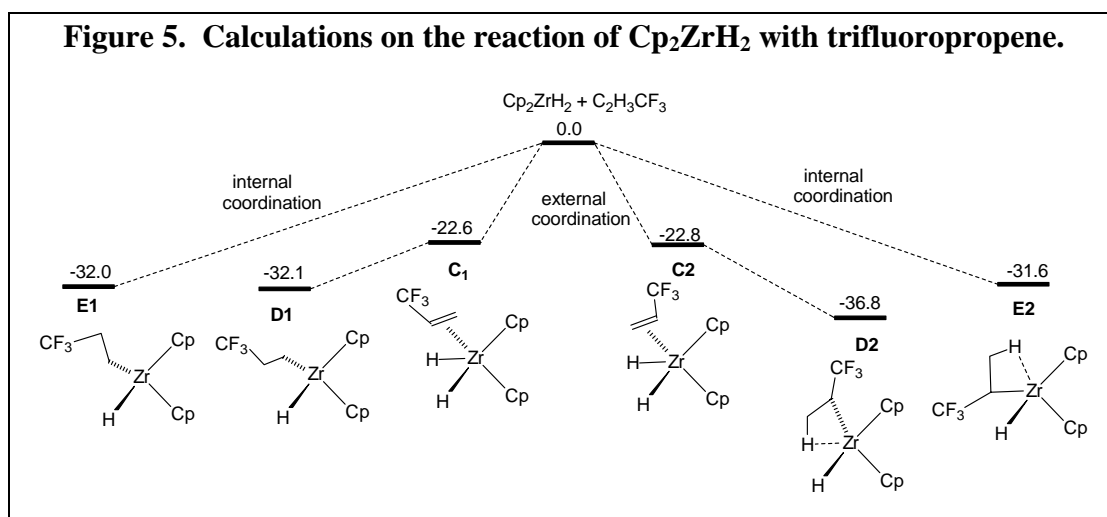
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7. C-F Bond Cleavage Studies

We have completed experimental and computational studies of the reactive system $\text{Cp}^*_2\text{ZrH}_2$ + perfluoroolefins. Perfluoroolefins 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 $\text{Cp}^*_2\text{ZrH}_2$ + non-perfluoroolefins. Reaction with perfluoropropene gives first the selective formation of *E*-CHF=CF₂. Further reaction with zirconium hydride leads to complete defluorination with no further intermediates being seen (eq 3).

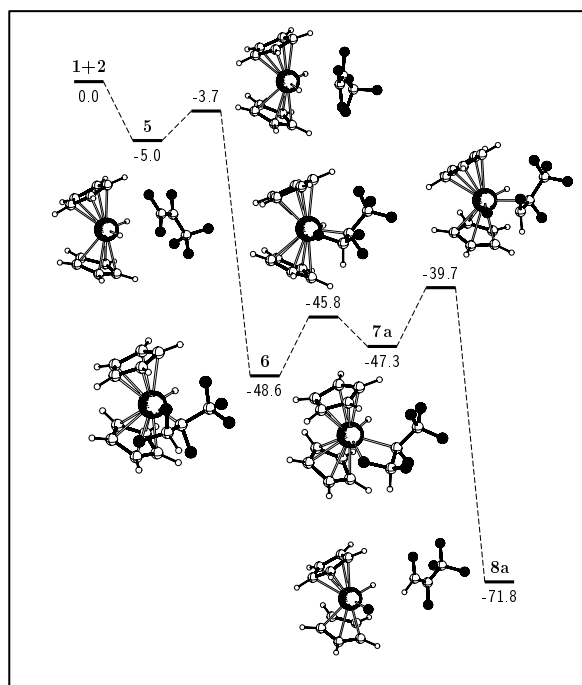


The mechanism for the reaction could involve hydridic attack on the olefin with H/F metathesis, or an insertion/elimination mechanism. The olefin could approach centrally, between the two hydrides, or laterally, with the two hydrides remaining cis to each other. In order to investigate these possibilities, 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. Reaction of trifluoropropene was first examined, which has been shown experimentally to undergo an insertion/ β -fluoride elimination pathway. The calculations were able to reproduce the selective internal insertion product, and confirm a β -fluoride elimination step (Figure 5).

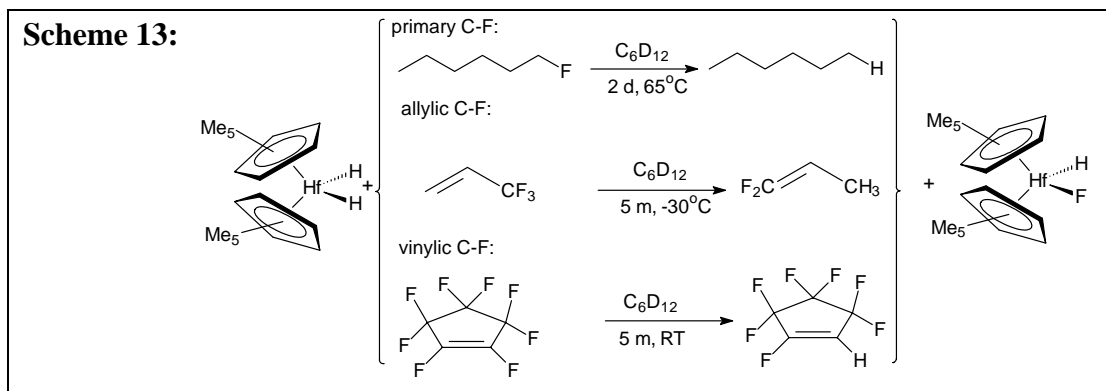


Further calculations were then completed for Cp_2ZrH_2 reacting with perfluoropropene. The results show that interaction of the olefin internally with Cp_2ZrH_2 leads to olefin insertion followed by an external β -fluoride elimination. Other pathways were investigated but all were found to lie at higher energies (Figure 6).

Figure 6. Calculations on the reaction of Cp_2ZrH_2 with perfluoropropene.



We have now 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 13). The lower reactivity of the hafnium complex is attributed to its larger M-H bond strength.



We are now working on completion of our investigation of the C-F cleavage in cyclic perfluoroolefins with Cp^*ZrH_2 . These appear to be a special class of substrate, in that the

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**Publications appearing during the current grant cycle acknowledging DOE support,
December 1, 2004 - November 30, 2007:**

Manuscripts in print:

1. “Defluorination of Perfluoropropene using $\text{Cp}^*_2\text{ZrH}_2$ and Cp^*_2ZrHF : A Mechanistic Investigation from a Joint Experimental-Theoretical Perspective,” Eric Clot, Claire Megret, Bradley M. Kraft, Odile Eisenstein, and William D. Jones, *J. Am. Chem. Soc.*, **2004**, *126*, 5647-5653.
2. “Cleavage of Carbon-Carbon bonds in Alkyl Nitriles Using Nickel(0),” Juventino J. García, Alma Arévalo, Nicole M. Brunkan, and William D. Jones, *Organometallics*, **2004**, *23*, 3997-4002. (DOE)
3. “On the Nature of Carbon-Hydrogen Bond Activation at Rhodium and Related Reactions,” William D. Jones, *Inorg. Chem.* **2005**, *44*, 4475-4484. (DOE, NSF)
4. “Alkane Coordination Selectivity in Hydrocarbon Activation by $[\text{Tp}'\text{Rh}(\text{CNneopentyl})]$: The Role of Alkane Complexes,” Andrew J. Vetter, Christine Flaschenriem, and William D. Jones, *J. Am. Chem. Soc.* **2005**, *127*, 12315-12322. (DOE)
5. “Bis- μ -2,3,5,6-tetrafluoro-trifluoromethyl-benzenethiolate-bis(3,5-cyclooctadiene)-dirhodium(I),” William D. Jones, Juventino Garcia, and Hugo Torrens, *Acta Cryst. E*, **2005**, *61*(11), m2204-m2206. (NSF)
6. “Kinetics and Mechanism of Dealkylation of Coordinated Isocyanide in $\text{Fe}(\text{PMe}_3)_2(t\text{-BuNC})_3$,” Christine L. Tennent and William D. Jones, *Can. J. Chem.* **2005**, *83*, 626-633. (DOE)
7. “The Synthesis and Structural Properties of $[\text{M}(\text{dippe})(\eta^2\text{-C}_4\text{H}_4\text{S})]$ 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. (DOE, NSF)
8. “Activation of Aromatic, Aliphatic, and Olefinic Carbon-Fluorine Bonds Using $\text{Cp}^*_2\text{HfH}_2$,” Ryan D. Rieth, William W. Brennessel, and William D. Jones, *European Journal of Inorganic Chemistry*, **2007**, *18*, 2839-2847. (DOE)
9. “The Activation of Alkyl Cyanides Using a Rhodiumtrispyrazolylborate Complex,” Andrew J. Vetter, Ryan R. Rieth, and William D. Jones, *Proc. Nat. Acad. Sci.* **2007**, *104*, 6957-6962. (DOE)
10. “Structural and Dynamic Properties of Propane Coordinated to $\text{TpRh}(\text{CNR})$ from a Comparison between DFT and Experiment Results,” Eric Clot, Odile Eisenstein, and William D. Jones, *Proc. Nat. Acad. Sci.* **2007**, *104*, 6939-6944. (DOE)
11. “Experimental and Theoretical Examination of C—CN and C—H Bond Activations of Acetonitrile Using Zerovalent Nickel,” Tülay A. Ateşin, Ting Li, William W. Brennessel, Sébastien Lachaize, Juventino J. García, and William D. Jones, *J. Am. Chem. Soc.* **2007**, *129*, 7562-7569. (DOE, NSF)

12. "Cleavage of Carbon-Carbon Bonds of Diphenylacetylene and its Derivatives *via* Pt Complexes: Tuning the C-C Bond Formation Energy toward Selective C-C Bond Activation," Ahmet Gunay and William D. Jones, *J. Am. Chem. Soc.*, **2007**, ASAP. (DOE)

Other Manuscripts/Reviews:

13. "Synthesis, Structure, and Reactivity of [Ir(dippe)(μ -Cl)]₂, [Ir(dippe)₂][Ir(dippe)Cl₂], and [Ir(dippe)₂]Cl," Stephen S. Oster and William D. Jones, *Polyhedron*, **2004**, 23, 2959-2965.
14. "Isomerization of 2-methyl-3-butenenitrile 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. (NSF)
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Recent Special Recognitions Received by the PI:

ACS Award in Organometallic Chemistry, 2003

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

Charles F. Houghton Professor of Chemistry, 2000-

July 2000- 2003: Chairman, Department of Chemistry

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.

Speaker at Reaction Mechanisms Conference, Northwestern Univ., 2004.

Co-organizer of Symposium on Activation of Unreactive Bonds in Organic Synthesis, Pacificchem, Honolulu, 2005.

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

Keynote Speaker, Netherlands' Catalysis and Chemistry Conference (NCCC VIII), Noordwijkerhout, Holland, 2007.

Professeur Invité, Université Paul Sabatier, Toulouse, France, 2007.