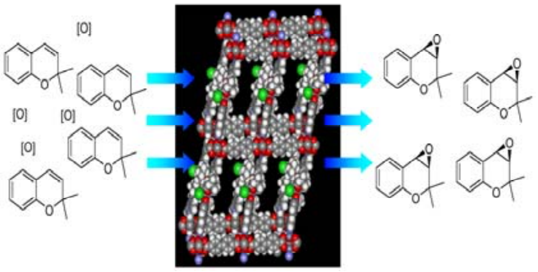
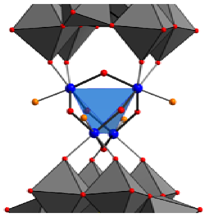
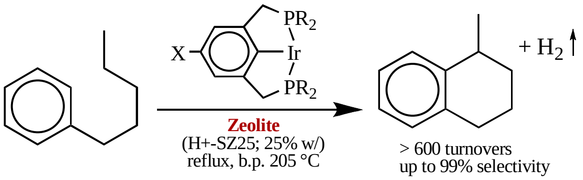
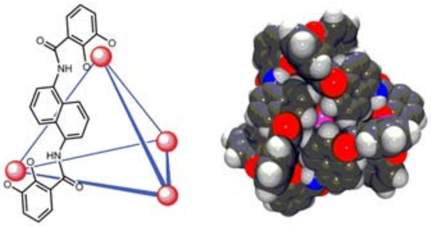
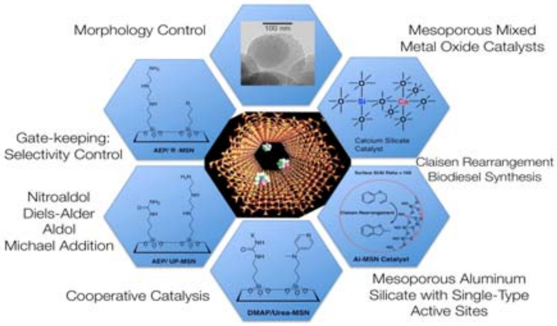
Frontiers in Molecular Catalysis Science

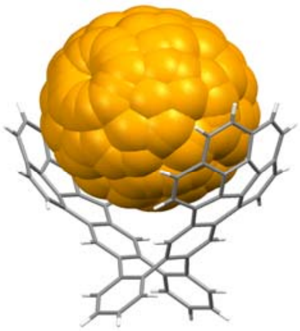












Meeting of the Catalysis Science Program
Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
U.S. Department of Energy
Annapolis, Maryland
May 18-21, 2008

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Office of Science
U.S. DEPARTMENT OF ENERGY

Frontiers in Molecular Catalysis Science

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Cover figures (top left to bottom right):

1. S. Nguyen, J. Hupp: chiral epoxidation of chromene catalyzed by chiral (salen)Mn in metal organic framework
2. C. Hill, et al.: water oxidation catalyst, Rb8K2[{Ru4O4(OH)2(H2O)4}(γ-SiW10O36)2]·25H2O
3. A. Goldman: tandem dehydrogenation catalysis with a pincer-ligated iridium complex
4. R. Bergman, K. Raymond: “nanovessels” for controlling stereo-, chemo- and/or regioselectivity
5. V. Lin et al.: multifunctional mesoporous nanoparticles for selective catalysis and biofuel applications
6. A. Sygula, P. W. Rabideau: double concave hydrocarbon catcher for buckminsterfullerene C60

This document was produced under contract number DE-AC05-060R23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

FOREWORD

The 2008 Catalysis Science Program Meeting is sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (OBES), U.S. Department of Energy. It is being held on May 18-21, 2008, at the Doubletree Hotel Annapolis, Annapolis, MD. The purposes of this meeting are to discuss the recent advances in organometallic, inorganic and bioinspired chemistry and catalysis, to foster exchange of ideas and cooperation among participants, and to discuss the new opportunities for catalysis and chemical transformations at the interfaces with other disciplines and technologies, including nanoscience, hydrogen fuel generation and storage, solar energy conversion and bioinspired chemistry.

Catalysis activities within OBES emphasize fundamental research aimed at understanding and controlling the chemical reactivity of fluid and condensed matter. The long-term goal of this research is to discover the fundamental principles and develop the techniques to predict structure-reactivity relations. Such knowledge, integrated with advances in synthesis, instrumentation, characterization, and theory, will help us to control chemical reactions along desired pathways. Ultimately, this new knowledge will result in chemical and materials processes to efficiently convert fossil and renewable resources, or to generate, convert and store energy, with minimum impact to our environment.

Special thanks go to our invited speakers, who will expose us to recent advances in their fields, to the program investigators and their students, postdocs, and collaborators, for their dedication to the continuous success and visibility of the OBES Catalysis Science Program, and to the session moderators, for their invaluable help. We also thank the Oak Ridge Institute of Science and Education staff, Ms. Margaret Lyday and other contributing staff members of ORISE for the logistical and web support and the compilation of this volume.

Andreja Bakac[1], Aaron Sadow[1], Michael Chen[2] and Raul Miranda[2]

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Office of Basic Energy Sciences
U.S. Department of Energy

MEETING OVERVIEW
2008 DOE/BES Catalysis Sciences Meeting
May 18 - 21, 2008 Annapolis, MD

Time	Sunday, May 18	Monday, May 19	Tuesday, May 20	Wednesday, May 21
7:00 AM		**Continental breakfast** Upper Lobby	**Continental breakfast** Upper Lobby	**Continental breakfast** Upper Lobby
8:15				
8:30		**Monday morning session** Coastal	**Tuesday morning session** Coastal	**Wednesday morning session** Coastal
9:00				
10:00				
11:00				
11:15				**Lunch buffet** Outside Coastal
noon		**Lunch buffet** Outside Coastal	**Lunch buffet** Outside Coastal	
12:30 PM				
1:00				
2:00				
2:15				Meeting Adjourns
3:00				
4:00	**Poster set-up begins** Mainsail **Registration** Upper Lobby			
4:30				
5:00		**Dinner** Coastal	**Dinner** Coastal	
5:30	Registration concludes for the day; **Dinner** Coastal			
6:00				
6:15		**Monday evening session** Coastal	**Tuesday evening session** Coastal	
6:45				
7:00	**Sunday evening session** Coastal			
8:25			**Social Hour/Posters** Mainsail	
8:30	**Social Hour/Posters** Mainsail			
8:40		**Social Hour/Posters** Mainsail		

AGENDA

Sunday Evening, 18 May 2008
Session Chair: William Evans (California-Irvine)

5:30 – 6:45	Dinner
7:00 – 7:10	Welcoming Remarks
7:10 – 7:55	**Invited Talk: Catalysis by Design: A Predictive Approach of Heterogeneous Catalysis via Surface Organometallic Chemistry** Jean-Marie Basset (Laboratoire de Chimie Organométallique de Surface)
7:55 – 8:30	**Nanocluster Catalysts Formation and Stabilization Fundamental Studies** Richard Finke (Colorado State University)
8:30 – 11:00	**Social Hour / Poster Session**

Odd-Numbered Posters*

*All posters may be set up starting on Sunday 4:00 pm, will stay posted during the entire meeting, and must be taken down by Tuesday midnight at the latest. Poster presenters must stand by their poster on Sunday (odd-numbered) and Monday (even-numbered). All poster presenters are encouraged to circulate and interact but be available for questions on the Tuesday session.

Tom Autrey - **Control of Hydrogen Release and Uptake in Condensed Phases**	P1
Perla B. Balbuena - **Theory-Guided Design of Nano-Nanoscale Multimetallic Nanocatalysts for Fuel Cells**	P3
Perla B. Balbuena - **Modeling Catalyzed Growth of Single-Wall Carbon Nanotubes**	P5
Robert G. Bergman - **Exploratory and Mechanistic Investigations of C-H Activation Reactions and their Applications to Catalysis and Organic Synthesis**	P7
Theodore A. Betley - **New Approaches to Driving Multielectron Redox Chemistry**	P9
Paul J. Chirik - **Understanding Nitrogen Fixation**	P11

Peter C. Stair - **Nanostructured Membrane Catalysis** P43

T. Don Tilley - **Molecular Precursor Methods for the Controlled Generation of Active and Selective Catalytic Sites on an Oxide Surface** P45

L. Keith Woo – **Gold Metal-Catalyzed Reactions of Isocyanides and CO with Amines and Oxygen** P47

Monday Morning, 19 May 2008
Session Chair: Paul Sharp (Missouri-Columbia)

7:00 – 8:15	Breakfast
8:30 – 9:15	**Invited Talk: Multifunctional Mesoporous Nanoparticles for Selective Catalysis and Biofuel Applications** Victor Lin (Iowa State/Ames Laboratory)
9:15 – 9:50	**Transition Metal Mediated Transformations of Small Molecules** Ayusman Sen (Pennsylvania State University)
9:50 – 10:20	Coffee Break
10:20 – 10:55	**Coordinative Supramolecular Catalysis** Joseph Hupp (Northwestern University)
10:55 – 11:30	**‘Flexible’ Heterogenization of (Salen) Mn Complexes for Catalyzing Selective Olefin Epoxidation—Lessons from Homogeneous and Biological Catalysis** SonBinh Nguyen (Northwestern University)
11:30 – 11:50	**Poster talk: Homolytic and Heterolytic S-H Bond Energies in Homogeneous Mo_2S_4 Complexes** Aaron Appel, Pacific Northwest National Laboratory
12:00	Lunch

Monday Evening, 19 May 2008
Session Chair: Paul Chirik (Cornell)

5:00 – 6:00	Dinner

6:15 – 7:00 **Invited Talk: Biocatalysis for Fuels and Industrial Chemicals: Enzymes, Whole Cells and Beyond**
Doug Cameron (Khosla Ventures, BioOils, LLC)

7:00 – 7:35 **Silane Activation on a Single-Site Oxorhenium(V) Oxazoline Catalyst: A New Mechanistic Paradigm for Hydrogen Production and Hydrosilation**
Mahdi Abu-Omar (Purdue University)

7:35 – 7:45 Break

7:45 – 8:20 **Mechanisms of Organometallic Copper Oxidase Reactions**
Shannon Stahl (University of Wisconsin-Madison)

8:20 – 8:40 **Poster talk: Ancillary Oxazolinylboron Ligands for Transition Metal Centers**
Aaron Sadow (Iowa State/Ames Laboratory)

8:40 – 11:00 **Social Hour / Poster Session**

Even-Numbered Posters

Andreja Bakac - **Thermodynamics of Oxygen Activation by Transition Metal Complexes** P2

Guillermo C. Bazan - **Catalysts for Selective Olefin Oligomerization and Polymerization** P4

John E. Bercaw - **Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds** P6

K. N. Raymond, R. G. Bergman - **Selective Organic and Organometallic Reactions in Water-Soluble Host-Guest Supramolecular Systems** P8

R. Morris Bullock - **New Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production** P10

Malcolm H. Chisholm - **Mechanistic and Synthetic Studies Aimed at the Development of Single-Site Metal Alkoxide Catalysts for the Generation of Polyesters and Polycarbonates** P12

Jorge M. Seminario - **Theory-Guided Design of Nano-Scale Multimetallic Nanocatalysts for Fuel Cells** P40

Paul R. Sharp – **Alkene Reactions of Platinaoxetanes and Platinum Oxo Complexes** P42

Andrzej Sygula - **Polynuclear Aromatic Hydro-Carbons with Curved Surfaces: Buckybowls** P44

David A. Vicic - **Mild Catalytic Methods for Alkyl-Alkyl Bond Formation** P46

Peter Zapol - **Computational Studies of Supported Vanadia Catalysts for ODH** P48

Tuesday Morning, 20 May 2008
Session Chair: Helena Malinakova (Kansas)

7:00 – 8:15	Breakfast
8:30 – 9:15	**Invited Talk: Photodriven Multi-Electron Transfer Reactions at Molecular Semiconductor Interfaces** Gerald Meyer (Johns Hopkins University)
9:15 – 9:50	**Principles of Selective O_2-Based Oxidation by Optimal (Multinuclear) Catalytic Sites** Craig Hill (Emory University)
9:50 – 10:20	Coffee Break
10:20 – 10:55	**Development and Application of New Catalysts for Heterocycle Carbonylation** Geoffrey Coates (Cornell University)
10:55 – 11:30	**Inorganic-Organic Molecules and Solids with Nanometer-Sized Pores** Andrew Maverick (Louisiana State University)
11:30 – 11:50	**Poster talk: C–H Oxidation Made Easy—by Amino Acid-Radical Forming Enzymes** Justine Roth (Johns Hopkins University)
12:00	Lunch

Tuesday Evening, 20 May 2008

Session Chair: Alan Goldman (Rutgers)

5:00 – 6:00	Dinner
6:15 – 7:00	**Invited Talk: Hydrogen Storage and Delivery Using Liquid Carriers** Guido Pez (Air Products and Chemicals, Inc.)
7:00 – 7:35	**Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer** Klaus Theopold (University of Delaware)
7:35 – 7:45	Break
7:45 – 8:05	**Poster talk: Catalysis Involving Low-Valent Main-Group Fragments and Synthons** Rory Waterman (University of Vermont)
8:05 – 8:25	**Poster talk: One and Two Electron Transformations of Iron Nitrido Complexes** Jeremy Smith (New Mexico State University)
8:25 – 11:00	**Social Hour / Poster Session** **All Posters**

Wednesday Morning, 21 May 2008

Session Chair: Aaron Sadow (Ames Lab/Iowa State)

7:00 – 8:15	Breakfast
8:30 – 9:15	**Invited Talk: Hydrogen Peroxide: The Ideal Oxidant. New Advances for its Synthesis and Some Catalytic Applications in the Selective Epoxidation of Simple Alkenes** Giorgio Strukul (Università di Venezia)
9:15 – 9:50	**Catalytic Hydrogenation of Carbon Monoxide and Olefin Oxidation** Brad Wayland (University of Pennsylvania)
9:50 – 10:00	Coffee Break
10:00 – 10:35	**Computational Studies of Ligand and Catalyst Design and Catalytic Mechanisms** Thomas Cundari (University of North Texas)

10:35– 11:15	General Discussion
11:15 – 12:30	Lunch
12:30 – 2:15	General Discussion (Cont’d) & Concluding Remarks

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Poster Presentations

Sunday Evening Sessions

Catalysis by Design: A Predictive Approach of Heterogeneous Catalysis via Surface Organometallic Chemistry

Jean-Marie Basset
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UMR5265 C2P2 CNRS-CPE-UCBL, 43 Bd 11 Nov. 1918
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Heterogeneous catalysis is a molecular phenomenon by which molecules react with surfaces to give new molecules or macromolecules via "surface organometallic fragments" which are "real intermediates" in any catalytic cycle. But the links between homogeneous catalysis and heterogeneous catalysis goes far beyond this simple unifying concept.

It is now possible by means of surface organometallic chemistry to design "single site" catalysts both on "oxides", on "metals" both taken in the broad sense.

This approach of "hybrid catalysis" is now at the origin of a new generation of catalysts, for which the discovery of new catalytic reactions or the improvement of known catalytic reactions can be predicted on simple grounds.

Examples will be given with the following catalytic reactions: Ziegler-Natta polymerization and depolymerisation, olefins and alkanes metathesis, methane coupling to ethane and hydrogen, cleavage of alkanes by methane, direct transformation of ethylene to propylene, dissociation of dinitrogen to amido imido complexes etc….

DE-FG02-03ER15453 **Richard G. Finke**

Nanocluster Catalysts Formation and Stabilization Fundamental Studies

Students: Lisa S. Ott, L.; Eric E. Finney, Clarie Besson, Chris Graham,
Joe E. Mondloch
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Goals

Our DOE-funded program has three primary goals: one goal is to determine which stabilizers and other factors are best for the formation, stabilization and catalytic activity of transition-metal nanoclusters; a second goal is to continue our mechanistic studies of the nucleation, growth and agglomeration of catalytically active transition-metal nanoclusters; and a third goal is to exploit custom-made nanoclusters in interesting catalytic reactions.

DOE Interest

Nanoclusters are metal particle catalysts closely analogous to the supported-metal particles in commonly used commercial heterogeneous catalysts. However, nanoclusters have the advantage of being soluble; *hence, they can be made and studied by powerful solution synthesis, spectroscopic characterization and kinetic methods.* Well-defined nanoparticle catalysts promise to be important in the development of the concepts and technical advances en route to achieving the “Holy Grail” of heterogeneous catalysis, namely single-site, high selectivity, and high activity metal-particle catalysts. Nanoparticles are also expected to have their own, unique catalytic reactivity.

Recent Progress

(1) Nanocluster Stabilization Fundamental Studies. We published 5 papers in the previously little investigated area of the factors that allow nanocluster stabilization while still permitting high catalytic activity;[1,2,3,4,5] this included the first review in the area.[5] Highlights of our discoveries include: (i) that putative “solvent-only” stabilized nanoclusters do not really exist[2]; instead, even the traditionally weakly coordinating anions BF_4^- provides considerable anion-based, charge-repulsion (i.e., DLVO-theory type[5]) stabilization; (ii) that organic polymers, long assumed to be superior nanoparticle stabilizers, are actually inferior unless anion-based charge-repulsion stabilization of the nanoparticles is also present[2]; and (iii) that halides are reasonable anionic-stabilizers of nanoparticles as typically believed, although not too much better than BF_4^-.[3] We also we able to show: (iv) that ionic liquids do provide excellent nanoparticle stabilization and others had implied, but that the imidazolium component of the ionic liquid can lead to oxidative addition to, and thus poisoning of, the surface of the nanoparticles.[4]

(2) Fundamental Studies of Nanocluster Nucleation, Growth and Agglomerations in Nature. Our studies in this area allowed us: (i) to publish only the third paper on the more general, 4-step mechanism for nucleation, growth and 2 types of agglomeration that we discovered in 2005, a paper which shows that primary variable turning on this mechanism is a large concentrations of coordinating ligand[6]; (ii) to understand an interesting supersensitivity we observed to the concentration of nanocluster precursor and the reaction temperature, effects that are likely important—but previously unrecognized—in many other nanocluster syntheses[7]; and (iii) to publish the first paper showing that there are two rate constants for bimolecular and novel autocatalytic agglomeration that one needs to measure as the preferred way to quantitate nanocluster stability in the future.[8] We were also able: (iv) to publish an invited, feature review.[9]

(3) Initial Investigations of the Broader Applicability of the Finke-Watzky (F-W) 2-Step Mechanism of Nucleation and Autocatalytic Growth in Other Parts of Nature. In what promises to be one of the largest and broadest impacts of our DOE funded mechanistic studies of nucleation and growth, we discovered that our 1997 2-step, F-W mechanism of slow, continuous nucleation (A —> B), followed by typically fast, autocatalytic growth (A + B —> 2B), applies to other, seemingly disparate areas of science. The first is: (i) an interesting organometallic catalyst formation reaction under study in Bob Bergman's group in which an Ir-Cl bond is replaced by a Me group from $SnMe_4$ to form an Ir-Me complex plus $SnMe_3Cl$. With Prof. Bergman and his postdoc Stuart Smith, together we showed that a poor, inefficient $Pt(P^tBu_3)_2$ precatalyst (A) chemically "evolves" to a much faster, effectively "smarter" $Pt(SnMe_3)(P^tBu_3)(Cl)$ catalyst (B) according to the generalized 2-step F-W mechanism of nucleation and growth.[10]

In a second, expected to be far reaching study, we showed that (ii) the F-W 2-step mechanism is the only kinetic treatment presently available able to deconvolute nucleation from growth rate constants for the 14 usable (non-prion) protein aggregation kinetic data set we could find in the literature.[11] Such protein aggregation is thought to be key underlying step in Alzheimer's, Parkinson's and Huntington's diseases. Learning how to control nucleation or growth are two promising therapeutic strategies one can envision. While these studies were funded with other monies (since they fall outside the specific scope of our current DOE grant), our paper does acknowledge our DOE grant for the long-term support that led to the original discovery of the F-W mechanism.[11]

(4) Nanocluster Catalysis Studies.

We also published one paper in which we were able to show that the true catalyst derived from placing $Pt(1,5\text{-}COD)Cl_2$ or $Pt(1,5\text{-}COD)(CH_3)_2$ under H_2 is a $Pt(0)_n$ nanocluster catalyst.[12]

Future Plans

In the coming year we plan to finish up several papers resulting from Eric Finney's Ph.D. thesis and a couple from Chris Graham's MS. thesis. We will also be continuing our investigations of other areas of Nature where the F-W 2-step mechanism for particle self-assembly discovered via our DOE funding might apply while also falling within the scope of our DOE grant emphasizing catalysis.

Publications (2006-2008)

1. L. Starkey-Ott, R. G. Finke, "Nanocluster Formation and Stabilization Fundamental Studies:[a] Investigating "Solvent-Only" Stabilization En Route to Discovering Stabilization by the Traditionally Weakly Coordinating Anion BF_4^- Plus High Dielectric Constant Solvents", *Inorg. Chem.* **45(20)** (2006) 8382-8393.
2. L. Starkey-Ott, B. J Hornstein, R. G. Finke, "A Test of the Transition-Metal Nanocluster Formation and Stabilization Ability of the Most Common Polymeric Stabilizer, Poly(vinylpyrrolidone), As Well As Four Other Polymeric Protectants", *Langmuir* **22** (2006) 9357-9367.
3. L. Starkey-Ott, S. Campbell, K. R. Seddon, R. G. Finke, "Transition-metal Nanocluster Formation and Stabilization Fundamental Studies: Ranking the Nanocluster Stabilizing Ability of Halides", J. *Nanoscience and Nanotechnology* **7** (2007) 2400-2410.
4. L. Starkey-Ott, R. G. Finke, "Evidence That Imidazolium-Based Ionic Liquids Can be Metal(0)/Nanocluster Catalyst Poisons in at Least the Test Case of Iridium(0)-Catalyzed Acetone Hydrogenation", *Inorg. Chem.* **46(24)** (2007) 10335-10344.
5. L. Starkey-Ott, R. G. Finke, "Transition-Metal Nanocluster Stabilization for Catalysis: A Critical Review of Ranking Methods and Putative Stabilizers", *Coord. Chem. Rev.* **251** (2007) 1075-1100.

6. E. E. Finney, R. G. Finke, "The Four-Step, Double-Autocatalytic Mechanism for Transition-Metal Nanocluster Nucleation, Growth and Then Agglomeration: Metal, Ligand, Concentration, Temperature, and Solvent Dependency Studies", *Chem. Mater.* **20** (2008) 1956-1970.
7. L. Starkey-Ott, R. G. Finke, "Supersensitivity of $Ir(0)_n$ Transition-Metal Nanoparticle Formation to Initial Ir Precursor Concentration and Reaction Temperature. Understanding Its Origins", *J. Nanoscience and Nanotechnology*, (2008) in press.
8. L. Starkey-Ott, R. G. Finke, "Transition-Metal Nanocluster Stabilization vs Agglomeration Fundamental Studies: A Quantitative Measurement of the Two Rate Constants for Agglomeration and Their Informative Temperature Dependence", *Chem. Mater.,* (2008), in press.
9. E. E. Finney, R. G. Finke, "Nanocluster nucleation and growth kinetic and mechanistic studies: A review emphasizing transition-metal nanoclusters." *J. Colloid and Interface Science,* **317(2) (**2008) 351-374.
10. S. E. Smith, J. M. Sasaki, R. G. Bergman, J. E. Mondloch, R. G. Finke, "Platinum Catalyzed Phenyl and Methyl Group Transfer from Tin to Iridium: Evidence for an Autocatalytic Reaction Pathway with an Unusual Preference for Methyl Transfer", *J. Am. Chem. Soc.*, **130** (2008) 1839-1841.
11. A. M. Morris, M. A. Watzky, J. N. Agar, R. G. Finke, "Fitting Neurological Protein Aggregation Kinetic Data via a 2-Step, Minimal / Ockham's Razor" Model: the Finke-Watzky Mechanism of Nucleation Followed by Autocatalytic Surface Growth", *Biochem.* **47** (2008) 2413-2427.
12. E. E. Finney, R. G. Finke, "Is it Homogeneous Pt(II) or Heterogeneous $Pt(0)_n$ Catalysis? Evidence That $Pt(1,5\text{-}COD)Cl_2$ and $Pt(1,5\text{-}COD)(CH_3)_2$ Plus H_2 Form Heterogeneous, Nanocluster Plus Bulk-Metal Pt(0) Hydrogenation Catalysts", *Inorganica Chimica Acta,* **359** (2006) 2879-2887.

Monday Morning Sessions

Multifunctional Mesoporous Nanoparticles for Selective Catalysis and Biofuel Applications

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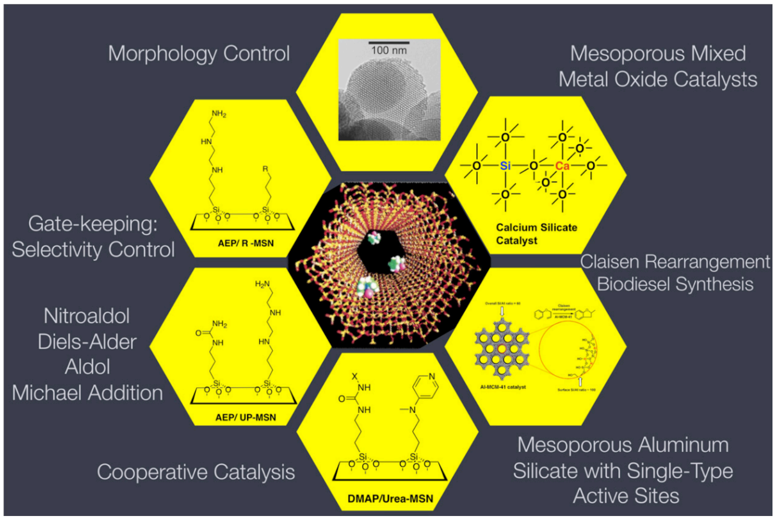
We have developed a synthetic strategy for multifunctionalization of mesoporous silica nanoparticle (MSN) materials. This method allows us to tune the relative ratio of different functional groups and the resulting particle morphology of MSNs. By introducing two organoalkoxysilanes as precursors in the co-condensation reaction, we can utilize one precursor with *stronger structure-directing ability* to create the desired pore and particle morphology and employ the *other* for selective immobilization of catalysts. As a proof of principle, we have synthesized and reported a series of bifunctionalized MSN-based heterogeneous catalysts for a variety of carbonyl activation reactions, such as aldol, Henry and cyanosilylation reactions. By varying the secondary group in the bifunctionalized MSN catalysts, we discovered that the selectivity of a nitroaldol reaction of two competing benzaldehydes reacting with nitromethane could be systematically tuned simply by varying the physicochemical properties of the pore surface-bound secondary groups, *i.e*. polarity and hydrophobicity.

Furthermore, we have reported a biomimetic cooperative catalytic system comprised of a series of bifunctionalized MSN materials with various relative concentrations of a general acid and a base group. We were inspired by the fact that enzymes engaged in carbonyl chemistry often employ both general acid and base catalytic residues in the active sites to cooperatively activate specific substrates. In this system, we have demonstrated that the general acid functionality could cooperatively activate substrates with the basic group in catalyzing various reactions that involve carbonyl activation. In addition to the organically functionalized MSN, we have developed a mixed oxide catalyst that contains both Lewis acidic and basic sites for the synthesis of biodiesel from various free fatty acid (FFA)-containing oil feedstocks. We have demonstrated that the acid and base functionalities could cooperatively catalyze both the esterification of FFAs and the transesterification of oils with short-chain alcohols (e.g. methanol and ethanol) to form alkyl esters (biodiesel). We envision that these multifunctionalized MSNs could serve as new selective catalysts for many other important reactions.



DE-FG02-84ER13295 **Ayusman Sen**

Transition Metal Mediated Transformations of Small Molecules

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Postdoctoral scholars: Sachin Borkar
Graduate students: Megan Majcher, David K. Newsham, Yiying Hong, Shikchya Tandukar, Rong Luo

Goals and Objectives

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance. The theme of the proposed research is the design of new systems for the synthesis of polymers incorporating polar monomers. In the process, we hope to address key questions concerning the steps involved in such polymerization reactions.

Significant Recent Achievements and Results

Below we briefly summarize some of our most important research achievements. Further details can be found in the publications listed at the end.

A significant fraction of the work during the current grant period has been devoted to catalytic systems for the copolymerization of simple alkenes with acrylate monomers. We have attempted to carefully delineate the fundamental reasons for the absence of efficient transition metal-based insertion polymerization catalysts for the copolymerization of acrylate monomers with alkenes. In particular, the formation of a species with an ester group on the α-carbon due to the favored 2,1-insertion of acrylate monomer makes the metal-alkyl species particularly prone to homolysis because of the enhanced stability of the resultant alkyl radical, one that is essentially the same as the propagating species in radical-initiated acrylate polymerization. We have also examined the validity of the different tests that are commonly employed to distinguish between metal-catalyzed insertion and radical polymerization processes.

Additionally, we have sought to find conditions that lead to an increase in the incorporation of simple alkenes in their radical-initiated copolymerization with polar vinyl monomers. We have shown that the addition of either soluble or insoluble Brönsted or Lewis acids to radical-initiated copolymerization of acrylate and methacrylate with non-polar alkenes resulted in increased monomer conversion and increased incorporation of the alkene (up to 40 mol%) into the polymer backbone. Studies indicate a strong correlation between the strength of the interaction of the acid (Brönsted or Lewis) with the acrylate carbonyl group and the acid’s ability to promote acrylate/methacrylate homo and copolymerizations. This effect is particularly dramatic for insoluble acids since only a small fraction of the sites on the surface of the acid can actually interact with the ester functionality. The insoluble, heterogeneous, acids can be recovered by simple filtration and reused without loss of activity.

Future Plans

During the upcoming year we intend to follow, for the most part, the lines of research outlined in the most recent proposal. The principal goal of the proposed research will continue to be the design of new systems for the formation of polymers with interesting architectures, particularly those involving the incorporation of polar monomers.

Impact on Science and Technologies of Relevance to DOE

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. Indeed, several high-volume commercial polymers are only accessible through metal-mediated routes. Hence, the achievement of a fundamental understanding of all aspects of such catalysis is an important goal. The Technology Vision 2020 report also cites the importance of developing new catalysts for customizing polymer properties. The theme of our research is the design of new metal-based catalytic systems for the synthesis of polymers incorporating polar monomers. For example, the copolymerization of functionalized vinyl monomers with non-polar alkenes remains an area of great interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise non-polar can greatly enhance the range of attainable properties.

Refereed Publications Based on DOE Grant (2006-present)

1. "Perspective on Metal-Mediated Polar Monomer/Alkene Copolymerization,"
   Ayusman Sen and Sachin Borkar,
   J. Organomet. Chem., **2007**, *692*, 3291.

2. "Intermediacy of Radicals in Rearrangement and Decomposition of Metal-Alkyl Species: Relevance to Metal-Mediated Polymerization of Polar Vinyl Monomers,"
   Megan Nagel and Ayusman Sen,
   Organometallics, **2006**, *25*, 4722.

3. "Methacrylate Insertion into Cationic Diimine Palladium(II)-Alkyl Complexes and the Synthesis of Poly(alkene-*block*-alkene/carbon monoxide) Copolymers,"
   Sachin Borkar, Hemant Yennawar, and Ayusman Sen,
   Organometallics, **2007**; *26*, 4711

4. "Copolymerization of Ethene with Styrene Derivatives, Vinyl Ketone, and Vinylcyclohexane Using (Phosphine-Sulfonate)Palladium(II) System: Unusual Functionality and Solvent Tolerance,"
   Sachin Borkar and Ayusman Sen, *submitted*.

5. “Effect of Lewis and Brönsted Acids on the Homopolymerization of Acrylates and Their Copolymerization with 1-Alkenes,”
Rong Luo, Ying Chen, and Ayusman Sen, *submitted*.

6. “Selective Heterogeneous Catalytic Hydrogenation by Recyclable Poly(allylamine) Gel-Supported Palladium(0) Nanoparticles,”
Yiying Hong and Ayusman Sen,
Chem. Mater., **2007**, *19*, 961.

7. “N-Heterocyclic Carbene-Palladium Complex Immobilized on Silica Nanoparticles. Recyclable Catalyst for High Yield Suzuki and Heck Coupling Reactions Under Mild Conditions,”
Shikchya Tandukar, and Ayusman Sen,
J. Mol. Catal. A: Chem., **2007**, *268*, 112.

8. “Cobalt Catalyzed Carbonylation of N-alkylbenzaldimines to N-alkylphthalimidines: Tandem C-H Activation and Cyclocarbonylation,” Jeffrey K. Funk, Hemant Yennawar, and Ayusman Sen, *Helvetica Chim. Acta*, **2006**, *89*, 1687.

DE-FG02-ER03-15457 **Joseph T. Hupp**

Coordinative Supramolecular Catalysis

Additional PI: SonBinh T. Nguyen
Students: Tendai Gadzikwa, Abraham Shultz
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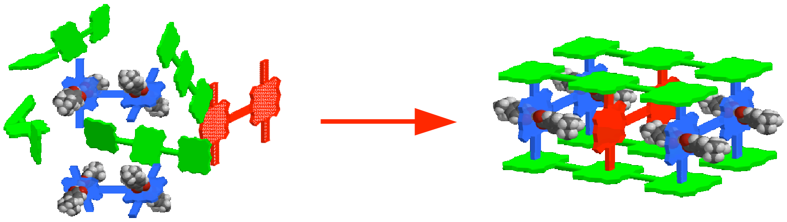
Collaborator: Randall Q. Snurr (Northwestern)

Goal

Exploit supramolecular coordination chemistry to devise catalysts that: a) capitalize on concepts used by Nature to accomplish catalysis in enzymatic systems, b) spontaneously assemble into highly functional forms, c) display enhanced stability relative to molecular catalysts, and d) display enhanced selectivity relative to molecular catalysts.

DOE Interest

Catalysts for complex and/or high-value-added reactions, such as syntheses fine chemical syntheses, often are homogenous molecular species. In many instances, the utility of such catalysts could be greatly increased if they could be isolated and thereby protected from self-degradation, and if they could be encapsulated in environments that: a) control substrate access & orientation, b) define chiral reactions spaces, and/or c) facilitate utilization of co-factors.



Recent Progress

Supramolecular assembly. Using porphyrins as building blocks and coordination chemistry as the building tool, we have succeeded in generating precise encapsulating structures for olefin epoxidation catalysts. As suggested by the diagram above, upon mixing of components the desired structures rapidly (seconds…) and spontaneously assemble into a single catalytic structure. The example shown comprises 18 porphyrins: Two function as active sites (oxygen-atom delivery sites), four serve to define the reaction environment in spatial and/or chiral fashion, and twelve serve to define further the dimensions of the reaction cavities and to organize the other six components. The solution-phase structures of catalytic supramolecular assemblies have been established by synchrotron based x-ray scattering and diffraction. The most sophisticated of the structures show both enantioselectivity and substrate size selectivity when deployed for olefin epoxidation. Notably, the selectivity is engendered entirely by the supramolecular reaction cavity, rather than by the active site.

Reversible covalent chemistry. Grubbs olefin metathesis chemistry has been used to convert initially coordinatively assembled supramolecular structures into covalently-stabilized (i.e. carbon-carbon bond stabilized) structures. These robust structures allow catalytically inactive metal sites to be replaced with active ones, offer orders-of-magnitude stronger binding of catalytic units, and permit supramolecular catalysts to be used in a much wider range of solvents.

Future Plans

This project comprises part of a broader ICEP effort to enhance catalyst utility, stability, and selectivity via coordinative assembly of higher-order structures and catalyst architectures (see accompanying abstract by **Nguyen**). Much of the future effort will be directed toward exploiting and improving upon the preliminary immobilization chemistry and array-assembly chemistry described by Nguyen. The immobilization chemistry includes membrane catalytic reactor chemistry, especially as it pertains to multi-stage catalysis. A portion of the future effort will also be directed toward utilizing further the reversible covalent chemistry described above in order to organize molecular components as selective dual-site catalysts.

Publications (2006-2008)

J. T. Hupp, "Rhenium-linked Multiporphyrin Assemblies: Synthesis and Properties," *Structure and Bonding*, E. Alessio Ed., **2006**, 121, 145-165.

S. J. Lee and J. T. Hupp, "Porphyrin-Containing Molecular Squares: Design and Applications," *Coord. Chem. Rev.*, **2006**, 250, 1710-1723.

S.-H. Cho, B.-Q. Ma, S. T. Nguyen, J. T. Hupp, and T. E. Albrecht-Schmitt, "A Metal-Organic Framework Material that Functions as an Enantioselective Catalyst for Olefin Epoxidation," *Chem. Commun.*, **2006**, 2563-2565.

A. B. F. Martinson, A. M. Massari, S. J. Lee, R. W. Gurney, K. E. Splan, J. T. Hupp, and S. T. Nguyen, "Organic Photovoltaics Interdigitated on the Molecular Scale," *J. Electrochem. Soc.*, **2006**, 153, A527-A532

S.-H Cho, T. Gadzikwa, M. Afshari, S. T. Nguyen, J. T. Hupp, "[Bis(catechol)salen]Mn^{III} Coordination Polymers as Support-Free Heterogeneous Asymmetric Catalysts for Epoxidation," *Eur. J. Inorg. Chem.* **2007**, 4863-4867.

S.-H. Cho, T. Gadzikwa, G. A. Emberger, R. Q. Snurr, S.T. Nguyen, and J.T. Hupp, "Synthesis of [Bis(pyridine)salen]Zn II–based Coordination Polymers and Their Application in Enantioselective Separations," *PMSE Preprints*, **2007**, 97, 95-96.

T. Gadzikwa, B. Zeng, Hupp, S. T. Nguyen, "Ligand elaboration as a strategy for engendering structural diversity in porous metal-organic framework compounds," *Chem. Commun. (revised)* **2008**.

T. Gadzikwa, G. Lu, C. L. Stern, S. R. Wilson, J. T. Hupp, S. T. Nguyen, "Covalent surface modification of a metal-organic framework: Selective surface engineering via Cu^{I}-catalyzed Huisgen cycloaddition," *Chem. Comm.*, **2008**, submitted.

DE-FG02-ER03-15457 **SonBinh T. Nguyen**

'Flexible' Heterogenization of (Salen)Mn Complexes for Catalyzing Selective Olefin Epoxidation—Lessons from Homogeneous and Biological Catalysis

Co-PI:	Joseph T. Hupp (NU Chemistry)
Collaborators:	Prof. Randall Q. Snurr (NU Chem. & Biol. Eng.), Prof. Linda J. Broadbelt (NU Chem. & Biol. Eng.), Prof. Donald Ellis (NU Chemistry and Physics), Dr. David A. Tiede (Argonne National Laboratory)
Post-docs:	Dr. Baoqing Ma, Dr. Suk-Joong Lee, Dr. Kyoung-Tae Youm, Dr. Eui-Hyun Ryu
Students:	Dr. So-Hye Cho, Ms. Tendai Gadzikwa, Mr. Abraham Shultz
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Goals. To fabricate highly selective, efficient, and environmental friendly heterogeneous catalysis using building blocks from homogeneous chemistry and inspirations from biological catalysis. This project comprises part of a broader effort at the Northwestern ICEP to enhance catalyst utility, stability, and selectivity via coordinative assembly of higher-order structures and catalyst architectures (see accompanying abstract by **Hupp**).

DOE interests. The selective oxidation of organics has long been an outstanding challenge in synthetic chemistry. Challenges including low catalyst lifetime, low selectivity (both chemo- and stereo), difficulty encountered in product separations, high environmental impacts, and high energy demands (as in the use of high-energy oxidants such as peroxides and hypervalent). By applying lessons from homogeneous and biological catalysis into heterogeneous designs, we can begin to address these challenges with more stable, more selective recyclable catalysts that have lower energy and environmental demands.

Research Plans. We target ***flexible*** auxiliary coordination, including coordination polymerization, of chiral homogenous catalysts as a strategy to obtain practically useful heterogeneous asymmetric catalysts for the selective epoxidation of olefins. Three solid-state catalytic designs were envisioned: the first is a catalytic membrane reactor where homogeneous catalysts is supported inside the nanopores of an anodic alumimum oxide (AAO) membrane, the second design involves a crystalline metal-organic framework (MOF) assembled using labile coordination interactions between coordination catalytic complexes and organic ligands; the third is an amorphous coordination polymer material employing stronger metal-ligand linkages.

Recent Progress.

(Salen)Mn-loaded AAO-based membrane catalytic reactor. Chiral (salen)Mn complexes containing catechol anchoring-groups were synthesized and immobilized on commercially available mesoporous aluminum oxide membranes (Figure 1).[1] In a bench-top oxidation of 2,2-dimethyl-2H-chromene, the catalytic membrane exhibited comparable activity and selectivity (82% yield, 81% ee) as the homogenous catalyst (86% yield, 86% ee). Even at the lowest loading of one catalyst 'monolayer', the membrane can be recycled several times with minimal loss of activity and selectivity. When the membrane was coupled to a catalytic flow reactor, flow rate up to 10 mL/h was obtained with reactant mixture in dichloromethane. In

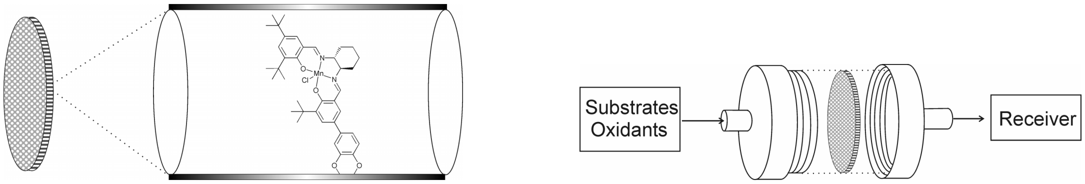


Figure 1. Left: A catalytic AAO membrane that has been loaded with a chiral (salen)Mn^{III} catecholate complex. For clarity, the complex was shown in scale. Right: A schematic diagram of the liquid-phase forced-through-flow catalytic membrane reactor for the enantioselective epoxidation of olefin substrates with iodosyl oxidants.

addition, the membrane can provide high turn-over frequency (> 100/min) while maintaining high selectivity (84% ee). In contrast to the unsupported catalyst complex which turns over only ~100 times, the membrane can yield ~2000 turn-overs/catalyst.

(Salen)Mn-based MOF for enantioselective epoxidation. A new microporous MOF compound featuring chiral (salen)Mn struts was synthesized and found to be a highly effective as an asymmetric heterogeneous catalyst for olefin epoxidation.[2] The (salen)Mn complex was incorporated into a pillared paddlewheel structure containing pairs of zinc ions at vertices together with biphenyldicarboxylate (bpdc) as the second ligand (Figure 1). The MOF maintains its porosity under repeated desolvation and resolvation, showing zeolite-like characteristics. Framework confinement of the (salen)Mn greatly enhances catalyst stability, imparts good substrate size discrimination, and permits readily catalyst separation and reuse. The observed enantiomeric excesses (ee) in the epoxidation of 2,2-dimethyl-2H-chromeme using this (salen)Mn-based MOF rival those of the free molecular catalyst, and they do not diminish even after the MOF catalyst was recycled three times. However, a small loss of activity was observed between cycles due to a minor (4-7%) loss of Mn after each catalytic run. This MOF fragmentation is most likely due to the lability of the zinc-pyridine bond.

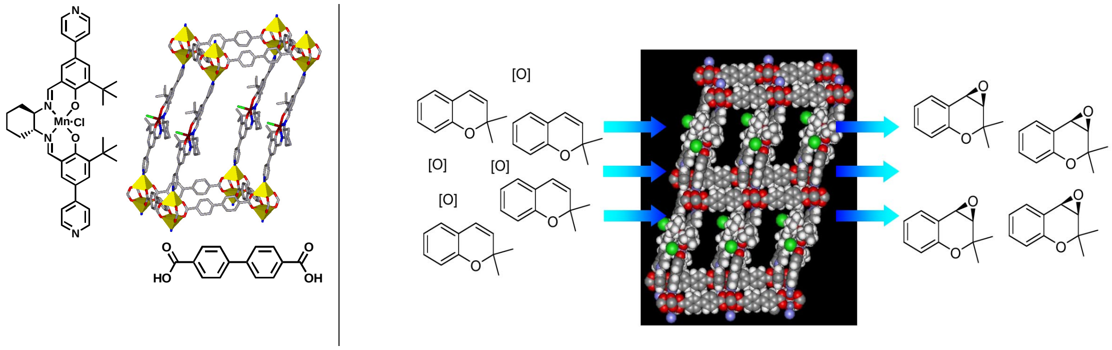
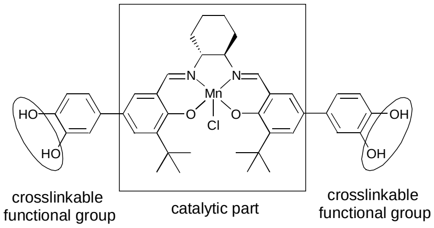


Figure 2. Left: A truncated unit cell of the catalytic microporous metal-organic-framework (MOF) material developed at Northwestern. This MOF features chiral (salen)Mn and biphenyldicarboxylate struts and is based on an anisotropic pillared paddlewheel structural motif. Right: The chiral epoxidation of chromene catalyzed by this MOF.

(Salen)Mn-based coordination polymers for enantioselective epoxidation. To partially address catalyst leaching issues, we employed stronger bis(metal-catecholate) linkages to heterogenize (salen)Mn complex **1** into an amorphous coordination polymer matrix using several metal ion linkers.[3] The resulting catalysts exhibit comparable catalytic activity to the homogeneous [bis(catechol)salen]Mn^{III} building block when used for the enantioselective epoxidation of 2,2-dimethyl-2H-chromene. Under practical oxidant concentrations, the copper-linked variant was recycled up to ten times with little loss of activity and no loss of enantioselectivity.



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Summary and Future Plans. Results thus far have confirmed the promises of our heterogenization strategies. Not only that solid-state site isolation of the homogeneous catalytic (salen)Mn motif prevents catalyst decomposition via bimolecular processes, akin to that observed in biocatalysis, it also enhances our ability to separate catalysts from the reaction and recycle them. Most encouragingly, the use of flexible linking chemistry in the heterogenization process did not adversely affect the enantioselectivity of the homogeneous components. Additionally, the size constraints of channels in AAO membranes or pores in our MOFs and coordination polymer enables effective discrimination of substrates based on size, a characteristics that is common in enzyme catalysis but difficult to achieve in homogenous small-molecule coordination chemistry.

Encouraged by the enhanced stability and effectiveness of the heterogenized chiral (salen)Mn complexes, whether via AAO membrane, MOF, or coordination polymers, we are currently exploring all of these strategies for improving the efficacy of homogeneous oxidation catalysts and extending their functionalities. Further improvement of these heterogeneous catalytic architectures includes the fabrication of 'multilayer' structures to improve catalyst stability as well as enabling multistage catalysis. The application of biological catalytic principles such as activity tuning via the manipulation of catalyst site[4] and cavity environment[5] are being pursued.

Representative Publications. underline indicates undergraduate and K-12 teacher co-authors, ***italics bold*** indicates corresponding authors

[1] *"Anodic Aluminum Oxide Catalytic Membranes for Asymmetric Epoxidation"* Cho, S.-H.; Walther, N. D.; ***Nguyen, S. T.***; ***Hupp, J. T.*** *Chem. Commun*. **2005**, 5331-5333.

[2] "*A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation*" Cho, S.-H.; Ma, B.; ***Nguyen, S. T.***; ***Hupp, J. T.***; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563-2565.

[3] "*[Bis(catechol)salen]Mn^{III} coordination polymers as insoluble asymmetric catalysts for epoxidation*" Cho, S.-H.; Gadzikwa, T.; Afshari, M.; ***Nguyen, S. T.***; ***Hupp, J. T.*** *Eur. J. Inorg. Chem.* **2007**, 4863-4867.

[4] "*Ligand elaboration as a strategy for engendering structural diversity in porous metal-organic framework compounds*" Gadzikwa, T.; Zeng, B.-S; ***Hupp, J. T.***; ***Nguyen, S. T.*** *Chem. Commun.* **2008**, revised.

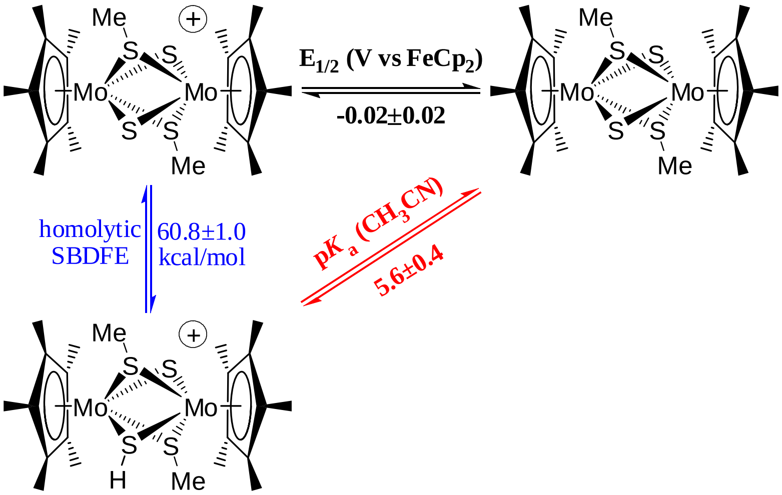
[5] "*Covalent surface modification of a metal-organic framework: Selective surface engineering via Cu^{I}-catalyzed Huisgen cycloaddition*" Gadzikwa, T.; Lu, G.; Stern, C. L.; Wilson, S. R.; ***Hupp, J. T.***; ***Nguyen, S. T.*** *Chem. Commun.* **2008**, submitted.

KC-03-02-01-0 **Project # 47319** **Aaron M. Appel**

Homolytic and Heterolytic S-H Bond Energies in Homogeneous Mo_2S_4 Complexes

Presenter: Aaron Appel
Lead PI: James Franz
Postdoc: Suh-Jane Lee
Contact: Aaron Appel; Pacific Northwest National Laboratory; P.O. Box 999, MS K2-57; Richland, WA 99352; aaron.appel@pnl.gov

Studying the formation and cleavage of S-H bonds is central to understanding the wide range of observed reactivities in molybdenum sulfide chemistry. Homogeneous CpMo(μ-S)$_4$MoCp based complexes have been extensively studied because of the abilities of these complexes to activate hydrogen and undergo bond forming reactions with a variety of hydrocarbons. However, very few bond energies have been determined for these small molecule analogs of hydrodesulfurization catalysts. A series of Cp*Mo(μ-SR)(μ-SR')(μ-S)$_2$MoCp* complexes have been synthesized and studied in order to develop thermochemical knowledge of these systems. Electrochemical data have been determined by cyclic voltammetry, and pK_a values have been determined by ^{1}H NMR. By combining the electrochemical data and pK_a values of these complexes, a substantial number of solution homolytic and heterolytic bond dissociation free energies have been determined, one example of which is shown below. Together, these data create a significant basis for understanding the thermochemistry of S-H bonds in molybdenum sulfide complexes.



References

Aaron M. Appel, Suh-Jane Lee, James A. Franz, Daniel L. DuBois, M. Rakowski DuBois, Jerome C. Birnbaum, and Brendan Twamley. "Formation and Reactivity of a Persistent Radical in a Dinuclear Molybdenum Complex." Submitted to *Journal of the American Chemical Society*

Monday Evening Sessions

Biocatalysis for Fuels and Industrial Chemicals: Enzymes, Whole Cells and Beyond

Douglas C. Cameron
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Biocatalysis is a broad, multifaceted topic. At one extreme, living organisms produce chemical catalysts such as acids and inorganic structures. At the other extreme, whole organisms and communities of organisms have catalytic activity. Between these extremes are enzymes and multiprotein complexes, such as cellulosomes and carboxysomes. Approaches to alter catalytic activities include protein engineering, laboratory evolution, metabolic engineering and synthetic biology. Successful processes for the production of fuels and chemicals from renewable resources will likely involve several different types of catalysis--both biological and non-biological catalysts. Several examples of such combined, "syncretic" processes will be presented.

DE-FG02-06ER15794 **Mahdi M. Abu-Omar**

Silane Activation on a Single-Site Oxorhenium(V) Oxazoline Catalyst: A New Mechanistic Paradigm for Hydrogen Production and Hydrosilation

Postdoc: Guodong Du
Students: Jeanette Cessarich, Mary Jones, and Erin Smith
Contact: Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907; mabuomar@purdue.edu

Goal

Investigate the kinetics and mechanisms of hydrogen release from organosilanes and hydrosilylation as catalyzed by oxo and imido complexes of high-valent rhenium. Establish the rate determining elementary steps and physical factors that govern kinetics of catalysis. Develop new catalyst systems for hydrogen release and utilization from liquid silanes.

DOE interest

Research in the chemical sciences can contribute to energy solutions in three ways, new sources of energy, preferably renewable; methods of energy storage and production via making and breaking of chemical bonds; and increased efficiency of chemical reactions (atom economy, mild conditions, 'green' chemistry, etc.). It is evident that chemical catalysis would play a central role in the latter two areas. Besides the immediate benefit of advancing a new mechanistic knowledge for the reactivity of organosilanes with transition metal oxo and imido complexes, our research has broader impact in the areas of hydrogen storage and production on-demand, and "green' and facile catalysis.

Recent Progress

Reduction reactions catalyzed by high-valent $Re(X)Cl_3L_2$ complexes (X = O or NAr, and L = PPh_3 or PCy_3): Aliphatic as well as aromatic aldehydes and ketones can be reduced with tertiary silanes to the corresponding protected alcohols in the presence of a catalytic amount (ca. 1 mol%) of $Re(X)Cl_3L_2$. These catalysts are reactive under ambient open-flask conditions, and tolerate many functional groups including alkenes, alkynes, and ethers, to name a few. Product yields are quantitative. A number of novel oxo and imido hydride complexes of rhenium have been synthesized (see structure, Figure 1) and their involvement in reduction of organic compounds investigated. Surprisingly, we found the isolable rhenium hydrides to be less reactive than the putative σ-complex formed in the early stages of the catalytic reactions. These findings reinforce the notion that the observation of "likely" intermediates in a catalytic cycle, generally, signals a nonproductive pathway.

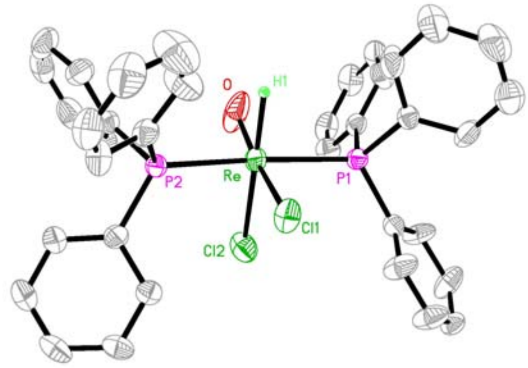

Fig. 1: Structure of $Re(O)(H)Cl_2(PPh_3)_2$.

Synthesis and reaction chemistry of chiral oxorhenium(V) complexes: Synthesis of chiral oxorhenium(V) complexes including a rare trinuclear cluster is described. We found these complexes to be effective catalysts for hydrosilylation of carbonyl compounds as well as for silane alcoholysis. However, the enantioselectivity for both reactions were low. An intermediate with a partially reduced imine ligand was identified.

Hydrogen release from liquid silane: We studied a binuclear nickel hydride catalyst for the conversion of liquid silane, analog of hydrocarbons, under ambient (mild) conditions to yield hydrogen and a polysilane material. We discovered the reaction can be carried out neat or in organic solvent such as toluene. However, in both instances the silicon product was a precipitate.

Activation of dioxygen on zirconium(IV) by confiscating electrons from the ligand: Through the utilization of redox active amido ligands, we prepared a bisamido zirconium(IV) complex and characterized it by crystallography and spectroscopic methods. We discovered that this zirconium complex despite having d^0 electron count is capable of activating dioxygen by confiscating electrons from the ligand to give a novel bisperoxo zirconium(IV) complex, which we characterized by single-crystal X-ray diffraction (Figure 2).

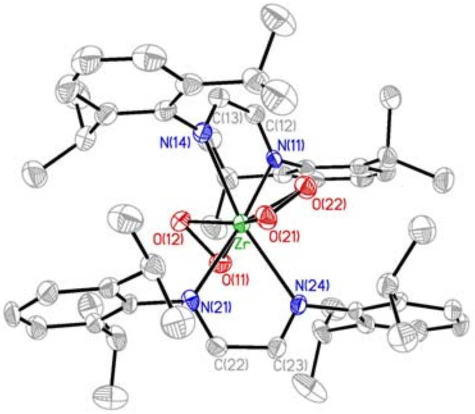

Fig. 2: Structure of bisperoxo zirconium(IV).

Future plans

Hydrogen release from liquid silane: We plan on completing the investigation of hydrogen release from neopentyl silane, study reaction kinetics, characterize the silicon product, and explore its rehydrogenation back to liquid silane.

Asymmetric reductions: Based on lessons learned from our rhenium chemistry we have designed and prepared $Mo^{VI}(O)_2$ and $Mo^{IV}(O)$ chiral salen complexes. We will develop their use as catalysts for hydrogenation and hydrosilylation of organic compounds.

Small molecule activation and 'green' chemistry: Our discovery of dioxygen activation by zirconium(IV) bisdiamido complex opens the door to very exciting new chemistry for us to explore in the context of hydrogen utilization and green chemistry. One venue is reaction with dihydrogen to make reactive zirconium(IV) hydride, which can in turn be employed in reactions with small molecules such as CO_2 and CO to make methanol or liquid fuels. We also plan to study the kinetics of the reaction of dioxygen with zircounium bisdiamido.

Publications 2006-2008

1. Ison, E. A.; Cessarich, J. E.; Du, G.; Fanwick, P. E.; Abu-Omar, M. M. "Synthesis of Cationic Oxorhenium Salen Complexes via μ-Oxo Abstraction and Their Activity in Catalytic Reductions" *Inorg. Chem.* **45** (2006) 2385-2387.
2. Guodong Du and Mahdi M. Abu-Omar, "Catalytic Hydrosilylation of Carbonyl Compounds with Cationic Oxorhenium(V) Salen" *Organometallics* **25** (2006) 4920-4923.
3. Guodong Du, Philip E. Fanwick, and Mahdi M. Abu-Omar, "Mechanistic Insight into Hydrosilylation Reactions Catalyzed by High Valent Re≡X (X = O, NAR, or N) Complexes: The Silane (Si-H) Does Not Add Across The Metal-Ligand Multiple Bond" *J. Am. Chem. Soc.* **129** (2007) 5180-5187.
4. Corneliu Stanciu, Mary E. Jones, Phillip E. Fanwick, and Mahdi M. Abu-Omar, "Multi-electron Activation of Dioxygen on Zirconium(IV) to Give an Unprecedented Bisperoxo Complex" *J. Am. Chem. Soc.* **129** (2007) 12400-12401.
5. Guodong Du, Phillip E. Fanwick, and Mahdi M. Abu-Omar, "Cationic Oxorhenium Chiral Salen Complexes for Asymmetric Hydrosilylation and Kinetic Resolution of Alcohols" *Inorg. Chim. Acta* (2008), In-press. (Special Issue in honor of Professor Robert J. Angelici).
6. Guodong Du and Mahdi M. Abu-Omar, "Oxo and Imido Complexes of Rhenium and Molybdenum in catalytic reductions" *Curr. Org. Chem.* (2008), In-press.

DE-FG02-05ER15690 **Shannon S. Stahl**

Mechanisms of Organometallic Copper Oxidase Reactions

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Goal

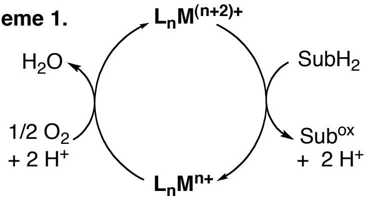
Our overall goals on this research project have two general themes:

(1) to gain a fundamental understanding of copper-catalyzed aerobic oxidation reactions that proceed via organometallic intermediates
(2) to apply insights from our mechanistic studies to the development of new aerobic oxidative coupling reactions.

Recent Progress

Organometallic oxidase reactions provide a versatile approach to the selective oxidation of organic molecules with molecular oxygen. Such reactions generally employ a two-stage catalytic mechanism, which consists of (1) metal-mediated oxidation of an organic substrate proceeding via organometallic intermediates followed by (2) aerobic oxidation of the reduced catalyst (L_nM^{n+}) (Scheme 1). Homogeneous palladium catalysts are widely used in such aerobic oxidation reactions. Other transition-metal catalysts are also known, but they have received substantially less attention and, in many cases, their mechanisms are poorly understood. In our DOE-funded project, we initiated an investigation of copper-catalyzed organometallic oxidase reactions in order to gain further insights into their reaction mechanisms and to explore new opportunities for aerobic oxidation reactions.

Scheme 1.



Our research in this project has focused on three complementary themes:

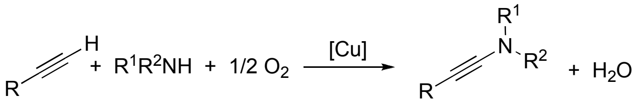
(1) Elucidation of the catalytic mechanism of copper-catalyzed C–N and C–O bond-forming reactions involving the aerobic oxidative coupling of aryl boronic acids and nitrogen or oxygen nucleophiles.

$$\underset{\text{R = aryl, vinyl}}{\text{R–B(OH)}_2} + \text{R}^1\text{R}^2\text{NH} + 1/2\ \text{O}_2 \xrightarrow{[\text{L}_n\text{Cu}]} \text{R–NR}^1\text{R}^2 + \text{HO-BX}_2 \qquad (1)$$

(2) Probing the fundamental reactivity of organometallic copper(III) complexes, in particular, carbon-nitrogen bond-forming reactions involving well-defined arylcopper(III) species

$$[\text{L}_n\text{Cu}^{\text{III}}\text{–Ar}]^+ + \text{R}^1\text{R}^2\text{NH} \longrightarrow \text{L}_n\text{Cu}^{\text{I}} + \text{Ar–NR}^1\text{R}^2 + \text{H}^+ \qquad (2)$$

(3) Development of Cu-catalyzed methods for the oxidative amidation of terminal alkynes as an efficient means of preparing ynamides



(3)

DOE Interest

The selective oxidation of organic molecules with molecular oxygen as the oxidant is of critical significance for the efficient use of hydrocarbon feedstocks. Insights gained from this work should reveal conceptual links between fundamental studies of metalloenzymes and model systems and the development of synthetically useful aerobic oxidation reactions.

Future Plans

Ongoing and future efforts will continue to probe mechanistic aspects of copper-catalyzed aerobic oxidation reactions and the reactivity of well-defined organocopper complexes. Computational methods will play an important role in complementing our experimental work in order to elucidate fundamental features of these reactions. Insights from these studies will provide a basis for our continued development of new organometallic oxidase reactions.

Publications Acknowledging DOE Support

Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130,* 833-835. "Copper-Catalyzed Aerobic Oxidative Amidation of Terminal Alkynes: Efficient Synthesis of Ynamides."

Ancillary Oxazolinylboron Ligands for Transition Metal Centers

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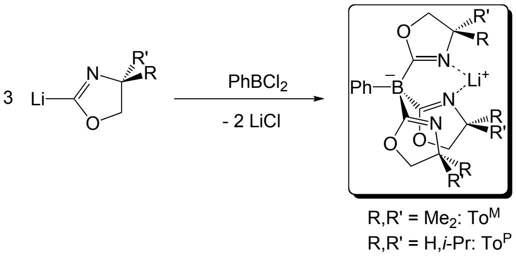
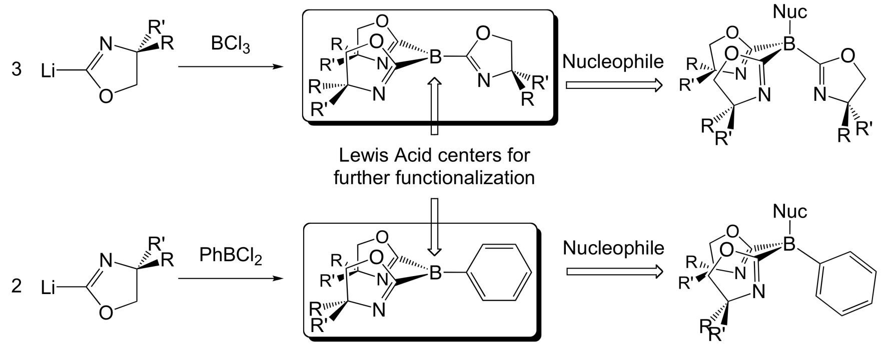
We are interested in transition metal centers that maintain similar coordination geometries under homogeneous and surface-supported conditions, allowing rational preparation of well-defined heterogeneous catalytic sites. Thus, we have developed a new family of 2-oxazolinyl-boron compounds to serve as tridentate ancillary ligands for homogeneous and supported organometallic chemistry. In particular, tris(2-oxazolinyl)phenylborate **To^{R-}** (using 4,4-dimethyl-2-oxazoline, **$[To^{M}]^{-}$**, and 4*S*-isopropyl-2-oxazoline, **$[To^{P}]^{-}$**) are easily prepared in a single flask. We can also prepare neutral bis(oxazolinyl)phenylboranes or tris(oxazolinyl) boranes as intermediates, and these intermediates provide routes to surface immobilized ligands.



$[To^{R}]^{-}$ monoanionic ligands are suitable for high valent early and low valent late transition metal centers. Thus far, yttrium(III), zirconium(IV), rhenium(I), ruthenium(II), and iridium(I) and (III) complexes have been prepared. Interestingly, early metal compounds are robust toward thermally induced decomposition; for example toluene solutions of $[Zr(\kappa^{3}\text{-}To^{P})Cl_3]$ are unchanged after 1 week at reflux. Likewise, addition of the acid $[HNEt_3]Cl$ to $Li[To^{R}]$ under anaerobic, dry conditions provides the protonated $H[To^{R}]$ without B–C bond cleavage. These studies provide support for the stability of the B–C linkages in the tris(oxazolinyl)borate ligands that will be critical for catalytic reactions.



The oxazolinyl imine functionality of the $[To^{R}]^{-}$ ligands facilitates characterization of its complexes. Solution and solid state ^{15}N NMR spectroscopies have proven particular valuable for characterizing complexes. For example, ^{1}H NMR and $^{1}H\text{-}^{15}N$ HMBC of $[Ir(To^{P})(\eta^{4}\text{-}C_8H_{12})]$ in benzene-d_6 indicate that the three oxazolinyl groups are equivalent due to rapid exchange, while solid state the ^{15}N NMR spectrum indicates that the compound exists as a mixture of κ^{2}- and κ^{3}-coordinated isomers (4-coordinate and 5-coordinate, respectively). We have seen that the ^{15}N NMR chemical shifts obtained from solution and solid state measurements are closely related; for example the chemical shift of 2H-4*S*-isopropyloxazoline (in solution) and the non-coordinated oxazoline in $[Ir(To^{P})(\eta^{4}\text{-}C_8H_{12})]$ (in the solid state spectrum) are -148 and -147 ppm (vs. nitromethane), respectively. These NMR techniques, in conjunction with infrared spectroscopy, allows for the characterization of well-defined organometallic sites in solution and on surface-supported materials.

Tuesday Morning Sessions

Photodriven Multi-Electron Transfer Reactions at Molecular Semiconductor Interfaces

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A significant challenge in the photochemical sciences is to couple photo-induced charge separation to multi-electron transfer (MET) catalysis. MET catalysis can avoid high-energy free radical intermediates to yield desired reaction products under mild conditions. The identification of molecular compounds capable of photodriven MET has proven to be extremely challenging. On the other hand, MET reaction products have been identified at illuminated semiconductor interfaces albeit generally with poor yields and broad distributions of reaction products.

In this presentation, the current status of our studies on photo-induced charge separation at sensitized mesoporous nanocrystalline (anatase) TiO_2 thin film interfaces will be reviewed.[1] The realization that photo-induced interfacial electron transfer occurs on ultrafast time scales opens up new opportunities for solar energy conversion. We have recently shown that sensitized ultrafast electron injection into anatase TiO_2 nanocrystals can be used to drive redox reactions that would be thermodynamically uphill from the thermally equilibrated excited state of the sensitizer.[2] This finding represents a molecular opportunity to exceed the Shockley-Queisser solar energy conversion limit.[3] Our ongoing efforts to couple this interfacial charge transfer with molecular catalysis will also be presented. Well-defined molecular catalysts (such as hemes) anchored to these TiO_2 thin films (heme/TiO_2) have been found to mediate MET reactions. The semiconducting nature of the mesoporous TiO_2 thin films has allowed the reactive catalyst state to be controlled with light and/or applied potential. Depending on the experimental conditions, illumination of heme/TiO_2 can result in the generation of conduction band electrons, $TiO_2(e^-)$, or in reduction of the ferrous heme to the formal iron oxidation state of one. In the former case, each ~ 20 nm diameter nanocrystal was found to store > 500 $TiO_2(e^-)$s upon illumination, the exact concentration could be controlled with surface coverage and irradiance. Comparative kinetic studies showed that heme/$TiO_2(e^-)$ reduced organohalide acceptors much more rapidly than did $TiO_2(e^-)$s alone. The reduction of CCl_4 by heme/$TiO_2(e^-)$ yielded stable (protoporhyrinato)Fe(II)CCl_2 carbene compounds in high (> 60%) yield.[4] Studies with radical clocks demonstrate a 4.5 microsecond time scale for the delivery of two electrons to a substrate.[5] Reaction mechanisms and studies of other photodriven redox reactions at sensitized catalytic semiconductor surfaces will be discussed.

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DE-FG02-03ER15461 Djamaladdin G. Musaev, Craig L. Hill, and Keiji Morokuma

Principles of Selective O2-Based Oxidation by Optimal (Multinuclear) Catalytic Sites

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Students: Zhen Luo, Daniel A. Hillesheim, Khaled Sarker, Rui Cao, Iourii Geletii, Yu Hou, Kevin O’Halloran
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Goals

Develop a combined experimental and theoretical approach to elucidate the mechanisms of selective (non-radical), reductant-free, O_2-based oxidation of organic substrates catalyzed by metal oxide cluster systems (polyoxometalates or “POMs”) with two or more proximal and synergistically interacting metal centers. The objectives entail clarification of the structural, solution and catalytic properties of two classes of complexes: those with two adjacent d-electron transition metals (formula: $\gamma\text{-XM}^1\text{M}^2(\text{OH})_2(\text{M}_{\text{FW}})_{10}\text{O}_{38}{}^{n-}$) and the new Late Transition Metal Oxo (LTMO) complexes.

DOE Interest

The proposed research addresses the catalytic selective oxidation of organic substrates by O_2. Realization of synthetic catalysts capable of such transformations remains a monumental challenge. The most promising such catalysts in chemistry and biology remain those with multiple proximal d-electron-containing metal centers. The POM complexes targeted herein, those with two adjacent d-electron-containing metals and the LTMO complexes, address core issues of intellectual and potential practical importance and provide a foundation for addressing principles central to realizing optimal synthetic catalysts and understanding related catalytic biological processes. One reaction (of several) the goals of this effort address that impacts energy transportation and utilization significantly is the catalytic O_2-based oxidation of methane (96% of natural gas) selectively at high conversion to methanol, a process that has yet to be achieved satisfactorily by a non-biological catalyst.

Recent Progress

Our ongoing program focuses in part on oxidatively robust POM complexes in which a catalytic active site interacts with proximal metal centers in a synergistic manner. Two classes of such POM complexes are of particular interest: (**I**) those with two adjacent d-electron transition metals (γ-M_2-Keggin complexes) and (**II**) the newly developed Late Transition Metal Oxo (LTMO) complexes.

1. The team has prepared, characterized new polyoxometalates containing two proximal d-electron-containing. The $\{\gamma\text{-M}_2\text{SiW}_{10}\}$ POM system has been established to be the most versatile oxidatively stable dinucleating (binding 2 metals) ligand system in the literature to date. $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ catalyzes peroxide-based epoxidation with extraordinary selectivities (>99

% of epoxide) and efficiencies (>99 % epoxide based on oxidant). We have (a) elucidated factors controlling catalyst, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, stability, and nature of the reactive intermediates; and (b) constructed of a defensible mechanism based on existing and new data.

2. We have designed and constructed the first homogeneous (molecular) catalyst for H_2O oxidation to O_2 that is free of oxidatively unstable organic structure of any kind. This complex, $Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-SiW}_{10}O_{36})_2]\cdot 25H_2O$ (**3**), is a derivative of the $\{\gamma\text{-M}_2\text{SiW}_{10}\}$ system we have been probing in some depth and contains 4 Ru centers that have reduction potentials in the exact range needed to oxidize H_2O. We first demonstrated that **3** (Figure 1) can be reversibly oxidized and reduced by 4 electrons (cyclic voltammograms in Figure 2), a critical prerequisite for the oxidation of H_2O, i.e. eq 1, and then we demonstrated that **3** catalyzed eq 1 using strong oxidants (e.g. “oxidizing equivalents” in eq 1 = $[Ru(bpy)_3]^{3+}$, etc.)

$$2\ H_2O + 4\ [\text{oxidizing equivalents}] \rightarrow O_2 + 4\ H^+ + 4\ [\text{reducing equivalents}] \qquad (1)$$

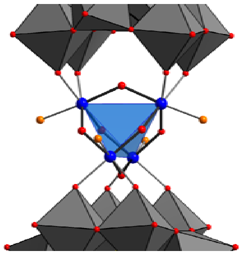

Figure 1. Structure of the polyanion in **3**, highlighting the central $[Ru_4(\mu\text{-O})_4(\mu\text{-OH})_2(H_2O)_4]^{6+}$ core (ball-and-stick representation, Ru: blue, μ-O: red, $O(H_2)$: orange, H omitted for clarity) and the slightly distorted Ru_4 tetrahedron (transparent blue). The polytungstate fragments are shown as gray polyhedra; Si as yellow spheres.

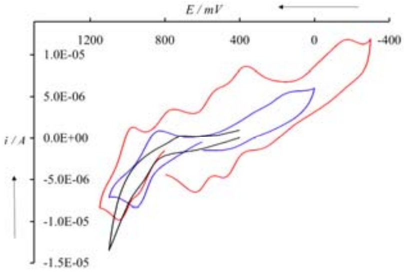

Figure 2. CVs of 1 mM **3** in 0.1 M HCl (pH 1.0, red curve), in 0.4 M sodium acetate buffer (pH 4.7, blue curve), and of 0.6 mM **3** (pH 7.0, black curve). Scans start at the rest potentials, 800, 600 and 400 mV, respectively and potentials are relative to a Ag/AgCl (3 M NaCl) reference electrode.

3. The first terminal Au-oxo and Pd-oxo complexes were prepared. Both Au-oxo and Pd-oxo complexes have been shown to transfer oxygen atoms to organic substrates. The Pd-oxo complex activates O_2, and both of these new classes of complexes appear to catalyze oxidations by O_2 without the requirement for a reducing agent. Such catalytic “aerobic” oxidations have been sought for 30 years and remain of considerable interest because they are green (require only air with no reducing agent) and are 100% oxygen atom efficient.

4. The “peroxo” mechanisms of the H_2O_2-based epoxidation catalyzed by divanadium-substituted-γ-Keggin $[\gamma\text{-1,2-H}_2\text{SiV}_2\text{M}_{10}\text{O}_{40}]^{4-}$ (where M = W and Mo) have been analyzed at the DFT level. A new “peroxo” mechanism (that starts from the peroxo intermediate with a $\{VO\text{-}(\eta^2\text{-OO})\text{-}VO\}$) core) of the studied reactions were compared with the “hydroperoxy” mechanism (that involves a $\{VO\text{-}(\mu\text{-OOH})(\mu\text{-OH})\text{-}VO\}$) active species), previously reported by our team.

5. The mechanism of interaction between the di-Ru-substituted-γ-Keggin $[\gamma\text{-1,2-H}_2\text{SiRu}_2\text{W}_{10}\text{O}_{40}(H_2O)_2]^{4-}$ and the O_2 molecule has been elucidated at the DFT level. It was shown that this reaction is an exothermic process and occurs with a small energy barrier.

6. The mechanism of the ethylene epoxidation by the $\{H_2SiO_4[WO(O_2)_2]_2\}^{2-}$ polyperoxytungstate (PPT) (Figure 3) was elucidated by computational means. It was shown that this epoxidation process is very facile, occurs with an energy barrier of only 12-17 kcal/mol, and is highly exothermic. Interestingly, an O-atom transfer from the “bridging” peroxo ligand to olefin occurs with a few (2-3) kcal/mol lower barrier than that from the “terminal” peroxo ligand.

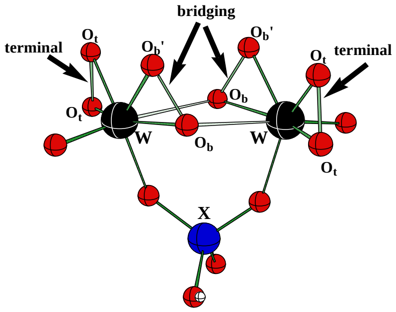

Figure 3. Schematic presentation of the polyperoxytungstate (PPT), and its possible reactive peroxo ligands.

It was shown that the reaction

$$\{H_2SiO_4[WO(O_2)_2]_2\}^{2-} + C_2H_4 \rightarrow \{[W(O)_2(O_2)][H_2SiO_4][WO(O_2)_2]\}^{2-} + OC_2H_4$$

is a very facile process, occurs with an energy barrier of only 12-17 kcal/mol, and is highly exothermic. Interestingly, an O-atom transfer from the “bridging” peroxo ligand to olefin occurs with a few (2-3) kcal/mol lower barrier than that from the “terminal” peroxo ligand.

Future Plans:

Further elucidate: (1) the thermodynamic stability of γ-M_2-Keggin in aqueous media for different M’s (d-electron metals); (2) the reactivity of divacant lacunary species and polyperoxotungstates (PPTs), $\{X^{n+}O_4[WO(O_2)_2]_4\}^{n-}$, which could be degradation products of γ-M_2-Keggin complexes in aqueous media; and (3) the physicochemical and structural (geometric and electronic) properties of γ-M_2-Keggin complexes, where M = V^{IV}, Mn^{III}, Cr^{III}, Ru^{III} and others, and correlating this information with the catalytic oxidation activity of these complexes. (4) Design and synthesis of new LTMO complexes of Ir, Pd and Au, and elucidate their stability and reactivity by combined experimental and computational approaches.

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DE-FG02-05ER15687 **Geoffrey W. Coates**

Development and Application of New Catalysts for Heterocycle Carbonylation

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Goal

The goal of this research project is the development of new catalysts for heterocycle carbonylation. The project focuses on three main objectives: 1) the development of a new generation of heterocycle carbonylation catalysts with improved activities and selectivities; 2) the application of heterocycle carbonylation catalysts to access high-value organic synthons and to synthesize monomers for unique polymer architectures; and 3) the study of the mechanisms of heterocycle carbonylation in a range of fundamentally new catalytic transformations.

Recent Progress

Recent work has focused on the development and application of a class of bimetallic $[\text{Lewis Acid}]^{+}[Co(CO)_4]^{-}$ catalysts that efficiently carbonylate epoxides to β-lactones. In the last funding period, significant advances were made in understanding the detailed catalytic mechanism of epoxide and lactone carbonylation. On the basis of these results, new catalysts with improved properties were developed. Three of these catalysts are now commercially available through the Aldrich Chemical Company. In addition, the application of these catalysts for the carbonylation of other heterocycles was developed. Major findings that occurred during the prior project period include:

- Study of the mechanism of epoxide carbonylation to β-lactones;
- Development of a new catalyst for low pressure epoxide carbonylation;
- Development of a new catalyst for epoxide double carbonylation to succinic anhydrides;
- Study of the mechanism of β-lactone carbonylation;
- Development of a multicomponent synthesis of 1,3-oxazinane-2,4-diones from epoxides, isocyanates, and CO;
- Catalytic synthesis of isotopically labeled anhydrides for mechanistic study;
- Catalytic synthesis of β-lactones that inhibit acetylcholinesterase;
- Catalytic synthesis of highly fluorinated β-lactones and their corresponding poly(3-hydroxybutyrate)s;
- Development of a new catalyst for the synthesis of substituted 3-hydroxy-δ-lactones;
- Development of a new catalyst for oxazoline carbonylation.

Future Work

Future work will focus on the development of a new set of catalysts that addresses a group of diverse challenges. We will explore new applications for our family of bimetallic carbonylation catalysts, while maintaining our focus on efficient catalytic reactions for the production of both useful monomers and synthetically relevant, bioactive molecules. Finally, we will undertake studies to fully understand the detailed mechanisms of new heterocycle carbonylation catalysts.

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DE-FG02-01ER15267 **Andrew W. Maverick**

Inorganic-Organic Molecules and Solids with Nanometer-Sized Pores

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Goal

We are constructing porous inorganic-organic hybrid molecules and solids that contain coordinatively unsaturated metal centers.

DOE Interest

We expect to use the approaches outlined here to prepare new porous molecules and solids that expose reactive metal sites to the interiors of enclosed cavities and channels. Possible applications of the resulting materials include catalysts, sensors, and thin-film membranes for separations, all of which may derive improved selectivity from the placement of the active metal sites inside the cavities.

Recent Progress

1. Extended solids

We have continued our work on the new isocyano-β-diketone ligand HacphNC (see Figure 1). This is designed to bind to two different kinds of metal ions through its two ligand moieties, and the high affinity of its isocyanide functional group for metals is expected to favor octahedral coordination.

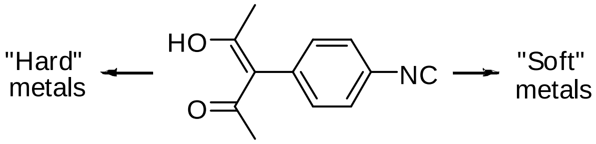

Figure 1. The isocyano-β-diketone ligand HacphNC.

We previously reported the preparation of complexes with “hard” metals, i.e. $Cu(acphNC)_2$, $Zn(acphNC)_2$, and $Al(acphNC)_3$. Preliminary results now indicate that the isocyanide moieties in these complexes, or in the free HacphNC ligand, can be used to coordinate to “soft” metals such as Au(I), Cu(I), Mn(I), and Fe(II). The experiments with Mn(I) and Fe(II) are the most promising, because these metals are likely to form the $(acphNC)_6M$ that will be needed in the construction of heterobimetallic 3D porous materials.

2. Molecular systems

a) Molecular squares and related species for H_2 storage: In the previous report, we described the properties of the β-diketonate molecular squares $Cu_4(m\text{-pba})_4$ and related species (see Figure

2). These hollow molecules, which have diameters of ca. 14 Å, accommodate guest molecules such as fullerenes (C_{60}, C_{70}) and 4,4′-bpy.

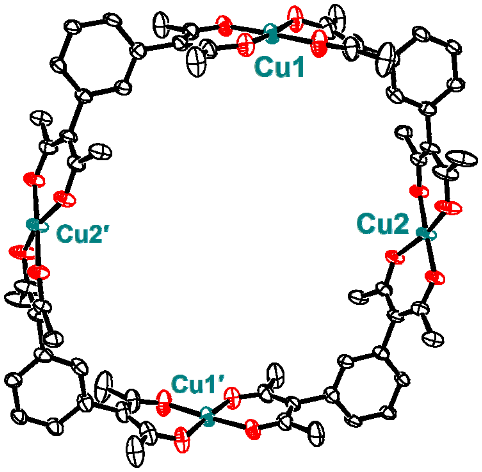

Figure 2. The β-diketonate molecular square $Cu_4(m\text{-pba})_4$. (Cu···Cu ~14 Å).

At the 2006 contractors' meeting, conversations with Giselle Sandí (Argonne) led to collaborations on H_2 storage measurements. These were performed by Sandí at Argonne; they showed H_2 uptake of ca. 0.6% by weight at room temperature (75 atm), a relatively high figure for a porous metal-organic material. Meanwhile, the adsorption properties of these molecular systems are not expected to be affected by loss of crystalline structure, as can happen with extended solids such as metal-organic frameworks (MOFs).

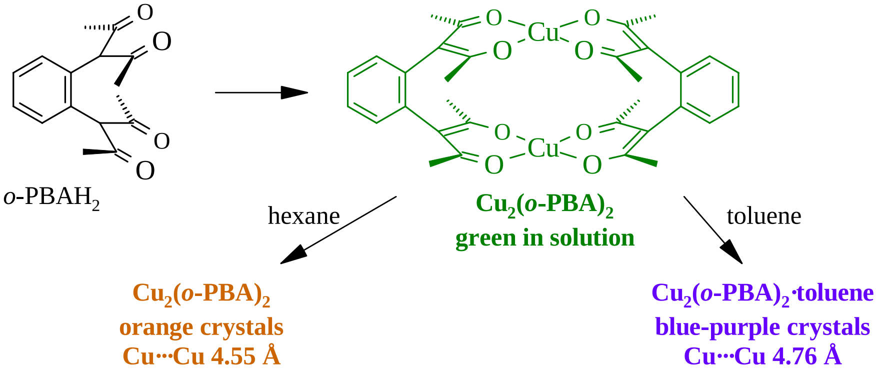

Figure 3. The bis(β-diketone) o-pbaH_2 and its binuclear Cu complexes.

These H_2 storage measurements encouraged us to consider measurements on other related materials. For example, we previously reported the preparation of the analogous *ortho* isomer of the ligand, o-pbaH_2, and its Cu complexes (see Figure 3), which are surprisingly strained *dimers* rather than the expected trimers. For H_2 storage measurements with $Cu_2(o\text{-pba})_2$, we collaborated with Dr. Alan Cooper (Air Products). Samples of $Cu_2(o\text{-pba})_2$ showed much lower H_2 storage, <0.01%. We believe this is because the internal cavity in the host is too small even for storage of the small guest H_2.

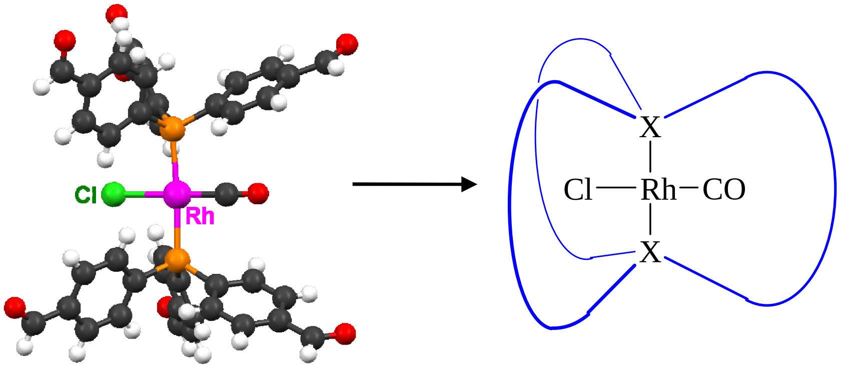

Figure 4. The Rh(I) complex of the trialdehyde ligand $P(C_6H_4CHO)_3$ (see crystal-structure drawing at left) should react with diamines to produce the caged Rh complex shown at right. This reaction appears to generate considerable polymeric material, but some soluble material, the latter being the desired product. Its structure and properties are now being studied.

b) Caged catalysts: An alternative approach to supramolecular catalysts is to construct a framework around a catalytic site in order to provide selective access of one type of substrate over another. We have used the trialdehyde $P(C_6H_4\text{-}4\text{-}CHO)_3$ to prepare a Rh(I) complex, and condensed it with diamines; see reaction in Figure 4. The supramolecular product of this reaction should serve as a homogeneous catalyst for hydrogenation or hydroformylation, but only for substrates that can enter the space between the "arms" of the compound.

Future Plans

1. Extended solids
    a. C-bound complexes of the isocyanide ligand HacphNC will be characterized further.
    b. HacphNC will be used in attempts to assemble 3D extended solid materials.
2. Molecular species
    a. We are developing ligands with flexible and polar substituents, in order to improve the solubility of the supramolecular products in a variety of solvents.
    b. We have treated our β-diketones with NH_3 to prepare ketoenamines. Complexes of these new β-diketone analogs should exhibit improved NMR and electrochemical properties, which will make possible new host-guest reactivity.
    c. The Rh-functionalized phosphine system will be studied further, in order to find conditions for improving yield and purity of the supramolecular product. This material will then be used in homogeneous catalysis experiments.

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C–H Oxidation Made Easy—by Amino Acid-Radical Forming Enzymes

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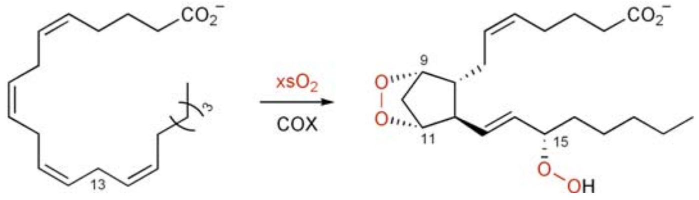
In an effort to understand how C–H oxidizing enzymes may be utilized in the production of oleo-fuels and chemical commodities, this presentation will focus on two tyrosyl radical-forming heme enzymes: cyclooxygenase (COX) and the "simpler" homologue rice α-oxygenase (RαO). COX mediates the first step in prostaglandin biosynthesis from arachidonic acid (Eq 1) while RαO metabolizes saturated as well as unsaturated fatty acids by oxidation at the 2-position (Eq 2). Common strategies for effecting regio and stereospecific insertion of O_2 into the substrate C–H bond have been illuminated through detailed mechanistic and biophysical studies. Thermodynamic considerations reveal an interesting paradox concerning the H• affinities of the tyrosyl radicals proposed to initiate fatty acid oxygenation. How these factors relate to the intra-protein redox reactions, by which Tyr• is produced in the first place via heme oxidation, will be discussed.

(1)



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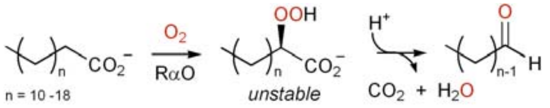

Tuesday Evening Sessions

Hydrogen Storage and Delivery Using Liquid Carriers

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In our concept of a “non H_2 gas” hydrogen energy infrastructure the carrier is an organic liquid which can undergo a reversible catalytic addition of hydrogen. Thus, the hydrogen “loaded” liquid can be catalytically dehydrogenated at the point of use which may be a stationary or mobile location. The concept will be illustrated by the performance of N-ethylcarbazole but also of other N- and O-heterocyclic molecule liquid carriers. The catalytic dehydrogenation requires an input of heat at temperatures of 150-200 ° which may be difficult to realize with PEM fuel cell sources. To address this we’ve developed the concept of autothermal liquid carriers, compositions that in appropriate catalytic dehydrogenation reactor systems could provide both the stored hydrogen and the thermal energy that is required to liberate it.

DE-FG02-92ER14273 **Klaus H. Theopold**

Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer

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Goal

Characterize the mechanisms of, and prepare catalysts for ‘proton coupled electron transfer’ (PCET) to metal bound fragments derived from the most abundant small molecules (i. e., O_2 and N_2).

DOE Interest

There are many important chemical challenges that are tied to this fundamental reaction. Among these are:

- metal catalyzed oxidations of organic molecules utilizing O_2 as the oxidant
- reduction of O_2 to water close to the thermodynamic potential – i. e., the cathode of any fuel cell based on reactions with O_2
- fixation of nitrogen at modest temperatures and pressures
- transfer of reduced nitrogen species to organic substrates

Any one of these problems has obvious implications for the generation and/or utilization of energy on a large scale.

Recent Progress

Hydrogen atom tunneling: The abstraction of hydrogen atoms from organic molecules by metal oxo complexes is an archetypical reaction in oxidation catalysis and bioinorganic chemistry. Moving the lightest of all atoms, hydrogen transfer reactions occasionally exhibit experimental evidence of involving quantum mechanical tunneling. The circumstances that favor tunneling and the question whether the latter can be facilitated – e. g. in the evolution of an enzyme – are subjects of current interest.

The reaction of $[Tp^{t\text{-Bu,Me}}Cr(O)(pz'H)]BARF$ (**1**) with 9,10-dihydroanthracene (DHA) produced $[Tp^{t\text{-Bu,Me}}Cr(OH)(pz'H)]BARF$ and anthracene. Kinetic isotope effect measurements using 9,9,10,10-tetradeuterioanthracene (DHA-d_4, 99.6 %D) revealed $k_H/k_D(295K) = 21.6$. While these kinetic isotope effects certainly imply C-H(D) bond breaking in the rate determining step, their values are unusually large. H/D kinetic isotope effects substantially in excess of 7-9 are often considered an indication of a tunneling contribution, although this is not a sufficient condition by itself. Two further criteria used to support hydrogen atom tunneling are i) a difference in the activation enthalpy of the H and D transfer that is larger than the difference in the zero point energies of the bonds broken ($\Delta(\Delta H^{\ddagger}) > 1.2$ kcal/mol), and ii) a significant difference in the pre-exponential factors resulting from an Arrhenius analysis ($A_H/A_D < 0.7$). Therefore we have determined the activation parameters for the reactions of **1** with DHA and DHA-d_4.

Figure 1 shows Eyring plots for both reactions, and lists the activation parameters derived from both Eyring and Arrhenius analyses of the temperature dependencies of the rate constants. It is readily apparent that the two additional tests for quantum mechanical tunneling are met. Indeed, the deviations are extreme; thus the case for tunneling of the hydrogen atom is unambiguous. The observation of H-atom tunneling in this PCET is reminiscent of similar results in our earlier cobalt dioxygen chemistry.

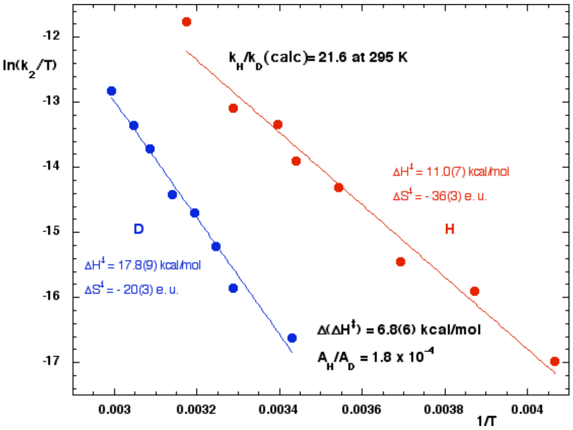
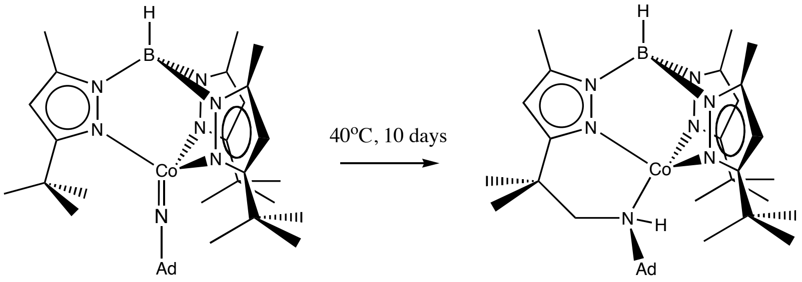


Figure 1. Activation parameters for the abstraction of H or D from dihydroanthracene.

Cobalt Imido Compexes: In lieu of a terminal cobalt oxo complex of the type 'TpCo=O', which has eluded us so far, we have investigated the synthesis and reactivity of the isolectronic imido derivatives $Tp^{t\text{-Bu,Me}}Co{=}NR$ (R= Me, Et, ^{t}Bu, Ad). The reactivity of the imido complexes resembles the oxo species in that it is dominated by C-H activation of the ligand (see Scheme 1).



Scheme 1. Insertion of imido ligand into a primary C-H bond of the $Tp^{t\text{-Bu,Me}}$-ligand

The presumed mechanism for this reaction involves a H-atom abstraction, and therefore we have measured rates and isotope effects. In this system, the isotope effects are relatively small, but the Eyring plots (for C-H and C-D insertion) show distinct curvature, beyond anything that can be explained by tunneling. We suggest that this behavior reflects a temperature dependent switch in the rate determining step of the reaction, and DFT calculations support that notion.

Iron Chemistry: The prevalence of iron in oxidation enzymes and the position of this element between chromium and cobalt (which have figured prominently in our earlier work) has motivated an exploration of $Tp^{tBu,Me}Fe$ chemistry. We have prepared the dinitrogen complex $(Tp^{tBu,Me}Fe)_2(\mu\text{-}N_2)$, see Figure 2. In solution, the dinuclear N_2 complex exists in equilibrium with its mononuclear analog $Tp^{tBu,Me}Fe(N_2)$.

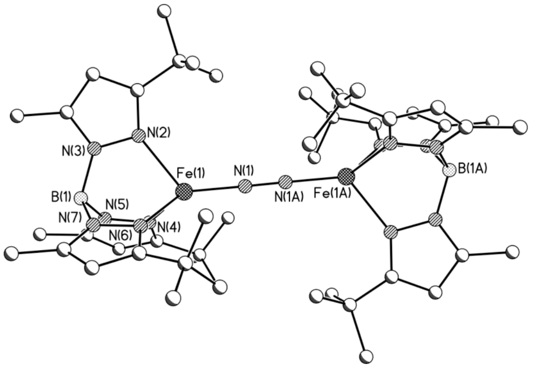
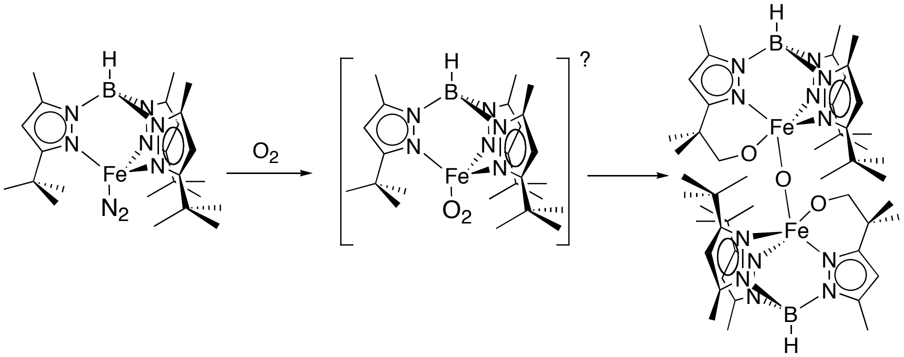


Figure 2. The molecular structure of $(Tp^{tBu,Me}Fe)_2(\mu\text{-}N_2$

These substitutionally labile compounds react rapidly with a wide variety of ligands, for example, they provide an entry point into dioxygen chemistry of the $Tp^{tBu.Me}Fe$ fragment.The reaction of $(Tp^{tBu,Me}Fe)_2(\mu\text{-}N_2)$ with O_2 yielded the binuclear Fe(III) complex shown in Scheme 1.

Scheme 1



This reaction is yet another example of an O_2-activation that leads to a hydrogen atom abstraction from an unactivated C-H bond; it is related to chemistry we have observed with Co(III) imido complexes of the type Tp'Co=NR. Speaking of imido complexes, reaction of $(Tp^{tBu,Me}Fe)_2(\mu\text{-}N_2)$ with organic azides has yielded novel iron imido complexes, such as the structurally characterized $Tp^{tBu,Me}Fe$=NAd and $Tp^{tBu,Me}Fe$=N(3,5-Me_2Ph). Their reactivity is currently being screened.

Future plans

We are investigating the reduction of N_2 upon coordination to chromium. To encourage PCET, we are preparing redox-active ligands, i. e., ligands that utilize metallocene moieties for both steric protection and electron delivery.

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Catalysis Involving Low-Valent Main-Group Fragments and Synthons

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Group 4 metals supported by triamidoamine ligands are effective catalysts in the synthesis of element–element bonds in the main group. Zirconium complexes of the general type $(N_3N)ZrX$ ($N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$; X = anionic ligand) have been demonstrated to undergo selective P–P bond formation by dehydrocoupling of primary and secondary phosphines [1]. Based on mechanistic study, which established that bond formation proceeds via σ-bond metathesis steps, heterodehydrocoupling schemes involving P–Si and P–Ge bond formation have been discovered using these same catalysts [2]. Recently, these systems have been shown to generate low-valent species by direct or indirect routes resulting in the catalytic preparation of element–element double bonds. Thus, $(N_3N)ZrX$ complexes dehydrocoupled 2,6-dimesityphenylarsine ($dmpAsH_2$) to give the diarsene product, dmpAs=Asdmp. Study on the related mesitylarsinido complex, $(N_3N)ZrAsHMes$ supported the hypothesis that extrusion of a low-valent arsenic fragment (an arsinidene, "AsR") termed via α-arsinidene elimination occurs [3]. Indirect generation of a phosphinidene synthon has been achieved via a combination of insertion and rearrangement. Zirconium primary phosphido complexes, $(N_3N)ZrPHR$, reacted rapidly with isocyanides to give insertion products, $(N_3N)ZrC(PHR){=}NR$. These products thermally rearrange to form amido ligands featuring phosphaalkene (P=C) linkages [4]. Recent developments suggest that this transformation can be made catalytic, which is the first catalytic synthesis of phosphaalkenes.

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One and two electron transformations of iron nitrido complexes

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Iron(IV) nitrido complexes supported by strongly donating tris(carbene)borate ligands are prepared in high yield by photolysis of precursor iron(II) azido complexes. Structural and spectroscopic investigations have been used to elucidate the electronic structure of these complexes. The nitrido ligand is electrophilic and reacts with triarylphosphines to produce iron(II) phosphinaminato complexes by a bimolecular mechanism. The nitrido complexes react with hydrogen atom sources (e.g TEMPO-H) to produce NH_3 by a mechanism that is proposed to involve multiple hydrogen atom transfer steps. Similarly, reaction with carbon-based radicals allows for the assembly of N-C bonds.

Wednesday Morning Sessions

Hydrogen peroxide: the ideal oxidant. New advances for its synthesis and some catalytic applications in the selective epoxidation of simple alkenes

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Nowadays hydrogen peroxide is being considered the ideal oxidant for many applications, mainly because of its environmental acceptability, water being its reduction product. However, the industrial production of hydrogen peroxide relies almost completely on the hydroquinone process that is run only on a very large scale and is highly energy consuming. Distributed production on small scale facilities can be performed by direct synthesis from H_2/O_2 catalyzed by noble metals. This process has always been considered with some reluctancy because of intrinsic safety problems. Recent attempts to carry out the reaction in a safe manner have relied either on the use of devices keeping hydrogen and oxygen separate (e.g. membrane reactors or modified fuel cells) or operating with powder catalysts outside the explosion limits. In both cases Pd catalysts have shown some promising results in terms of activity, selectivity and hydrogen peroxide productivity operating at room temperature and atmospheric pressure.

Among the applications of hydrogen peroxide in organic synthesis, the epoxidation of simple unfunctionalyzed terminal alkenes such as propene, 1-hexene, 1-octene, etc. has always been very challenging because of their intrinsically poor reactivity. Devising new catalysts capable of activating the substrate instead of the oxidant is crucial. New soft Pt(II) Lewis acid catalysts can be prepared showing exceptional activity in this reaction using commercial 35% H_2O_2 as the oxidant, mainly because of the poor reactivity of noble metals towards water, a reactant that should be avoided with ordinary, oxophilic Lewis acids. Unprecedented selectivity is observed in the epoxidation of dienes (terminal and internal double bonds). Enantioselectivities up to 87% are observed using chiral-diphosphine modified catalysts. The system can be easily run also in water medium using surfactants as dispersing agents. Mechanistic insight shows that the reaction proceeds via direct activation of the olefin by the metal, followed by nucleophilic attack of the oxidant.

DE-FG02-86ER13615 **Bradford B. Wayland**

Catalytic Hydrogenation of Carbon Monoxide and Olefin Oxidation

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Goal

This program encompasses a set of objectives for the development of new strategies, catalyst materials, and media for the activation of CO, H_2, CH_4, C_2H_4, O_2, CH_3OH, H_2O, and related substrates relevant to the conversion of carbon monoxide, alkanes, and alkenes to organic oxygenates. One central objective is the design and synthesis of metal complexes that manifest reactivity patterns associated with potential pathways for the hydrogenation of carbon monoxide including routes where CO reacts to produce metallo-formyl (M-CHO), dimetal ketone (M-C(O)-M), and dimetal dionyl (M-C(O)-C(O)-M) species. Ancillary goals include development of hydrocarbon oxidations that utilize dioxygen, exploring the range of substrate reactions in water and ionic liquid media, and expansion of the thermodynamic database for organo-metal processes in a range of reaction media.

DOE Interest

The goals of this program in small molecule transformations are directed toward advancing the DOE-BES core objective to innovate new technologies that provide fuels and chemical feedstock by processes with minimum environmental impact and that are derived from abundant and sustainable sources. Unusual forms of metal promoted carbon monoxide reduction and coupling provide new opportunities to utilize CO produced from both biomass and coal in the formation of fuels and organic materials. Evaluation of the scope and thermodynamics for organo-metal substrate reactions in water provides a foundation for the rational design of catalytic processes in water.

Recent Progress

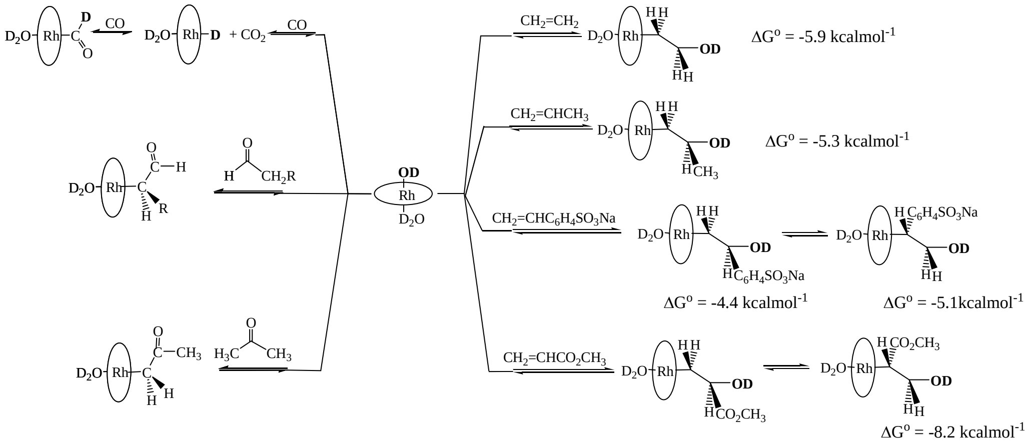
Tethered bis-metalloporphyrin complexes for reactions where two metal sites occur in the transition state: The broad objective for this aspect of our program was to evaluate the effects that result from tethering two or more metal complexes together so as to provide pre-organization for transition states that involve several metal centers. The primary objectives were in activation of saturated hydrocarbons which continues as a focus area for organometallic catalysis research. Substrate reactions of the dirhodium(II) derivatives were used to illustrate the effectiveness of this strategy. The dirhodium(II) complex of the mesityl derivative is a bimetalloradical, and the lower steric demanding phenyl derivative gives a diamagnetic Rh^{II}-Rh^{II} bonded complex.

Reactions with CO: The *m*-xylyltethered tetraphenylporphyrin derivative ((TPP)Rh^{II}(*m*-xylyl)Rh^{II}(TPP)) has a weak Rh^{II}-Rh^{II} bond and reacts readily with CO (P_{CO} < 1atm) to form a one-carbon bridged dimetal ketone (M-C(O)-M). The more sterically demanding mesityl derivative ((TMP)Rh^{II}(*m*-xylyl)Rh^{II}(TMP)) prohibits Rh^{II}-Rh^{II} bonding and the one-carbon bridge, and reacts with CO to produce the two-carbon bridged dirhodium diketone complex. Carbon monoxide reductive coupling to form a C-C bonded dionyl unit (-C(O)-C(O)-) is currently accessible only through this class of sterically demanding rhodium(II) porphyrin species.

Organo-metal reactivity and thermodynamic studies in water: Application of organometallic transformations in water as a means to circumvent the use of organic solvents is a prominent current theme of environmental and energy related catalysis research. The exceptionally broad range of H_2, CO, and hydrocarbon substrate reactions for group 9 metalloporphyrins previously observed in hydrocarbon media have been systemically evaluated in water. Each of the (por)Rh-H reactions with unsaturated substrates including CO, H_2CO, and CH_2=CH_2 that produce M-CHO, M-CH_2OH, and M-CH_2CH_3 complexes that were first recognized in organic media now have been observed to have a parallel process in water. These classes of metal hydride reactions with unsaturated substrates play a central role in many of the most important catalytic processes such as hydrogenations, hydroformylation, and many related transformations.

A major objective of this study was advanced by obtaining equilibrium thermodynamic values for reactions of tetra(*p*-sulfonatophenyl)porphyrin rhodium hydride ((TSPP)Rh-H) with carbon monoxide, formaldehyde, and ethene as a bench mark for late transition metal hydride addition reactions with unsaturated substrates. Determination of equilibrium constants for reactions of CO, CH_2O, and CH_2=CH_2 with the hydride provides the first opportunity to compare experimental thermodynamic values for reactions of a metal hydride with this important series of substrates. Thermodynamic studies on a common set of processes in organic and aqueous media provide quantitative criteria for the comparison and prediction of substrate reactivity patterns, and to aid in identifying the origins of the factors contributing to medium effects.

Regioselectivity and Equilibrium Thermodynamics for Addition of Rh-OH to Olefins in Water: Addition of the Rh-OH unit in (TSPP)Rh-OH complexes with olefins to form β-hydroxyalkyl complexes is a new class of substrate reactions that was recently observed. Equilibrium thermodynamic values for these reactions are the only data available for this type of process. These reactions are the entry point into olefin oxidation processes to form aldehydes, ketones, and epoxides.



Future Plans

Incorporation of CO and olefin substrate reactions into catalytic cycles for carbonylation and oxidation processes is a high priority future objective. Tuning of substrate reactivity by medium effects will be extended to ionic liquids that support ionic species but are weak donors. Substrate reactivity and thermodynamic studies will be expanded to water and alcohol O-H bond reactions with cobalt, rhodium, and iridium macrocyclic complexes. Design of metal complex appended amphiphilic block copolymers that self-assemble into nano-structured arrays for catalysis applications is a new direction for this program.

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DE-FG02-03ER15387 **Thomas R. Cundari**

Computational Studies of Ligand and Catalyst Design and Catalytic Mechanisms

Postdoc:	Dr. Nathan J. DeYonker
Graduate Students:	Tom Grimes (Ph.D. ’07), Khaldoon Barakat (Ph.D. ’07), Adriana Dinescu (Ph.D. ’07), Aaron Pierpont, Glenn Morello
Collaborators:	Brent Gunnoe (NCSU), Pete Wolczanski (Cornell U.), Abul Kazi (UA-Pine Bluff), Angela Wilson (UNT), Kirk Peterson (WSU)
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Goal:

Our research focuses on development of improved computational methods for modeling transition metal chemistry, the application of such methods to organometallic catalysis, and integration of modeling and simulation with the research of leading experimental groups to study catalytic mechanisms relevant to the DOE-BES mission. Through the combination of the aforementioned foci, we seek to identify promising next-generation catalyst/ligand systems for further computational and experimental research.

DOE Interest:

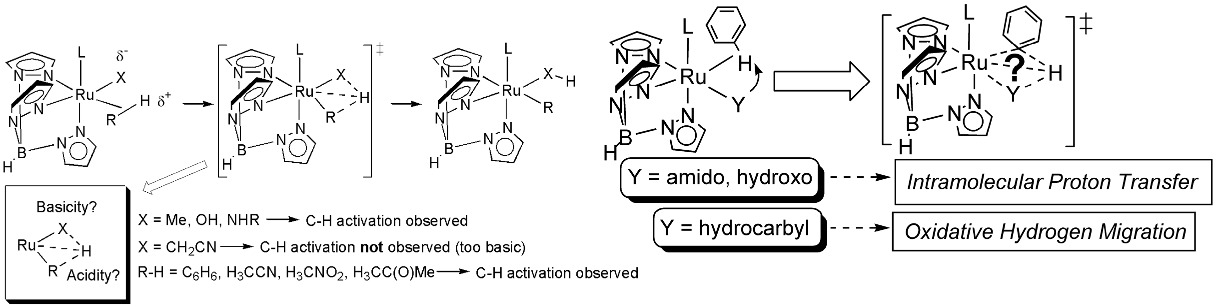
Understanding the fundamental principles by which steric and electronic manipulation of a metal and/or ligand affect reaction mechanisms and thus activity and selectivity is essential in the design of improved catalysts. Transition metal catalysis plays a pivotal role in numerous current and future technologies that are central to the DOE mission. Areas that are vital to the DOE-BES research portfolio include the more efficient utilization of hydrocarbon resources from petrochemical and natural gas feedstocks, and as these become scarcer, more practical routes to the use of alternative hydrocarbon feedstocks like biomass.

Recent Progress

Significant recent progress under the aegis of **DE-FG02-03ER15387** support has been made on several research fronts, including the role of spin states in transition metal catalysis, catalytic group transfer to alkenes and alkanes, catalytic arene functionalization, and quantitative thermochemistry for transition metals and transition states. We will focus here on the latter two research thrusts.

Catalytic arene functionalization:

Aromatic hydrocarbons remain an important feedstock for the synthesis of higher-valued derivatives at the industrial and commodity chemical scales. Indeed, given their prevalence in biomass, the importance of catalysis involving aromatics will only grow in the future. Research in C-H activation and arene functionalization in conjunction with fellow DOE-BES contractor T. Brent Gunnoe’s group (North Carolina State University) elucidated several important factors affecting the activity and selectivity of catalysts direct for arene functionalization (*e.g.*, ethylene plus benzene to ethylbenzene). Several studies were conducted – a theory/experiment Hammett analysis of C-H bond activation rates of substituted benzenes, the C-H bond activation of hetero-substituted aliphatics (MeCN, acetone, THF, *etc.*), and benzene C-H activation by d^6 transition metal scorpionates. Taken together, this research is leading to an improved understanding of metal/ligand control of catalysts for olefin hydroarylation (schematic depictions shown below in Scheme 1), for example, (a) the importance of controlling acid/base properties of the metal vis-à-vis activity/selectivity of C-H activation of functionalized hydrocarbons, (b) the crucial balance between substrate access and C-H bond strength/acidity in effective catalysis of functionalized substrates, and (c) the fundamental shift in C-H activation mechanism with activating ligands that have available lone pairs.



Scheme 1

Accurate Energetics: Transition Metals and Transition States:

The emphasis of our research program remains the investigation of catalyst systems and mechanisms, and the integration of leading-edge theory with cutting-edge experimental research to identify promising new chemistry that can lead to more efficient utilization of hydrocarbons. However, our group also continues to pursue new and innovative computational strategies that can benefit BES-DOE contractors (and thus the DOE mission) both near and long term.

Energies are the key to catalyst design. This simple observation, coupled with the importance of transition metal-based catalysts, immediately indicates the great potential for computational approaches for the accurate calculation of transition metal thermodynamics. Thus, the Cundari group has put considerable collaborative effort into the development of methods for prediction of accurate metal thermodynamics. Despite tremendous improvements in theory and simulation over the past decade by numerous groups, calculation of accurate metal energetics (e.g., to a target chemical accuracy of 1 – 2 kcal/mol) for chemically diverse families of complexes remains an unrealized goal. We have made considerable advances to extend our ccCA (correlation consistent composite approach) method to achieve the long-range goal of quantitative transition metal thermodynamics.

Another area of obvious importance to catalysis, is the prediction of reaction barrier heights. The ccCA method was applied to a standard benchmark set of reactions comprised of both hydrogen-transfer reactions and non-hydrogen transfer reactions (*i.e.*, heavy-atom transfer, S_N2, and unimolecular reactions). The ccCA method was compared against G3B for the same set of reactions. Error metrics indicate that ccCA achieves "chemical accuracy" with a mean unsigned error (MUE) of 0.89 kcal/mol with respect to the benchmark data for barrier heights; G3B has a mean unsigned error of 1.94 kcal/mol. Further, the greater accuracy of ccCA for predicted reaction barriers is compared to other benchmarked literature methods, including density functional (BB1K, MUE = 1.16 kcal/mol) – which was specifically developed to accurately predict rates - and expensive, wavefunction-based (QCISD(T), MUE = 1.10 kcal/mol) methods.

Future work:

Catalytic Activation of Hydrocarbon

We will continue to collaborate with the Gunnoe group in both theory-led and experimental-led studies of novel olefin hydroarylation complexes with enhanced activity and selectivity. Thrust areas in include: (a) identify/characterize novel catalysts that can maintain activity with a phosphine coligand (to control desired regiochemistry for olefin hydroarylation), and (b) model non-ruthenium complexes with enhanced activity.

Accurate Energetics: Transition Metals and Transition States:

Postdoctoral associate, Dr. Nathan DeYonker, is interfacing with DOE scientists to incorporate ccCA into PNNL's NWChem quantum chemistry package. This work will aid greater dissemination of the ccCA methodology to the scientific community, and will accelerate ever larger modeling efforts for which accurate thermochemistry is essential. In a parallel research effort with the Wilson group at UNT we seek to improve ccCA to the point of it being a "black box" method for larger, more experimentally relevant transition metal complexes, which can thus yield chemically accurate thermodynamics for materials incorporating elements from across the periodic table.

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Poster Sessions

AL-08-380-019 **R. J. Angelici, A. Bakac, V. S. - Y. Lin, M. Pruski, A. Sadow, K. Woo**

Homogeneous and Interfacial Catalysis in 3D Controlled Environments

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Goal

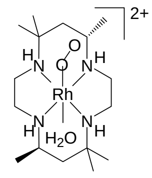
Discover new catalytic principles in solutions and on surfaces. Develop new catalysts and specific catalytic systems for targeted reactions that are important to the missions of the DOE, such as oxygen activation, hydroamination, polymerization, and others. Develop new synthetic methods for the preparation of mesoporous oxide catalysts with well-defined pore/particle morphology and surface properties.

Recent Progress

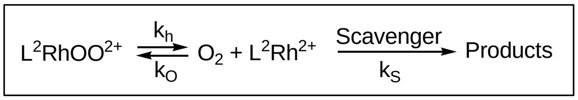
(1) Oxygen activation by transition metal complexes. Coordination and stepwise reduction of molecular oxygen at metal centers in industrial, laboratory, and biological oxidations generates a number of reactive intermediates. A great majority of mechanistic work with transition metal-activated oxygen has focused on oxidations of organic substrates but little is known about the reactions of metal-based intermediates with substrates or with organic and inorganic transients. This chemistry is the topic of our research.

Superoxochromium(III) complexes $L(H_2O)CrOO^{2+}$ ($L = (H_2O)_4$ and N_4 macrocycles) oxidize hydroperoxo complexes of rhodium and cobalt in an apparent hydrogen atom transfer (HAT) process, i e.

$$L(H_2O)CrOO^{2+} + L(H_2O)RhOOH^{2+} \rightarrow L(H_2O)CrOOH^{2+} + L(H_2O)RhOO^{2+}.$$

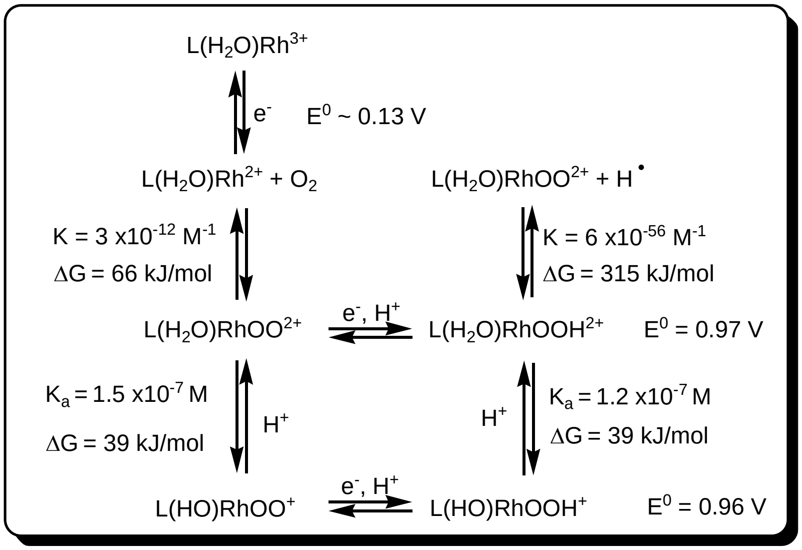


$L^2(H_2O)RhOO^{2+}$



These reactions have rate constants in the range 17 – 135 M^{-1} s^{-1} and exhibit a deuterium kinetic isotope effect of 2.5 – 3.0. The rates of oxidation of $L(H_2O)RhOOH^{2+}$ by $Cr_{aq}OO^{2+}$ are comparable to those for the oxidation of the corresponding hydrides despite the >80 kJ/mol difference in the driving force for the two reactions. Nitroxyl radicals (X)TEMPO (X = H, 4-OH, and 4-oxo) also reduce $Cr_{aq}OO^{2+}$ and $Rh(NH_3)_4(H_2O)OO^{2+}$ to the corresponding hydroperoxo complexes. The kinetics of $RNO^{\bullet}/LMOO^{2+}$ reaction are largely acid independent for $Cr_{aq}OO^{2+}$, but acid catalysis dominates the reactions of the rhodium complex. This emerging trend in oxidations with superoxo complexes seems directly related to the thermodynamics of electron transfer: the weaker the oxidant, the more important the acid-assisted path. Thermodynamic data, including reduction potentials, bond dissociation free energies, and acidity constants have been obtained for macrocyclic superoxo and hydroperoxo rhodium(III) complexes, $L^2(H_2O)RhOO^{2+}$ and $L^2(H_2O)RhOOH^{2+}$. Our approach utilized a combination of kinetic and equilibrium measurements tailored specifically for these intermediates. The type of information obtained here is rare in the realm of oxygen activation owing to the short lifetimes and low concentrations of reaction intermediates. The reduction potential for the $L^2(H_2O)RhOO^{2+}/L^2(H_2O)RhOOH^{2+}$ couple, $E^0 = 0.97$ V vs NHE, almost independent of pH, was determined in equilibrium measurements with suitable substrates. Thermochemical calculations yielded the bond-dissociation free energy of the $L^2(H_2O)RhOO\text{-}H^{2+}$ bond, BDFE = 315 kJ/mol at 298 K, which is over 60 kJ/mol smaller than that for the parent H_2O_2. The kinetics of disappearance of $L^2(H_2O)RhOO^{2+}$ in the presence of several oxidants yielded information on the energetics of the $Rh\text{-}O_2$ bond and the value of the homolysis rate constant, $k_h = 2.18 \times 10^{-4}$ s^{-1} at 25.0^0 C.

The equilibrium constant for O_2 binding to $L^2(H_2O)Rh^{2+}$ is 10^9-fold greater than that for the cobalt analog, $L^2(H_2O)Co^{2+}$. This difference is attributed to the lower reduction potential of the rhodium complex.



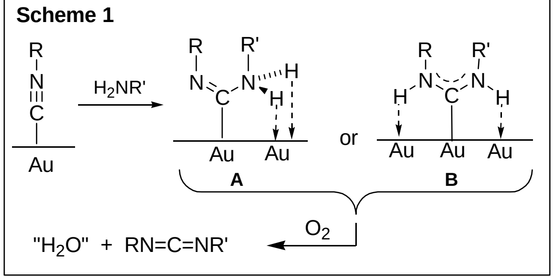
Triarylphosphine oxides, $OPAr_3$, do not readily exchange oxygen with standard solvents. The transfer of isotopically labeled oxygen from a donor to PAr_3 therefore provides unequivocal demonstration of the mechanism. Phosphines also serve as standards in determinations of aqueous protonation constants, K_H, for other substrates. These determinations are based on proton transfer equilibria between the species of interest and a phosphonium ions of known K_H. We have now found that the literature K_H's of triarylphosphines are incorrect, and that the actual values are several orders of magnitude lower than reported. Our determinations are based on two independent methods, ^{31}P chemical shifts, and kinetics of debromination of a vicinal dibromide.

$$\boxed{HPPh_3^+ + H_2O \rightleftharpoons PPh_3 + H_3O^+ \quad K_H = 1.5\ M^{-1}\ (\text{in } 1{:}1\ H_2O/CH_3CN)}$$

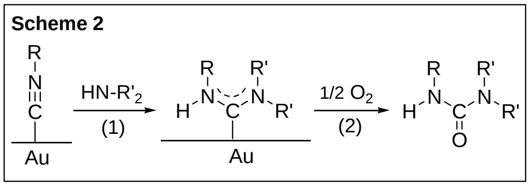
(2) Organometallic chemistry and catalysis on bulk gold metal. Isocyanides (C≡N–R) adsorbed on gold surfaces react with primary amines in the presence of oxygen or air to give carbodiimides. Kinetic studies using gold powder as a catalyst suggested that the reaction involves nucleophilic attack of the amine on the adsorbed isocyanide (Scheme 1). Secondary amines (HNR'_2) also react, but the number of hydrogen atoms in this system precludes the formation of the carbodiimide; ureas are formed instead. Our proposed mechanism (Scheme 2) again involves nucleophilic attack (step **1**) on the adsorbed isocyanide followed by reaction (step **2**) of the diaminocarbene intermediate with O_2. The details of the reaction with O_2 in step **2** have no simple precedents. We next explored the reaction of primary amines and O_2 with CO, which is isoelectronic with isocyanides but does not adsorb on bulk gold surfaces under the mild conditions in our work. Nevertheless, we find that gold powder does catalyze the reaction of CO with primary amines and O_2 to give isocyanates, which react further to give ureas.

$$R{-}C{\equiv}N + H_2N{-}R' + 1/2\ O_2\ (1\ \text{atm}) \xrightarrow[\text{Hexane}]{\text{Au, 60 °C}} R{-}N{=}C{=}N{-}R' + H_2O$$

Scheme 1



Scheme 2



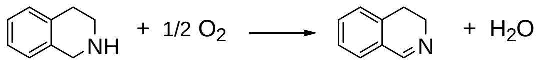
These reactions occur at 45 °C, 0.7 atm CO, and 0.3 atm O_2. The formation of isocyanates in the first step parallels the formation of carbodiimides in the reactions with isocyanides. The mechanism is believed to involve nucleophilic attack of the amine on adsorbed CO in analogy to the reaction of isocyanides (Scheme 1).

$$\boxed{C{\equiv}O + NH_2\text{-}R + 1/2\ O_2 \xrightarrow{Au} \text{"}H_2O\text{"} + O{=}C{=}N\text{-}R \xrightarrow{NH_2\text{–}R} O{=}C(NHR)_2}$$

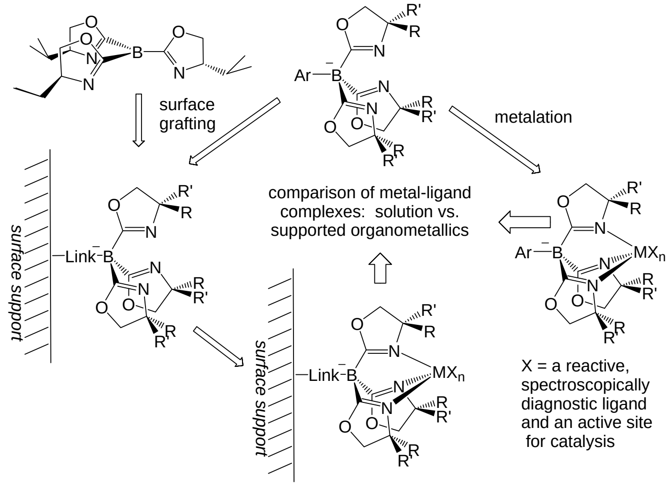
In a very different type of reaction, gold catalyzes oxidative dehydrogenation of benzylic amines to give imines. Diisopropylamine also gives the corresponding imine but the reaction is slower. The mechanisms of these dehydrogenation reactions are not known, but the gold surface must activate, in some manner, the C–H and N–H bonds, as well as O_2.

The gold-powder catalyzed reactions described here are significant because they involve a bulk form of gold. Decades of study have shown that bulk gold has very low catalytic activity. It is only recently that gold nanoparticles (< 5 nm) have been found to be highly active for several reactions including the oxidation of carbon monoxide. Not only do the preparations of supported nanogold catalysts require special care but their activities usually decline with use. In contrast, the large gold particles (~10^3 nm) used in this work are highly active and may be recycled many times.

$$PhCH_2NHCH_2Ph + 1/2\ O_2 \longrightarrow PhCH_2\text{-}N{=}CHPh + H_2O$$



(3) Modular boron bridged (oxazoline) ligands. These ligands serve as ancillary frameworks for homogeneous and supported organometallic chemistry. We have prepared a few classes of 2-oxazoline-boron compounds. In particular, tris(2-oxazolinyl)phenyl borate **To**$^{R-}$ (using 4,4-dimethyl-2-oxazoline, **To**$^{M-}$, and 4*S*-isopropyl-2-oxazoline, **To**$^{P-}$) serve as ancillary ligands for soluble organometallic compounds. We isolated yttrium(III), zirconium(IV), rhenium(I), ruthenium(II), and iridium(I) and (III) complexes of $[To^R]^-$. Additionally, the $[To^R]^-$ ligands facilitate the identification and comparison of species in solution and in the solid state. Solution and solid state ^{15}N NMR and ^{11}B NMR spectroscopies were used to characterize these complexes. For example, solid state ^{15}N NMR spectrum of $[Ir(To^P)(\eta^4\text{-}C_8H_{12})]$ indicates that the compound exists as a mixture of κ^2- and κ^3-isomers (4- and 5-coordinate, respectively). Additionally, the ν(C=N) stretching frequencies in the infrared spectrum, correlated with results from computation models, identify the metal's coordination environment and compare solution and supported structures.



(4) New and efficient synthetic route to mesoporous mixed oxide catalysts. The feasibility of our new method has been demonstrated in the synthesis of a mesoporous calcium silicate mixed oxide material for the transesterification reaction in biodiesel synthesis. In contrast to other reported mixed oxides, where the different oxides are usually distributed in domains and separated from each other, our mesoporous silica/calcium oxide catalyst shows a homogeneous distribution of calcium and silicon oxides as confirmed by solid-state ^{29}Si NMR spectroscopy. This new synthetic method is also useful for producing a mesoporous aluminum silicate (Al-MS) material. Solid-state NMR studies showed that the aluminum atoms are tetrahedrally coordinated and are stable up to at least 400 ºC. The double resonance $^{27}Al\text{-}^{29}Si$ NMR experiment provided first direct evidence that all Al atoms are surrounded by Si atoms forming Al-O-Si bonds in the framework. The silicon to aluminum atomic ratio at the surface $(Si/Al)_s$ is estimated at around 100, which exceeds the overall Si/Al ratio of 60. Reactivity study of the mesoporous aluminosilicate shows excellent catalytic reactivity for the Claisen rearrangement of allyl phenyl ether, despite the low surface concentration of Al.

We demonstrated remarkable new capabilities of solid-state NMR spectroscopy by combining fast magic angle spinning (at 2-3 million rpm) with new multiple RF pulse sequences. The latest exploit was to seek sensitivity gain in heteronuclear correlation (HETCOR) spectroscopy of MSN's through the detection of high-γ (^{1}H) rather than low-γ (e.g., ^{13}C, ^{15}N) nuclei. This so-called indirect detection method has been hitherto impossible due to the lack of adequate ^{1}H homonuclear decoupling schemes. The technique yielded well resolved two-dimensional (2D) ^{13}C-^{1}H HETCOR spectra of surface-bound species under natural abundance within minutes, a result that earlier would have been considered unrealistic. The first ^{15}N-^{1}H spectrum of surface species bound to a surface was acquired, also without isotope enrichment. Most recently, we measured the indirectly detected through-bond 2D ^{13}C-^{1}H spectra of surface species. In another study, solid-state NMR and DFT calculations were used to refine the structures of covalent linkages formed during organic functionalization of silicas. The geometry of NMR-derived structures was optimized by our collaborators using molecular mechanics and *ab initio* methods. Subsequently, DFT calculations of ^{29}Si, ^{13}C and ^{1}H chemical shifts were performed, which agreed very well with the experiments.

DOE Interest

Our research addresses homogeneous activation of molecular oxygen, catalytic chemistry on bulk metal surfaces, design of new ligands and catalytic systems that function in both homogeneous and 3D environments, and design, synthesis and application of functionalized mesopores in catalysis. This work combines the most attractive features of homogeneous and heterogeneous catalysis, addresses the underlying principles of activation of organic molecules on metal surfaces, and provides a framework for new selective catalytic conversions involving bond activation and hydrocarbon functionalization. All of these issues are central to DOE mission.

Future work

Determination of reduction potentials and exchange kinetics for hydrogen atom or and/or proton-coupled electron transfer (PCET) in the chemistry of metal-activated oxygen. An understanding of the rate constants and trends in hydrogen atom transfer reactions of metal superoxo complexes, including the unexpectedly slow reactions with rhodium hydrides, requires the knowledge of the O-H bond energies and exchange rate constants for superoxo-hydroperoxo couples in water. We will design methods and carry out kinetic measurements on cross reactions (HAT and electron transfer), to obtain the needed parameters from thermochemical cycles (for bond energies) and Marcus relationship (for kinetics of self reactions).

Catalytic oxidation chemistry with Fe(IV). Our recent work on generation, characterization, and reactivity of $\mathrm{Fe^{IV}_{aq}O^{2+}}$ in water has shown that 2-electron oxidations, which are a prerequisite for catalysis, take place by both oxygen atom and hydride transfer, but the latter often competes with the undesirable one-electron processes, such as HAT. Future studies will focus on identifying reaction conditions, substrates, and ligands that favor the 2-e chemistry which should lead to efficient iron catalysts.

Formation and reactivity of carbene species on gold surfaces. In order to probe more broadly the reactivity of carbenes on bulk gold, we will seek to create carbenes on Au using several new methods. These will follow known reactions of transition metal complexes that give carbene complexes. It should be emphasized that Au metal differs from metals in coordination complexes. Thus, the proposed reactions will also test the postulate that ligand reactions in metal complexes are a useful guide to reactions on metal surfaces.

Catalytic applications of yttrium and zirconium complexes. Given the symmetry and easily accessed chirality of $[\mathrm{To^R}]^-$ ligands, we are developing olefin insertion-based catalyses including hydroamination and polymerization, for which selectivity and activity remain key issues. The zirconium complexes, when activated with methylaluminoxane, catalyze ethylene polymerization. We are preparing well-defined cationic alkyl complexes to further investigate the selectivity of insertion polymerization.

Influence of the mesopore environment on catalyst selectivity and activity. Our ability to anchor multiple types of groups on mesopore walls allows us to tether not only the catalyst but also other functional moieties. The influence of these auxiliary groups will be directed toward achieving various catalyst functions, such as enantioselectivity. These studies will use the concept of gatekeepers, which will be tested.

Cooperative catalysis inside mesopores. To study how various functional groups could synergistically catalyze a reaction in a 3-D controlled environment, we will functionalize the surface of mesopores with two to three different types of catalytically active moieties and vary the relative ratio and spatial distribution of these functionalities. As a proof of principle, functional groups that can serve as general acids and bases will be introduced to study the selective carbon-carbon bond formation and carbonyl activation.

Characterization of cooperative catalysts. We will use the sensitivity and the resolving power of indirectly detected 2D and 3D X-^{1}H correlation NMR spectroscopy to characterize the topology of increasingly complex molecular structures on the catalyst surface. Our preliminary results indicate that by introducing additional spin recoupling pulse sequences, we can study the distances between different types of functional groups, e.g., in acid-base cooperative catalysts.

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DE-AC05-76RLO 1830 **Tom Autrey**

Control of Hydrogen Release and Uptake in Condensed Phases

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Goal

The objective of our research is to expand fundamental insight into hydrogen rich materials that will provide the basis for developing new hydrogen storage systems. We propose that: (i) hydrogen release from materials comprised of electron-rich and electron-poor sites, i.e., protonic and hydridic hydrogen, is greatly enhanced, (ii) metal (M_4 and/or M_6) clusters are important species in the catalysis of hydrogen release and uptake, and (iii) nanoscale effects and interfacial interactions enhance kinetics and modify thermodynamics of hydrogen storage materials.

DOE Interest

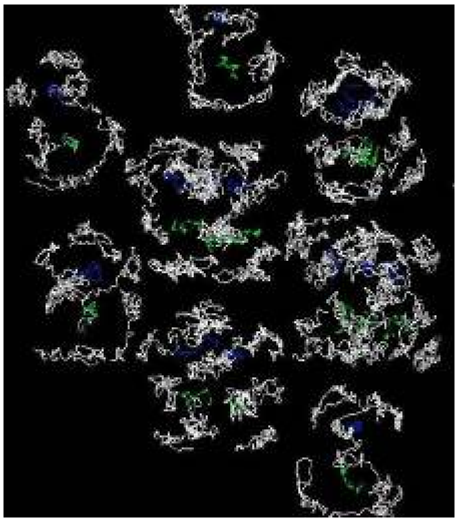
The US DOE issued a Grand Challenge for Basic Research in Hydrogen Storage calling for significant new breakthroughs to develop novel materials to store hydrogen on-board fuel cell powered vehicles. Our research uses a combination of experiment and theory to develop fundamental insight into the chemical and physical properties that control the structure and dynamics of compounds composed of protonic and hydridic hydrogen is the focus of our research. The effects resulting from nanoscaling of hydrogen rich materials and interfacial interactions are explored. This research will result in knowledge that will lead to the development of new materials that release and absorb hydrogen at moderate temperatures and pressures. In consequence, the work specifically addresses the focus area "Novel Materials for Hydrogen Storage" and the "Design of Catalysts at the Nanoscale" of the Hydrogen Fuel Initiative.

Recent Progress

The NH_xBH_x series of compounds composed of protonic $NH^{\delta+}$ and hydridic $BH^{\delta-}$ hydrogen has been a focus of our research. Our work integrates experimental and molecular modeling tools to develop a description of the long-range, average or static structure of a crystalline hydrogen rich material and then progressively addresses more complex and collective phenomena. This begins by establishing a framework of local structure that is enhanced by an understanding of the dynamics using experimental probes sensitive to a broad range of length and time scales in conjunction with state-of-the-art molecular simulation methods outlined in Table 1. This 'multi-level' approach provides a comprehensive understanding of molecular crystals, (AB) $NH_3 \rightarrow BH_3$, (ABH2) $[NH_4][BH_4]$, (DADB) $[NH_3BH_2NH_3][BH_4]$ and can be readily extended to other studies of complex condensed matter systems.

Complexity	Average Structure	Local Fluctuations	Large Amplitude Fluctuations	Collective Phenomena
Phenomena	Average Structure	Vibrational Dynamics	Rotational Dynamics	Molecular Transformations
Theory	Minimum Energy Structures, Thermal Ensembles of Configurations	Normal Mode Analysis, Power Spectra	Potentials of Mean Force, Nudged Elastic Band calculations of minimum energy path	Characterizing catalytic pathways and mechanisms
Experiment	NPD, XRD	Raman, IR, INS	^{2}H NMR, QENS	NMR, XAFS

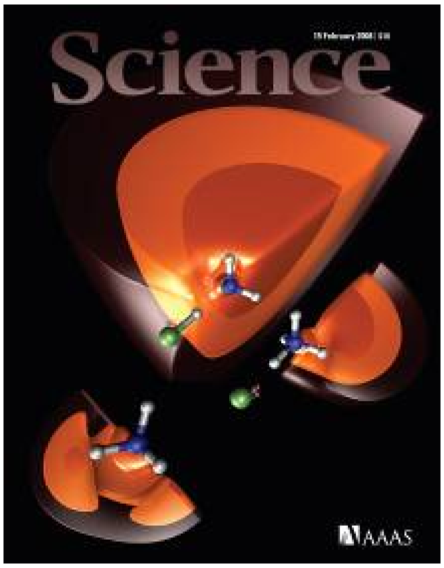
Average Structure. The structure of the orthorhombic phase of AB obtained from Rietveld analysis of the Neutron Powder Diffraction (NPD) data was measured from 10 - 275 K to compare with results from dynamics modeling. Figure on right is MD simulation of AB for 7 ps at 275 K. (H atoms in white, B in green, N in blue). Modeling shows the H is extremely dynamic and accounts for the large thermal ellipsoids observed in the neutron powder diffraction data obtained for $^{11}BD_3ND_3$.



Local Fluctuations. The phase transition in a single crystal of AB was studied using Raman spectroscopy as a function of temperature from 80 to 330 K. The orthorhombic to orientationally disordered tetragonal phase transition at 225 K was clearly evident from the decrease in the number of vibrational modes. This work was recently published in *JCP*.

Large Amplitude Fluctuations in Structure. Variable temperature ^2H (D)-NMR experiments on the orthorhombic phase of ND_3BH_3 and NH_3BD_3 spanning the static to fast exchange limits of the ND_3 and BD_3 motions were investigated to gain insight into the rotational dynamics. New values of the electric field gradient (EFG) tensor parameters have been obtained from the static ^2H spectra for the borane and amine hydrogens are compared. This work was recently accepted for publication in *JPC A*.

Complex Phenomena. We have suggested that proton transfer is a key step in the decomposition of solid AB (PCCP 2007). In collaboration with Kit Bowen at John Hopkins University we used *ab initio* electronic structure theory to help elucidate the mechanism of proton transfer in NH_4Cl. In contrast to accepted acid-base behavior in solution, single molecules of NH_3 and HCl do not react to form the ionic salt, $NH_4^+Cl^-$, in isolation. Using anion photoelectron spectroscopy and *ab initio* electronic structure theory the interaction of an excess electron with the hydrogen bonded complex $NH_4\cdots HCl$ was investigated. The results were recently published and featured on the cover of *Science*.



X-ray absorption fine structure (XAFS) is used to determine the structure of the rhodium cluster present during the catalyzed dehydrocoupling of amine boranes under operando conditions. We show how a variety of XAFS strategies can be used in combination with other analytical methods to differentiate homogeneous from heterogeneous catalysis. This work was recently published in *JACS*.

Future Plans

An overarching goal of this effort is the expansion of fundamental knowledge about the properties and processes of molecular and nanoscale systems in complex environments that are relevant to chemical and physical processes associated with hydrogen storage. *Specifically, we seek to develop a better understanding of molecular processes in hydrogen-bonded materials that have alternating electron-rich and electron-poor sites capable of covalently binding* $H^{\delta+}$ and $H^{\delta-}$, *respectively*. Priority will focused on four key topics:

NH_4BH_4 (ABH2). Molecular simulation predicts a *stable* zincblende structure, but Experiment shows a rock-salt type structure at room temperature that decomposes with a half-life of hours. Is there a low temperature phase transition from the disordered rock-salt to ordered zincblende structure as predicted by simulation? What triggers the phase transition? What is the enthalpy of H_2 loss to for DADB?

Better understanding of the structure and dynamics of ABH2 could lead to insight that would enable approaches to stabilize ABH2 at higher temperatures (i.e., >> 230K)

NH_3BH_3 (AB). There are two temperature ranges where significant changes in the average structure are observed; (1) just below the phase transition (<220 K) we observe anomalous hysteresis in the vibrational spectrum and (2) at temperature >340 K we observe disruption in the dihydrogen bonding network that appears to facilitate isomerization to DADB . What is happening to the dihydrogen bonding interactions at these two critical temperature ranges? What is triggering the phase transition? How does dihydrogen bonding affect the long-range correlated motions? This insight will enhance the understanding of the role of dihydrogen bonding on the structure and dynamics of AB.

$[NH_3BH_2NH_3][BH_4]$ DADB. We observe up to 3 different BH_4^- resonances in the solid state ^{11}B NMR spectra of DADB at room temperature. At 320 K we see these species collapse to one BH_4^- resonance. At room temperature is this a mixture of DADB and 'mistreated' DADB? What is the average structure of DADB (as a function of temperature)? At lower temperatures <200 K, do we see a transformation of DADB to "DADB II". What happens to the structure at higher temperatures, >320 K? It is important to gain insight into the average structure of DADB as a function of temperature as we have learned in the previous period a DADB-like compound significantly reduces the induction period for H2 release from AB.

Catalysis. In the catalyzed release of hydrogen from amine boranes we observed a mixture of both Rh_4 (ca. 80%) and Rh_6 (ca. 20%) clusters by XAFS spectroscopy under *operando* conditions. Using FEFF fitting procedures of the experimental XAFS data we narrow down the likely number of species to 5 likely candidates. Are the Rh_4 and Rh_6 clusters in equilibrium or formed by separate pathways? Can we use simulation and modeling to identify the active catalyst species starting with initial guesses from FEFF predictions? (As Rh_4 and Rh_6 catalyst cluster candidates are indentified we will synthesis the metal clusters and test their catalytic activity). A combination of experiment with simulation and modeling will enable unique insight that will permit the identification of active catalytic species.

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AL-08-380-019 **Andreja Bakac**

Thermodynamics of oxygen activation by transition metal complexes

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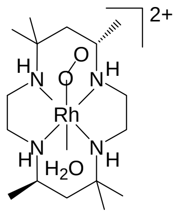
Hydrogen atom transfer between superoxochromium(III) complexes $L(H_2O)CrOO^{2+}$ (L = $(H_2O)_4$ and N_4 macrocyclic ligands) and hydroperoxo complexes of rhodium and cobalt is facile and irreversible, establishing that the OO-H bond in hydroperoxo complexes of chromium is stronger than for the other two metals.

$$L(H_2O)CrOO^{2+} + L(H_2O)RhOOH^{2+} \rightarrow L(H_2O)CrOOH^{2+} + L(H_2O)RhOO^{2+}$$



$L^2(H_2O)RhOO^{2+}$

A combination of kinetic and equilibrium measurements designed specifically for these complexes yielded an estimate of the OO-H bond dissociation free energy (BDFE) for a hydroperoxo complex, and the reduction potentials and acidity constants for the macrocyclic rhodium ions. The reduction potential for the $L^2(H_2O)RhOO^{2+}$/ $L^2(H_2O)RhOOH^{2+}$ couple, E^0 = 0.97 V (NHE), was determined in equilibrium measurements with the $ABTS^{2-}/ABTS^{\bullet -}$ couple over a wide range of pH.

$$L^2(H_2O)RhOO^{2+} + ABTS^{2-} \overset{H^+}{\rightleftharpoons} L^2(H_2O)RhOOH^{2+} + ABTS^{\bullet -}$$

The acidity constants of the coordinated molecules of water in $L^2(H_2O)RhOOH^{2+}$ (pK_a = 6.9) and $L^2(H_2O)RhOO^{2+}$ (pK_a = 6.6) were obtained by spectroscopic and kinetic titrations. The combination of the pKa values with the reduction potential in acidic solutions yielded the reduction potential E = 0.95 V for the $L^2(HO)RhOO^{+}/L^2(HO)RhOOH^{+}$ couple. Thermochemical calculations yielded the bond-dissociation free energy of the $L^2(H_2O)RhOO\text{-}H^{2+}$ bond, BDFE = 315 kJ/mol at 298 K. The kinetics of disappearance of the superoxorhodium complex $L^2(H_2O)RhOO^{2+}$ in the presence of several oxidants (H_2O_2, $(NH_3)_5CoBr^{2+}$, and $IrCl_6^{2-}$) in both air-free and air-saturated aqueous solutions yielded the information on the energetics of the Rh-O_2 bond. The value of the rate constant k_h = 2.18 (± 0.37) × 10^{-4} s^{-1} at 25 ^{0}C was the same irrespective of the oxidant, consistent with the homolysis scheme. A strong correlation exists between the equilibrium constant for O_2 binding to reduced metal complexes and the reduction potential for the non-oxygenated couple.

$$L^2RhOO^{2+} \underset{k_O}{\overset{k_h}{\rightleftharpoons}} O_2 + L^2Rh^{2+} \xrightarrow[k_S]{\text{Oxidant}} \text{Products}$$

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DE- FG02- 05ER15729 **Perla B. Balbuena**

Theory-guided design of nanoscale multimetallic nanocatalysts for fuel cells

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Goal

Determine trends for catalytic activity towards the oxygen reduction reaction and stability against dissolution of Pt-based alloy nanocatalysts exposed to acid medium. Reactivity and stability trends sought as a function of surface composition and atomic distribution in the first 2-3 surface layers. Investigate possible mechanisms for metal dissolution. Analysis of surface segregation phenomena in Pt_3M systems for a large number of metals M. Developing and testing new computational approaches to characterize the catalytic interface.

DOE Interest

This research will allow design of catalysts for the oxygen reduction reaction with much better activities and durabilities; simultaneously advancing the fundamental and applied aspects of catalytic reactions such as the physics, the chemistry, methods, and development of accurate guidelines for rational design.

Recent Progress

Catalytic activity: Ab-initio based thermodynamic rules were developed to obtain a preliminary design of bimetallic catalysts that may substitute Pt. Variations in atomic distribution (mixed vs. ordered structures) analyzed in small clusters and extended surfaces of Pt_xPd_y at fixed overall composition revealed polarization effects caused by specific electronic density distributions determining trends in reactivity. Other bimetallic and trimetallic systems investigated to characterize their ability for modifying Pt reactivity. An interesting parallelism between metalloenzymes and bimetallic nanocatalysts for the oxygen reduction reaction. Ionic complexation to dendrimers sites was investigated as a first stage for elucidating nanoparticle synthesis.

Stability of nanocatalysts against dissolution: Development of a systematic thermodynamic analysis based on DFT calculations, to characterize stability against dissolution of platinum and other elements in mono- or multimetallic ensembles. Under the hypothesis that the formation of a surface oxide growth is the initial stage for catalyst dissolution, we investigated thermodynamics and kinetics of oxygen penetration into the subsurface of Pt and Pt-alloys and found important differences in the activation barriers for migration of atomic oxygen into the subsurface of specific alloy compositions compared with pure Pt (Figure 1). We investigated surface segregation phenomena, and we developed and applied a new methodology to calculate potential shifts for the onset of surface oxide growth for Pt and Pt-alloys. All these indicators are novel tools for the characterization of metal dissolution and therefore constitute basic guidelines for durable catalyst design.

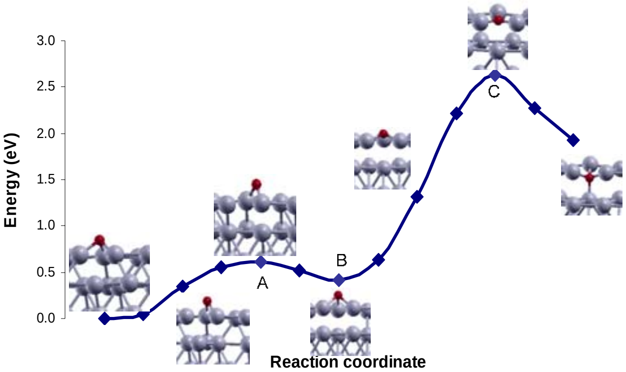

Figure 1. MEP for adsorbed O diffusing from fcc to hcp (B) to the tetrahedral subsurface site. (Gu and Balbuena, JPCC, 2007)

Development of new computational methodologies for the catalytic interface: The effect of the bulk on a finite cluster is accounted for through a combined Green function—DFT approach developed by one of the PIs. This procedure was further refined to deal with alloy bulk materials, and applied to Pt_xCo_y systems.

Future Plans

Thermodynamics and kinetics of surface segregation in nanoalloys under reaction conditions. We will investigate the thermodynamic and kinetic factors that may determine the surface composition of an alloy of given overall composition. This analysis is expected to provide guidance not only for alloy design but also for the selection of an appropriate synthesis process. The analyses will include ordered alloys, core-shell structures, and monolayers of one element deposited over a substrate. The effect of the adsorbed species on the process will be determined.

Effect of the environment on the evolution of the catalytic surface. We will study the surface evolution at corner and edge sites due to the effect of adsorbed O, OH, and surrounding water molecules, especially in acid medium. Using a slab model, we will simulate the behavior of alloy stepped surfaces to investigate surface segregation when atomic oxygen is adsorbed on the surface under one monolayer of water. The goal of these static DFT studies will be to characterize the geometry and energetic characteristics of the system after segregation of one of the metals to the surface under water and under acidic water.

Publications (2006-2008)

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DE FG02-06ER15836 **Perla B. Balbuena**

Modeling catalyzed growth of single-wall carbon nanotubes

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Goal

Investigate the reasons for chirality selectivity obtained in the process of catalyzed growth of single-wall carbon nanotubes including the influence of the catalyst shape, size, and electronic properties, and of the type of substrate on such selectivity.

DOE Interest

Single-wall carbon nanotubes (SWCNTs) have high potential as components of micro and nanoelectronic devices, in nanomedical applications, and as catalytic supports, because of their interesting mechanical, electrical, and chemical properties. These properties are strongly related to the type of nanotube, i.e, to their diameter and chirality. We expect that our studies will contribute to the understanding of nanotube growth and therefore, will provide guidance to synthesis methods towards fabrication of nanotubes of specific types. In addition, developing an improved understanding and control of the catalytic reaction where a C-containing precursor forms carbon over metal catalysts is important in a variety of fuel-processing technologies.

Recent Progress

Aromaticity and reactivity as functions of nanotube chirality and length: We have evaluated the nucleus independent chemical shift –a response of a chemical system containing aromatic rings to a magnetic field) as a measure of aromaticity for nanotubes of similar diameter but different chirality (arm-chair, near arm-chair, and near-zigzag), and simultaneously the reaction energy for adding a C_2 radical to the same group of one-end closed SWCNTs. These two properties were compared as functions of nanotube length and chirality. Our results show how the aromatic character varies from the open end (where the nanotube grows according to the root growth model), to the closed end. The aromaticity correlates with the reaction energy for the growth reaction only for some chiralities. Density functional theory was used for all the calculations.

Catalyst-nanotube cap interactions as functions of nanotube chirality: We have evaluated the nanotube cap-cluster interactions for several nanotube chiralities using density functional theory. Initially, a Cobalt cluster of 9 atoms has been studied. Various properties such as polarization (see Figure 1), electronic levels and structure of the frontier orbitals, and addition of C_2 radicals to the nanotube open edge were comparatively analyzed and the results related to the relative abundance of nanotubes found experimentally.

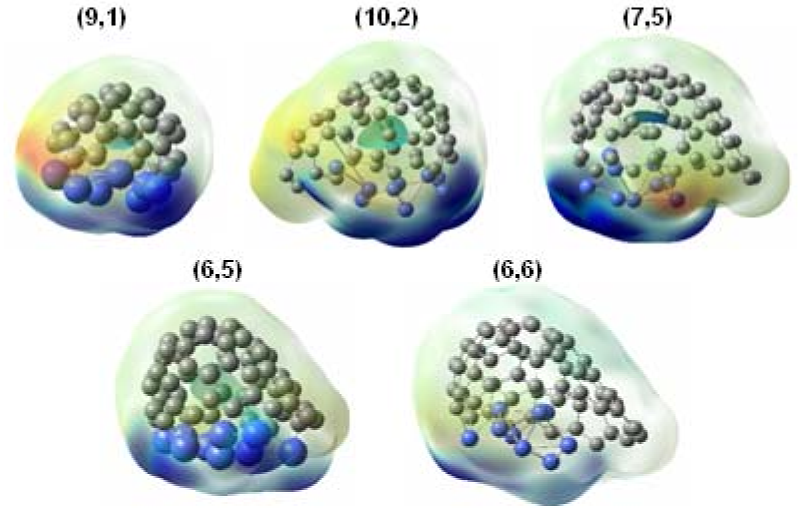

Figure 1. Electrostatic potential mapped on an electron density isosurface. Notice how the polarization of the system decreases as the chirality changes from zig-zag to armchair.

Future Plans

Cluster-cap structure and dynamics: Studies are in progress to evaluate physical, chemical, and electronic properties of metallic clusters of 15 atoms in contact with caps of different chiralities. Ab initio molecular dynamics simulations in selected systems will be performed to investigate the time evolution of these systems at the synthesis conditions.

Substrate-catalyst interactions: The effect of the substrate (MoC) on the adsorption of C atoms or C_2 radicals in Co clusters will be investigated using density functional theory. Preliminary work has focused on the adsorption of small Co clusters on the MoC substrate simulating the intial stages of formation of Co clusters on such surfaces. Future studies will include the adsorption and dissociation of CO on the cluster/substrate composite system.

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DE-FG03-98-ER14910 **Guillermo C. Bazan**

Catalysts for Selective Olefin Oligomerization and Polymerization

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Goal

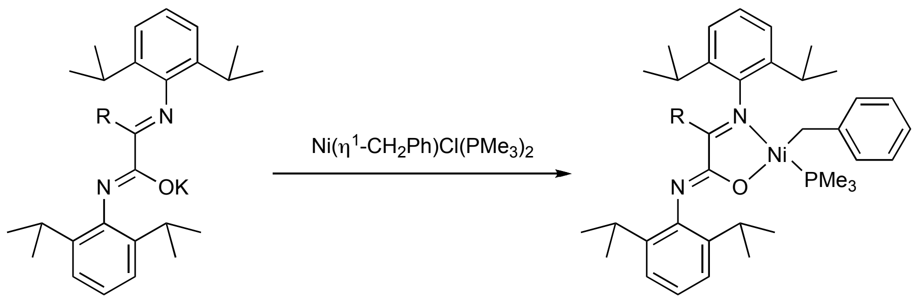
To develop organometallic polymerization initiators that increase the options available for chemical synthesis and industrial processes and that contribute toward a better management of petrochemical resources.

DOE Interest

Polyolefins constitute a large fraction of materials derived from petrochemical resources. Better methods for their preparation and processing thus improve our management of oil and its derivatives. Additionally, materials that modulate the interfacial energies of polyolefins and polar commodity plastics should substantially increase the scope of applications for polyolefins by allowing their incorporation into polymer "alloys".

Recent Progress

i) α-Iminocarboxamide Nickel Complexes: Synthesis and Uses in Ethylene Polymerization A series of *N,O*-bound, neutral nickel complexes containing α-iminocarboxamide, η^1-CH_2Ph and PMe_3 ligands were synthesized to examine the effect of steric and electronic variations at the site adjacent to the imine functionality. EHT synthetic approach and types of complexes studied are shown in Scheme 1. These complexes were subsequently activated with $Ni(COD)_2$ for use in ethylene homopolymerization and ethylene/norbornene acetate (NBA) copolymerization reactions. As the bulk of the substituents is increased one observes a progressive decrease in the rate of ring rotation, a more crowded coordination sphere around nickel, increased monomer consumption activity and higher molecular weights of the products. Copolymerization reactions showed that the increased crowding around nickel decreases the reactivity of NBA relative to ethylene. As electron density is removed from the metal center, the catalytic species become more active toward ethylene and are more prone to interact with the functionality on NBA.

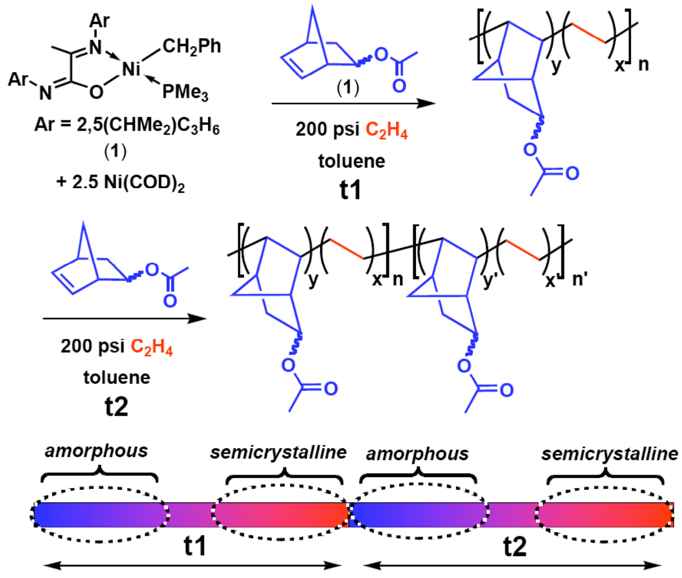


R = Me **1**, Et **2**, CH_2CHMe_2 **3**, $CHMe_2$ **4**,
Ph **5**, *p*-CF_3-Ph **6**, *p*-OCH_3-Ph **7**

Scheme 1. Synthesis and structures of α-iminocarboxamide nickel complexes.

ii) Synthesis of Pseudo-Tetrablock Copolymers with Ethylene and a Functionalized Comonomer.

The quasi-living characteristics of the polymerization of ethylene and NBA by **1**/Ni(COD)$_2$ opens the opportunity to access hitherto inaccessible polymer architectures. One example concerns tetrablock structures, which were prepared according to the process in Scheme 2. One begins the polymerization with a set concentration of NBA under a constant C_2H_4 pressure. The reaction is allowed to continue for a time t1, during which [NBA] decreases in the reaction medium, leading to an increase of C_2H_4 incorporation relative to NBA. After completion of t1, a second batch of NBA is added to the reactor, such that [NBA] is re-established to that at the beginning of the reaction. The reaction is then allowed to proceed for a time t2. The amount of NBA to be added at t1 is determined by stopping a polymerization at t1, determining the molar incorporation of NBA in the resultant copolymer and from this and the polymer yield determine the amount of NBA that was consumed in t1. The addition of more monomer at t1 results in a sudden increase in the incorporation of NBA, followed by a depletion process similar to that expected during t1. The end result is a backbone containing two similar tapered copolymer structures covalently joined in a head to tail fashion. The idea is schematically illustrated in Scheme 2, where the ratio of NBA (blue) to C_2H_4 (red) in the chain tapers to a point where the C_2H_4 content is sufficiently high that a semicrystalline segment is obtained. Each TCP



Scheme 2. Synthesis of pseudo-tetrablock copolymers.

segment provides for an amorphous and a semicrystalline component. Thus, each chain contains four distinct regions, similar to a tetrablock copolymer.

Future Plans

Our future plans are aimed at discovering new polymerization initiators that afford control over the structure of conjugated polymers. This departure is motivated by the function of these novel optoelectronic materials in emerging energy-related technologies such as organic solar cells. Specifically, we plan to (i) provide easy to use metal/ligand combinations that catalyze the controlled formation of conjugated polymers and (ii) obtain a better mechanistic understanding of what features of the catalytic site lead to optimal control. Our working hypothesis is that the chain-growth characteristics can be achieved in cross-coupling processes, such as the Suzuki-Miyaura reaction, due to the formation of π-bound intermediates, which hold the metal center bound to the product of the reductive elimination step, namely the last step in conventional catalytic cycles. Oxidative addition takes place without dissociation and leads to attachment of the metal center to one terminus of the polymer chain. Such conditions ultimately lead to the monomer always reacting with the growing chain and thereby chain-growth characteristics.

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DE-FG02-85ER13431 **John E. Bercaw**

Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

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Goal

Provide understanding of solvent and ligand effects on catalyst composition, counter-anion effects, and structures of alkyl aluminum adducts of catalysts for olefin polymerization in order to guide development of superior catalyst systems; develop chemistry of new “pincer” type ligands for early transition metals.

DOE Interest

New information on catalyst design and performance may lead to new types of polymers and/or new chemical transformations between hydrocarbons and transition metal centers, ultimately contributing to the development of catalytic reactions for the production of fuels, commodity and polymeric materials.

Recent Progress

Preparation of New Group 4 Precatalysts with New Bi- and Tridentate Ligands. Using either alkane elimination or salt metathesis methods, titanium, zirconium, and vanadium complexes have been prepared with new ligand systems featuring tridentate bis(phenolate)pyridine or bidentate bis(phenolate)benzene arrangements. When activated with MAO, these complexes are competent for the polymerization of propylene, 1-hexene, and ethylene/1-octene copolymers. Vanadium precatalysts exhibit the highest activity, and both zirconium and vanadium precatalysts give atactic polymer. Complexes of the tridentate bis(phenolate)pyridine ligand on titanium generate multiple catalytically active species as manifested by the interesting ^{13}C NMR pattern, showing a large [*mmmm*] pentad in the presence of otherwise atactic polypropylene, and consequent separation of the polypropylene into two fractions. Complexes of the bidentate bis(phenolate)benzene ligand on titanium generated a single catalytically active species which gives atactic polypropylene. The pyridine donor is most likely labile, thus accounting for the multiple catalytically active species.

Tantalum Imides with New Tridentate Ligands. A tantalum imido-amido-amine complex supported by a dianionic bis(phenolate)pyridine pincer ligand has been synthesized. This compound, [ONO]Ta(NPh)(NHPh)(NH_2Ph), (ONO = 2,6-(2,4-$(CMe_3)_2$-C_6H_2O)C_5H_3N) is currently being investigated as a catalyst for hydroamination of olefins, and its insertion chemistry is also being studied. DFT studies on the complex have shown that the C_2 symmetry of the bis(phenolate)pyridine ligand reduces π donation from the phenoxides that was previously seen in cases where the ligand possessed C_s and C_{2v} symmetry. This C_2 symmetry may allow for a large range of multiply bound tantalum species to be supported by the ligand.

Iron Compounds with a Bis(anilide)pyridine Ligand. A tridentate bis(aniline) pyridine ligand $2,6\text{-}NC_5H_3(2\text{-}(2,4,6\text{-}Me_3C_6H_2)\text{-}NHC_6H_4)_2$ has been synthesized. Deprotonation of the ligand and reaction with anhydrous ferrous chloride yields the iron complex as a THF adduct. This new complex is a ground state quintet and exhibits a distorted trigonal monopyramidal geometry, with the anilides and the THF occupying the basal positions and the pyridine at the apex. The geometrical and electronic properties of the complex are unique in the context of iron pincer complexes, thus making it a promising entry into the chemistry of this class of compounds.

Structural Studies of Zirconium Hydride Adducts with Alkylaluminums. In collaboration with Hans Brintzinger and his colleagues at Konstanz, the structures of zirconocene hydrides formed from reaction of zirconocene dichlorides and aluminum hydrides have been investigated via variable temperature NMR. Multinuclear clusters are proposed as the likely structures of these potential polymerization intermediates, and the stoichiometries and structural types are being correlated with cyclopentadienyl substitution and bridging groups for *ansa* zirconocenes.

Studies of Solvent Effects on Chromium-Catalyzed Ethylene Oligomerizations. Solvent effects in the trimerization and tetramerization of ethylene to 1-hexene and 1-octene with an aluminoxane-activated chromium catalyst bearing a diphosphine ligand have been investigated. While reactions in non-polar solvents exhibit poor activity at lower ethylene pressures, those in more polar solvents, such as chlorobenzenes and fluorobenzenes, are highly active and generate very little undesired polyethylene. Varying the solvent also has a significant impact on 1-hexene/1-octene selectivity. Experiments with potentially coordinating additives result in a higher tendency for 1-octene formation.

Future Plans

Preparation of New Group 4 and 5 Transition Metal and Iron Complexes with New Di- and Tridentate Ligands. Using metallation of the 2 position of 1,3-phenylene group of the *bis*(phenolate)benzene, we will attempt to generate a *neutral* zirconium system that is sufficiently electron deficient to promote olefin insertion and oligomerization/polymerization. Other synthetic targets include hydrides and alkylidenes to explore transformations for comparisions with the analogous metallocene complexes. New reaction chemistries of the Ta and Fe systems will be explored.

Structural Studies of Zirconium Hydride Adducts with Alkylaluminums and Solvent Effects on Chromium-Catalyzed Ethylene Oligomerizations. Experimental work on these topics is essentially complete, and manuscripts describing these topics are currently in draft form. A provisional patent on the solvent effects on the chromium catalysis is currently being converted to a full patent application.

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DE-AC02-05CH11231 **Robert G. Bergman**

Exploratory and Mechanistic Investigations of C-H Activation Reactions and their Applications to Catalysis and Organic Synthesis

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Goal

To develop new metal-catalyzed transformations of organic molecules and understand the mechanisms of their reactions, with a specific focus on processes that involve carbon-hydrogen (C-H) bond activation.

DOE Interest

Because of its fundamental and practical impact, the prospect of using transition metals to “activate,” in homogeneous solution, carbon-hydrogen bonds that are not located in the same molecule as the metal or adjacent to an activating functional group, has long been an important target of chemical research. This has been true since the late 1960’s, when it was identified as one of the most important goals of organometallic chemistry in an oft-quoted paper by Jack Halpern, a central figure in the field at that time. Following a few seminal papers which indicated that C-H bond activation was achievable, an exponentially increasing amount of research has taken place in this field; currently, these reactions are studied extensively by organic, inorganic, physical, theoretical, biological, and industrial chemists. The practical goal of this work is driven by the fact that direct activation of C-H bonds has the potential to simple organic molecules into more useful functionalized materials. The goal of industrial chemists has been to search for novel C-H activation routes to commodity chemicals (e.g., methane to methanol without over-oxidation). Organic and pharmaceutical chemists have been primarily interested in using C-H activation reactions to increase the repertoire of useful methods in organic synthesis, with a focus on increasing selectivity or efficiency in the production of fine chemicals, including physiologically active molecules. Processes that activate C-H bonds directly, rather than in more conventional multi-step processes that involve the introduction and removal of intermediate functional groups such as halogens, also lead to reduction in waste disposal and energy costs.

Recent Progress

Progress on this project has occurred in the following three areas.

Stable Alkane Complexes. In our initial work on carbon-hydrogen bond activation reactions of iridium (I) complexes, indirect evidence was obtained suggesting that alkane complex intermediates (species in which alkanes are weakly coordinated to the metal center before C-H bond activation occurs) intervene in the C-H activation process. However, persuasive evidence is lacking as to whether such species have ever been isolated. We have therefore initiated work designed to prepare and unambiguously characterize such species by using bi- and trinuclear systems to increase the total metal-alkane interaction energies. This research has been initiated through a computational search for the optimum structures of metals and ligands that will provide the largest interaction energies, carried out in collaboration with Prof. M. Head-Gordon (UC Berkeley). Our initial results indicate that with appropriately designed systems, metal-alkane interaction energies can approach 30 kcal/mol, which would make them stable at room temperature.

C-H Activation Reactions of Ir(III) Complexes. We have also made substantial progress on expanding the scope of the C-H activation reactions of cationic Ir(III) complexes and understanding their reaction mechanisms. In one study, we have uncovered unusual rearrangements that take place when cationic Ir(III) complexes react rapidly with heteroatom-substituted cyclopropanes, and have provided information about the mechanisms of these reactions.

Discovery and Study of C-H Activation Reactions Useful in Organic Synthesis. In an extensive collaborative study with the J. Ellman research group, we have developed a range of synthetic methods in which arenes and alkenes undergo carbon-hydrogen bond activation with rhodium catalysts, and the resulting intermediates react with alkenes and/or aryl halides to make new carbon-carbon bonds. Recently we uncovered ways to extend the C-H activation reactions to the β-hydrogens of α,β-unsaturated carbonyl compounds, and to couple the metal-functionalized atom to a second alkene. Several of these transformations involved the development of new rhodium-bound organic ligands that promote the coupling reactions effectively. In addition to synthetic methods development, the mechanisms of these new reactions have been extensively investigated through the use of both experimental studies (e.g., kinetics, isotope labeling) and computational studies.

Future Plans

We plan to pursue the following goals in the immediate future: (a) continuation of the computational search for ligands that will lead to predictions of stable, isolable alkane complexes; (b) use of the computational results to guide the synthesis of multidentate ligands capable of binding two and three rhenium centers, with the goal of gaining experimental access to alkane complexes that are stable enough to be fully characterized by NMR spectroscopy and X-ray diffraction under ambient conditions; (c) thorough investigation of the mechanism of directed C-H activation proceeding through N-heterocyclic carbene reactions promoted by protic acids; (d) search for general enantioselective C-H bond activation reactions; (e) development of metal-catalyzed C-H activation initiated arylation reactions; (f) development of tandem reactions initiated by C-H bond activation/alkene hydroarylation and -vinylation, followed by insertion of reactive organic partners, such as nitriles, allenes, and diazo compounds.

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DE-AC02-05CH11231 **K. N. Raymond, R. G. Bergman**

Selective Organic and Organometallic Reactions in Water-Soluble Host-Guest Supramolecular Systems

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Goal

The aim of this project is the use of rationally designed chiral supramolecular assemblies or "nanovessels" to alter and control the stereo-, chemo- and/or regioselectivies in the reactions of encapsulated guest molecules.

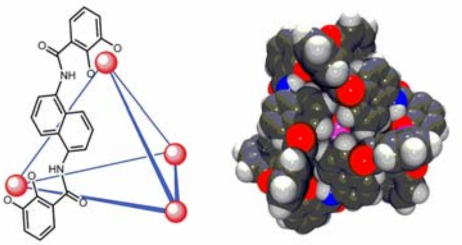
DOE Interest

The DOE Chemical Energy program supports basic research in the area of chemical transformations or conversions that are fundamental to new or existing concepts of energy production and storage. This includes the use of catalytic transformations as a means to reduce energy consumption and waste production. More specific goals of this project include using water-soluble supramolecular host molecules to catalyze chemical transformations to obtain products, rates and selectivities that are otherwise not possible in aqueous solution.

Recent Progress

The poster will present recent progress that has been made in a collaborative study being carried out by the R. G. Bergman and K. N. Raymond research groups. Several cationic organic and organometallic complexes have been shown to bind into the cavities of water-soluble chiral clusters or "nanovessels" (constructed earlier by the K. N. Raymond group) from metal salts and dicatecholate bridging ligands (Figure 1). Among these are reactive Ir(III) complexes that undergo Ir(III)/Ir(V) C-H oxidative addition reactions (discovered earlier by the R. G. Bergman group) when they are encapsulated in the nanovessel clusters in aqueous solution, leading to the first nanovessel intracavity C-H activation reactions. Substantial size- and shape selectivities have been observed in these reactions. Subsequently, aza-Cope and other pericyclic rearrangements have been found to

Figure 1



proceed in the nanovessel cavities; small quantitities of the nanovessels have been found to catalyze these reactions with accelerations up to 800-fold. Most recently, nanovessels have also been found to alter the acidities of organic bases by up to 4.5 pKa units. The pK_a-shift properties of the nanovessels has provided a way of carrying out acid-catalyzed hydrolyses in strongly basic aqueous solution, strongly catalyzing the hydrolyses of orthoformates and acetals. The velocities of the hydrolysis reactions mirror the classic rate behavior of enzymes, including Michaelis-Menten kinetics and competitive inhibition by strongly-binding guests. Hence we call them "nanozymes".

The unique interior environment of these nanovessels has also been used to encapsulate a variety of different guest types in addition to simple monocations. The hydrophobic host interior cavity has been exploited to encapsulate a range of neutral guest molecules such as linear and cyclic alkanes. Similarly, the hydrophobic interior has been used in concert with the preference for monocationic guests to allow for the formation and encapsulation of otherwise water-unstable iminium cations. The unique symmetry environment of the nanovessel allows for the observation of partially encapsulated guest molecules due to a reduction of the host symmetry during this process. When long, linear alkane chains are appended to a cationic guest molecule, the alkyl chain protrudes through one of four apertures in the host ligand framework, forming a “dangling arm” host-guest complex. This directly demonstrates how host distortion can accommodate guest exchange and allow substrates access to encapsulated reactive species.

Future Plans

The highly restricted volume of the clusters we are currently studying limits the range of substrates that can access the cavities. Therefore, an important area of future work will center on the design, synthesis and investigation of the host-guest dynamics of larger, water-soluble supramolecular assemblies, which should allow entrance of a much wider range of substrates. These include pyrene- and binaphthalene- based ligand scaffolds, which have been shown to have larger interior cavities as compared to the naphthalene-based nanovessel. The guest scope and reactivity of encapsulated guests will be investigated and compared with those of the well-studied naphthalene-based assembly. An important direction will involve encapsulation of positively charged (as well as possibly charge-neutral) organometallic catalytsts, and determination of whether they will exhibit rate accelerations in their intravessel catalytic reactions similar to those seen with the rearrangement reactions dicussed above, as well as selectivities that are not accessible using the unencapsulated catalysts. A particularly important goal will be to use enantiomerically resolved nanovessels, which we are now able to prepare, to investigate the possibility of carrying out catalytic enantioselective transformations of organic substrates within the nanovessels, without having to use resolved ligands bound to the encapsulated metal centers.

Studies will be also be focused on the host-guest chemistry of our naphthalene-based nanovessels, including further exploration of neutral guests, targeting arene and chiral hydrophobic guest molecules. The hydrophobic interior of the nanovessel will also be used to investigate transformations such as amide bond rotation, which proceed through a hydrophobic transition state. We plan to use the unique symmetry environment of the nanovessel to probe such fundamental processes as nitrogen inversion of encapsulated mono-protonated amines and the barrier to ring rotation of encapsulated metallocene complexes. Finally, the sensitivity of the host-guest exchange process will be probed via isotopic substitution of exchanging guest molecules and we expect differences in zero point energy between the ground and transition states to result in an inverse kinetic isotope effect during the guest exchange process.

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New Approaches to Driving Multielectron Redox Chemistry

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Goal

Design and synthesize metal complexes to drive multielectron redox transformations. One strategy involves the synthesis of polymetallic reaction sites to promote cooperative substrate binding and activation over several metal sites. A second strategy involves the design and synthesis of late-transition, high-oxidation state complexes to promote unusual bond making and breaking reactivity.

DOE Interest

The underlying science in both of the projects described should appeal to the DOE in three principle areas: (1) designer cathodes may be effective for small-molecule activation reactivity (e.g., CO_2 reduction) in a stoichiometric and electrocatalytic fashion; (2) designer anodes may be effective for driving difficult oxidation processes (e.g., water oxidation) for use in artificial photosynthetic devices; and (3), organometallic platforms are targeting bond activation processes to introduce functionality into otherwise unactivated C—H bonds (e.g., alkane hydroxylation for synthetic fuels).

Recent Progress

Polymetallic reaction site design and synthesis. Utilizing tris-amine ligand platforms, we were successful in synthesizing ligand scaffolds with three discrete monoanionic or dianionic binding sites. The amines bridge adjacent metal sites, while a covalently linked ligand protects the periphery of the trimetallic molecule to stabilize the trigonally coordinated metal sites. The three metals have a common, vacant coordination site in the molecule's core to promote cooperative substrate binding and activation. An example X-ray structure of such a complex is provided in Figure 1a.

Organometallics. An alternative means to driving multielectron redox transformations could involve stabilizing low-coordinate, high-oxidation state, late transition metals to participate in oxidative group-transfer processes. We have developed diamine and dipyrrolide frameworks to stabilize such species and are systematically investigating their efficacy to stabilize metal-ligand multiple bonds to promote aliphatic or aromatic C—H bond additions across the created M—L π bond. An example structure is shown in Figure 1b.

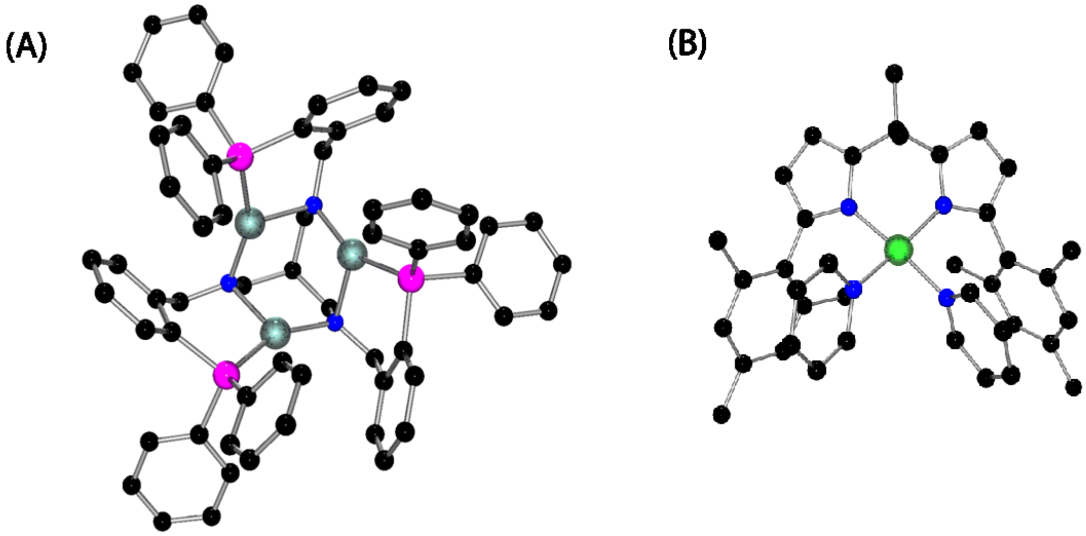

Figure 1. X-ray crystal structures of (a) recently synthesize trimetallic molecule and (b) Ni^{II} supported dipyrrolide complex.

Future Plans

As a new research group (lab initiated experimentation in October 2007), we have spent most of our efforts synthesizing new platforms targeting the described reactivity. With our synthetic efforts well underway, we have begun examining their ability to perform the desired multielectron redox functions. Our latest results in terms of small-molecule activation and group-transfer chemistry will be presented.

Publications

E. R. King and T. A. Betley, "Structural and electronic comparisons of the weak-field dianilide and strong-field, redox-active dipyrolide ligand frameworks," *Inorg. Chem.* (**2008**) *Submitted*.

KC-03-02-01-0 Project # 52775 R. Morris Bullock

New Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

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Goal

Our goal is to design, synthesize, characterize and optimize complexes based on inexpensive, abundant metals that exhibit high activity as electrocatalysts with low overpotentials for hydrogen oxidation and hydrogen production. A central focus is the integration of the capabilities of metal complexes to bind and heterolytically cleave hydrogen with the ability of pendant bases (typically amines that are covalently bonded to the ligand) to mediate proton transfer and assist heterolytic cleavage. This will involve catalyst design and synthesis as well as mechanistic and thermodynamic studies of complexes with and without pendant bases. Matching the proton acceptor ability of the amine (basicity) with the hydride acceptor ability of the metal will be a crucial feature in the design of highly active and energy efficient catalysts.

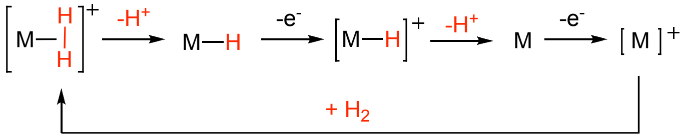
DOE Interest

The high biological activity of hydrogenase enzymes shows that inexpensive metals like Fe and Ni can function as effective catalysts for oxidation of hydrogen and hydrogen production. While Nature’s hydrogenase enzymes use iron and/or iron-nickel complexes, fuel cells for oxidation of hydrogen almost invariably require platinum. This project seeks to discover and develop the chemistry of metal complexes of inexpensive, abundant metals, for their use as electrocatalysts for hydrogen oxidation and hydrogen production. The motivation to design these molecular electrocatalysts based on inexpensive metals comes from the recognition that large-scale processes that require platinum will not be feasible, and that low-cost alternatives are needed to help hydrogen become more practical as an alternative fuel.

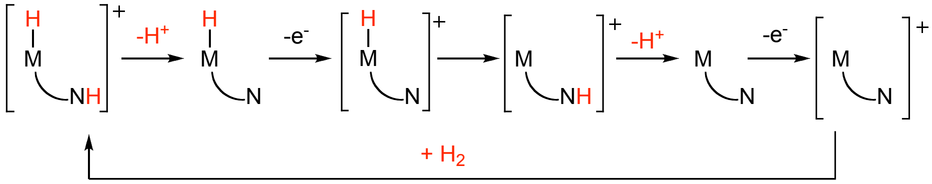
Recent Progress

Our approach emphasizes the roles played by both the first and second coordination spheres of the catalysts, and it attempts to integrate both features into catalysts in a manner similar to that achieved by enzyme systems. Our studies include synthesis of new metal complexes and determination of their thermodynamic properties such as pK_a values, electrochemical data, and derived bond dissociation energies. Reliable thermochemical data will help us to rationally evaluate the combinations of ligands and metals that are best suited for catalyzing the desired reactions. These complexes will then be tested as electrocatalysts for the oxidation of H_2 to H^+, and for the reverse reaction, the formation of H_2 through reduction of protons.

A generalized mechanism for oxidation of hydrogen in a metal complex is shown below starting with a dihydrogen (η^2-H_2) ligand bound to a cationic metal complex. Deprotonation of

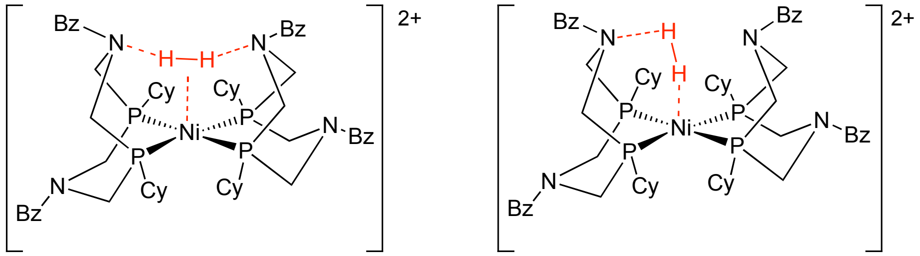


the cationic dihydrogen complex generates a neutral metal hydride, which is oxidized to an MH$^+$ species that exhibits increased acidity. After this complex releases a proton, it is oxidized. Addition of H$_2$ completes the catalytic cycle by regenerating the dihydrogen complex. Introduction of a pendant base can substantially lower the barriers for oxidation of hydrogen, as shown in generalized form here. Deprotonation of the NH leaves the M-H that can be oxidized, leading to enhanced acidity. In this example, a proton may be intramolecularly transferred from the M-H site to the nitrogen of the amine. Proton transfer from the metal to the amine will also place the proton in a more sterically accessible site for subsequent deprotonation by an external base.



Prior work showed that the nickel complex $[Ni(Et_2PCH_2NMeCH_2PEt_2)_2]^{2+}$ serves as a functional model for hydrogenases, catalyzing the oxidation of hydrogen to protons. In the absence of a proton relay, oxidation of H$_2$ occurs, but is slow and requires a significant overpotential (0.8 V). Introduction of an amine base lowers the overpotential by 0.7 V and improves the rate of catalysis by at least two orders of magnitude. Incorporation of a positioned pendant amine in a related complex, $[Ni(P^{R}{}_2N^{R'}{}_2)_2]^{2+}$, results in a much reduced barrier for hydrogen production, giving a turnover frequency of 350 mol H$_2$ per mole catalyst per second at 22°C, (overpotential ≈ 0.3 V). This catalytic rate is in the range found for the [NiFe] hydrogenase (700 s^{-1}, at 30°C). A critical feature for the design of highly active catalysts with low overpotentials is the ability to obtain a structure where minimal reorganization of the coordination sphere of the metal complex is required. (see Figure below)

How many positioned proton relays are involved in the activation of H$_2$? An alternative transition state for hydrogen oxidation that would be consistent with the observed kinetics and intermediates is the asymmetric activation of H$_2$ as shown in the right side of the figure. To test which structure is more likely, a nickel complex containing one cyclic diphosphine ligand with one positioned base and one diphosphine with no base, $[Ni(P^{Ph}{}_2N^{Bz}{}_2)(dppp)]$ (dppp is 1,3-bis(diphenylphosphino)propane), has been synthesized and structurally characterized. Thermodynamic studies of the corresponding Ni(II) complex indicate that H$_2$ addition in acetonitrile is exergonic by -4 kcal/mol. This value is more negative than that observed for the addition of H$_2$ to $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$, (-3.1 kcal/mol) which contains two positioned pendant bases. However the rate of H$_2$ oxidation for $[Ni(P^{Ph}{}_2N^{Bz}{}_2)(dppp)](BF_4)_2$ (<0.5 s^{-1}) is significantly less than that of $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$ (10 s^{-1}) in spite of the greater driving force for the former. This is consistent with the interpretation



that the activation of H_2 by these Ni complexes involves two positioned pendant bases (left side of the Figure above) as suggested by DFT calculations and the structure of the CO adduct of $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$.

In an effort to extend this work to other first row transition metals, new cobalt complexes containing the $P^{Ph}{}_2N^{Ph}{}_2$ ligand have been prepared and the ability of these complexes to catalyze the electrochemical reduction of protons to H_2 have been studied. In contrast to nickel complexes, for which optimal catalytic activity is obtained when two cyclic diphosphine ligands with pendant bases are coordinated to nickel, the catalytic activity for proton reduction observed for $[Co(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)](BF_4)_2$ was found to result from loss of a diphosphine ligand to form $[Co(P^{Ph}{}_2N^{Ph}{}_2)(CH_3CN)_3](BF_4)_2$ in the presence of acid. The latter complex has been structurally characterized and appears to be the true catalyst during the catalytic cycle for hydrogen production. $[Co(P^{Ph}{}_2N^{Ph}{}_2)(CH_3CN)_3](BF_4)_2$ has a catalytic turnover frequency of 90 s^{-1} with an estimated overpotential of 285 mV. In contrast to previously studied nickel complexes, two cyclic diphosphine ligands with pendant nitrogen bases are not required for high activity. However, a comparison of the catalytic activity of $[Co(P^{Ph}{}_2N^{Ph}{}_2)(CH_3CN)_3](BF_4)_2$ with that of $[Co(dppp)(CH_3CN)_3](BF_4)_2$, for which no catalytic activity is observable, indicates that the pendant nitrogen base is playing a key role in the catalysis of H_2 production.

Prior work with iron complexes containing ligands with pendant bases has shown that such complexes have thermodynamic properties favorable for catalytic hydrogen activation; however, the catalytic rates for these complexes are limited by slow hydrogen coordination/dissociation. Manganese complexes are being synthesized to investigate the effect of change in both the thermodynamics and kinetics relative to the iron catalysts. Complexes of the form $[Mn(P_2)_2(CO)(H_2)]^+$ and $Mn(P_2)_2(CO)H$ (where P_2 is a bidentate diphosphine ligand) have been synthesized, and the electrochemistry and acidity/basicity of these complexes are being investigated. Currently, mixed phosphine complexes of the form $Mn(P_2)(PNP)(CO)(H)$ (where PNP is a diphosphine ligand containing a pendant amine base) are being synthesized.

Future Plans

Further studies will seek to understand the necessity of two pendant bases for optimum performance in the Ni complexes, compared to the Co complexes that are active with only one diphosphine with a pendant base. Work on Mn was recently initiated, and has resulted in several new Mn complexes that are promising for future electrochemical and catalytic studies. Future studies will seek to optimize ligand structures to explore the feasibility of obtaining catalysts with high rates and low overpotentials.

Publications (Project started in the middle of FY 07)

"Hydrogen Production using a Cobalt-Based Molecular Catalyst with a Positioned Proton Relay," by G. Jacobsen, J. Yang, B. Twamley, A. B. Wilson, R. M. Bullock, M. Rakowski DuBois, and D. L. DuBois, invited paper submitted to *Energy and Environmental Science*.

"Hydrogen Oxidation with a Nickel Complex Containing One Positioned Pendant Base," by J. Yang, M. Rakowski DuBois, R. M. Bullock, B. Twamley, W. Shaw and D. L. DuBois, manuscript in preparation.

DE-FG-02-85ER13406 **Charles P. Casey**

Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis

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Research Goals and Specific Objectives

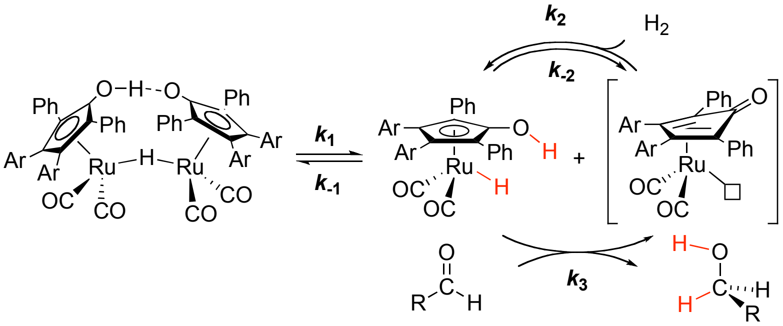
Our goal is to learn the intimate mechanistic details of reactions involved in homogeneous catalysis and to use the insight we gain to develop new and improved catalysts. Our work centers on the hydrogenation of polar functional groups. Specifically, we are concentrating on catalysts capable of simultaneously transferring hydride from a metal center and a proton from an acidic oxygen or nitrogen center to an aldehyde or ketone; reaction of the organometallic product with hydrogen regenerates the active reducing agent.

DOE Interest

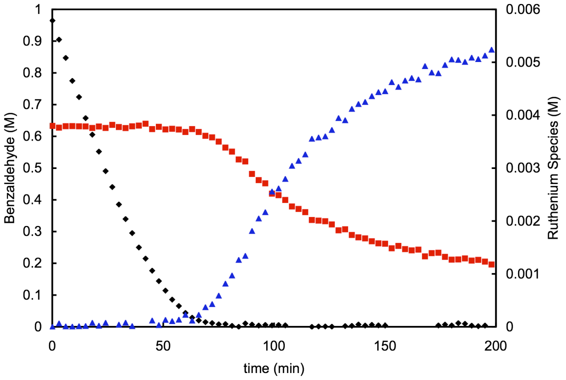
Better understanding of fundamental organometallic reactions and catalytic processes will aid and enable design of energy and material efficient chemical processes. Our work is contributing to the development of catalysts for the selective and mild hydrogenation of ketones and aldehydes; this will provide a modern green alternative to reductions by $LiAlH_4$ and $NaBH_4$, which require extensive work-up procedures and produce waste streams.

Recent Progress

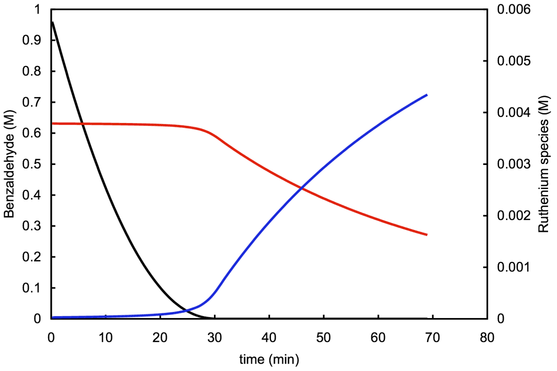
Spectroscopic Determination of Hydrogenation Rates and Intermediates During Carbonyl Hydrogenation Catalyzed by Shvo's Hydroxycyclopentadienyl Diruthenium Hydride Agrees with Kinetic Modeling Based on Independently Measured Rates of Elementary Reactions.[6] The rates of elementary reactions involved in the Shvo hydrogenation system were measured at temperatures ranging from -10 to 95 °C and were used to construct a kinetic model for the hydrogenation.



The rates of hydrogenation of aldehydes and ketones and the metal complexes present during catalysis were monitored at 60 °C under 35 atm H_2 using *in situ* IR spectroscopy. The kinetic model accurately accounts for the observations that (1) the bridging diruthenium hydride was the only observable ruthenium species until nearly all of the substrate was consumed, (2) the complex rate dependence on substrate, H_2 pressure, total ruthenium concentration, and solvent, and (3) observed rates were within a factor of 2 of those predicted by the kinetic model.

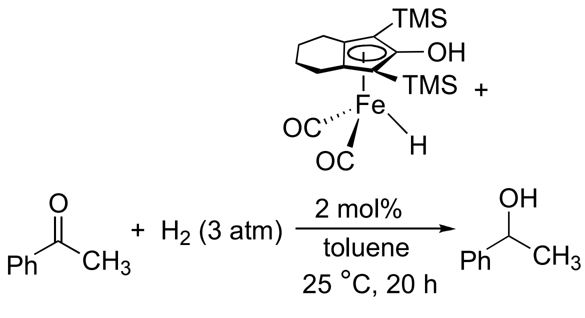


in situ IR Determination of concentrations of benzaldehyde (◆), **Ru-H-Ru (■)**, and **Ru-H (▲)** during hydrogenation of benzaldehyde under 35 atm hydrogen at 60 °C in toluene.



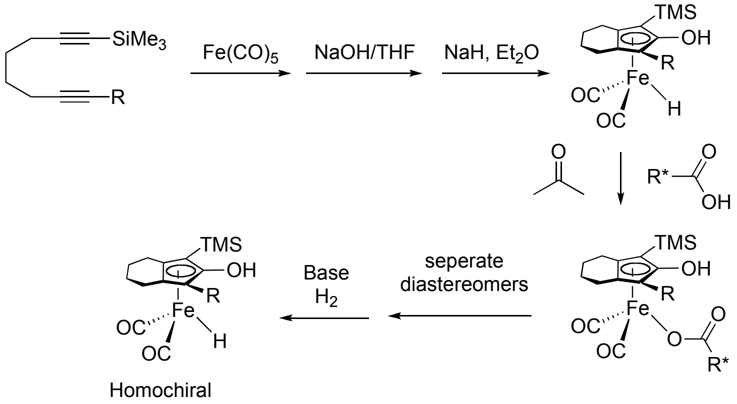
Kinetic modeling simulations of concentrations of benzaldehyde (**black**), **Ru-H-Ru (red)**, and **Ru-H (blue)** during hydrogenation of benzaldehyde under 35 atm hydrogen at 60 °C in toluene.

New Iron Hydrogenation Catalyst. We have discovered that iron complexes with electronically coupled acidic and hydridic hydrogens catalyze the hydrogenation of ketones under mild conditions. These hydrogenation catalysts show high chemoselectivity for aldehydes, ketones and imines and isolated C=C, C≡C, C-X, $-NO_2$, epoxides, and ester functions are unaffected by the hydrogenation conditions. Mechanistic studies have established a reversible hydrogen transfer step followed by rapid dihydrogen activation. The same iron complex also catalyzes transfer hydrogenation of ketones.



Future Plans

Develop an Enantioselective Iron Catalyst. We plan to synthesize a "planar chiral" version of the iron catalyst by replacing one trimethylsilyl group on the Cp ring by another group. This synthesis will involve use of diynes with different terminal substiutents. Reaction of the catalysts with a ketone in the presence of a homochiral carboxylic acid should produce two diastereomers of the carboxylic acid addition product. The diastereomers will be separated by chromatography or recrystalization. Reaction of the resolved carboxylic acid derivative with base and hydrogen should generate the desired homochiral iron hydrides which will then be tested as enantioselective hydrogenation catalysts.



Publications (2006-2008)

1. C. P. Casey, G. A. Bikzhanova, I. A. Guzei, "Stereochemistry of Imine Reduction by a Hydroxycyclopentadienyl Ruthenium Hydride," *J. Am. Chem. Soc.* **128** (2006) 2286-2293.
2. C. P. Casey, N. A. Strotman, S. E. Beetner, J. B. Johnson, D. C. Priebe, T. E. Vos, B. Khodavandi, I. A. Guzei, "The PPh_3 Substituted Hydroxycyclopentadienyl Ruthenium Hydride $[2,5\text{-}Ph_2\text{-}3,4\text{-}Tol_2(\eta^5\text{-}C_4COH)]Ru(CO)(PPh_3)H$ is a More Efficient Catalyst for Hydrogenation of Aldehydes," *Organometallics* **25** (2006) 1230-1235.
3. C. P. Casey, N. A. Strotman, S. E. Beetner, J. B. Johnson, D. C. Priebe, I. A. Guzei, "PPh_3 Substituted $[2,5\text{-}Ph_2\text{-}3,4\text{-}Tol_2(\eta^5\text{-}C_4COH)]Ru(CO)(PPh_3)H$ Exhibits Slower Stoichiometric Reduction, Faster Catalytic Hydrogenation, and Higher Chemoselectivity for Hydrogenation of Aldehydes over Ketones than the Dicarbonyl Shvo Catalyst" *Organometallics* **25** (2006) 1236-1244.
4. C. P. Casey and H. Guan, "An Efficient and Chemoselective Iron Catalyst for the Hydrogenation of Ketones," *J. Am. Chem. Soc.* **129** (2007) 5816-5817.
5. C. P. Casey, T. B. Clark, I. A. Guzei, "Intramolecular Trapping of an Intermediate in the Reduction of Imines by a Hydroxycyclopentadienyl Ruthenium Hydride: Support for a Concerted Outer Sphere Mechanism," *J. Am. Chem. Soc.* **129** (2007) 11821-11827.
6. C. P. Casey, S. E. Beetner, J. B. Johnson, "Spectroscopic Determination of Hydrogenation Rates and Intermediates during Carbonyl Hydrogenation Catalyzed by Shvo's Hydroxycyclopentadienyl Diruthenium Hydride Agrees with Kinetic Modeling Based on Independently Measured Rates of Elementary Reactions," *J. Am. Chem. Soc.* **130** (2008) 2285-2295.

FWP CH030201 **Christopher J. Chang**

Bioinspired Oxidation Catalysis of Energy Consequence

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Goal

The long-term goal of this research program is to develop bioinspired synthetic catalysts for oxygen-based reactions that rely on cheap and plentiful first-row transition metals. Our main focus is on the coordination chemistry of iron in various geometries to achieve this aim. Of particular interest are multielectron, multiproton oxygen activation, functionalization, and evolution pathways that form the basis for natural and synthetic carbon-neutral energy conversion cycles, with water splitting as the holy-grail catalytic reaction. Synthetic designs are biomimetic and guided by principles of natural metalloenzymes, which exert exquisite control over substrate reactivity at first-row transition metal sites by dual management of proton and electron inventories. This program seeks to capture the functional essence of biological energy conversion systems and extend their chemistry beyond the constraints of the protein environment.

Recent Progress

We have developed several new types of nitrogen-based ligand templates for first-row transition metal centers and have elaborated their coordination chemistry. A unifying design feature for all these scaffolds is the use of bioinspired donors that are electronically compatible with coordination to early, mid, or late metals. Included are pyrroles, imidzoles, and pyridines that can be incorporated into chelating frameworks. The synthesis and structural characterization of a variety of unsaturated iron complexes with coordination numbers ranging from two to five has been achieved without resorting to excessive steric bulk. The resulting iron compounds are competent for stoichiometric and catalytic group transfer reactions. In particular, a new three-fold symmetric non-heme iron pyrrole platform shows promising activity through the activation of nitrous oxide, a thermodynamically potent oxidant that is difficult to harness kinetically because it is a poor ligand.

DOE Interest

The proposed research program in bioinspired energy catalysis addresses the overall BES scientific/technical mission of developing predictive catalyst design principles by advancing three frontiers of catalytic research: (i) multielectron chemistry at cheap and abundant first-row transition metal centers, (ii) bond-making and bond-breaking reactions at energy-poor substrates, and (iii) coupling electron and proton transfer for catalytic transformations.

Future Plans

Spectroscopic and structural characterization of intermediates along stoichiometric and catalytic pathways will be pursued. We are particularly interested in high-valent iron-oxo intermediates and catalytic turnover with nitrous oxide, oxygen, or hydrogen peroxide as terminal oxidants. Manganese analogs will also be elaborarted. Reactions with other small-molecule substrates of energy consequence, including carbon dioxide, hydrogen, water, and protons, will also be evaluated.

"N_2O Activation and Oxidation Reactivity from a Non-Heme Iron Pyrrole Platform", Harman, W. H.; Chang, C. J. *J. Am. Chem. Soc.* **2007**, *129*, 15128-15129.

DE-FG02-05-R659 **Paul J. Chirik**

Understanding Nitrogen Fixation

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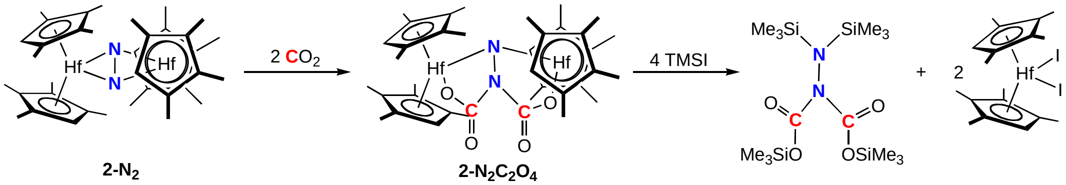
Goal

Develop soluble transition metal reagents for the transformation of atmospheric nitrogen into ammonia and other value-added nitrogen-containing molecules. The design and synthesis of these compounds is based on concurrent mechanistic studies aimed at elucidating the factors that govern the reactivity of coordinated dinitrogen.

Recent Progress

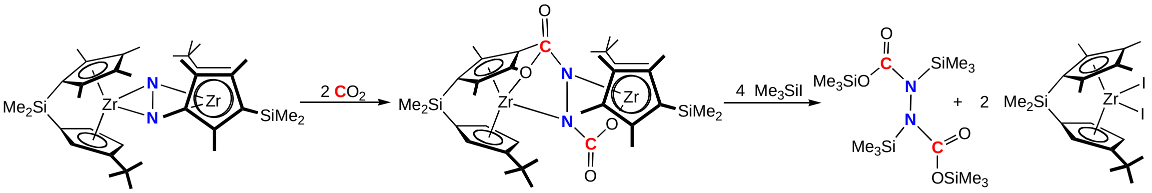
Our laboratory has continued the exploration of strongly activated group 4 metallocene dinitrogen complexes for assembly of new bonds to atmospheric nitrogen. More recently we have been focused on formation of nitrogen-carbon bonds with the goal of synthesizing nitrogen-containing organic molecules directly from atmospheric nitrogen.

The C_s symmetric hafnocene dinitrogen complex, **2-N$_2$**, is a robust molecule in solution and does not suffer from deleterious side-on, end-on isomerization of the N_2 ligand upon exposure to additional dinitrogen. Accordingly, this compound undergoes insertion and cycloaddition of various heterocummulenes with the metal-nitrogen bonds. Addition of two equivalents of CO_2 resulted in N-C bond formation where the heterocummulene inserted into two of the Hf-N bonds. The new product was characterized by multinuclear (^{1}H, ^{13}C, ^{15}N) NMR spectroscopy, infrared and X-ray diffraction studies. Notably, new N-C bonds were formed from two abundant and typically inert small molecules, N_2 and CO_2. The functionalized dinitrogen core can be further elaborated into free carboxylated hydrazine upon addition of the appropriate electrophile. Addition of excess Me_3SiI resulted in formation of the hafnocene diiodide complex (the precursor to the N_2 compound) and $(Me_3Si)_2N\text{-}N(CO_2SiMe_3)_2$. The new hydrazine, assembled from N_2 and CO_2, was characterized by NMR and IR spectroscopies and mass spectrometry.

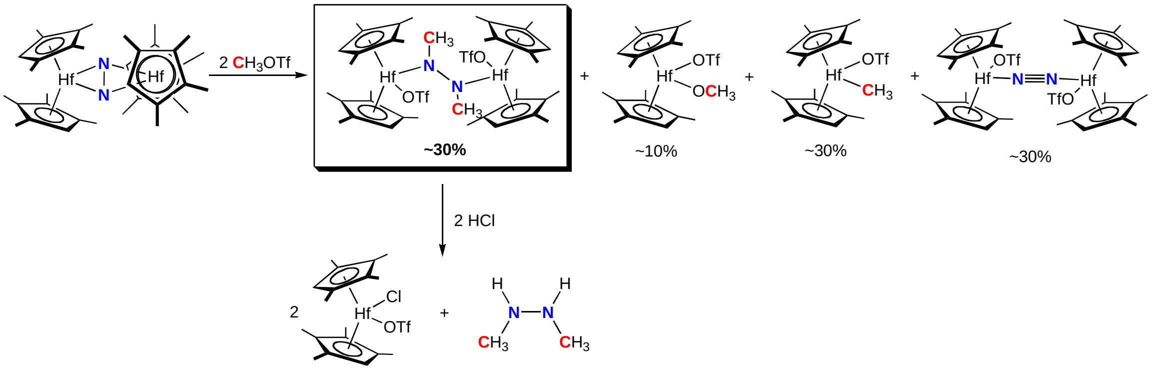


2-N$_2$ 2-N$_2$C$_2$O$_4$

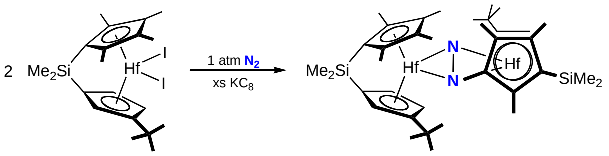
Following this initial discovery, we posited whether zirconocenes could be enticed into similar types of reactivity. Introduction of an [SiMe$_2$]-bridged bis(cyclopentadienyl) ligand into the metal coordination sphere was shown to suppress side-on, end-on isomerization and produce compounds with strongly activated N-N bonds. Addition of two equivalents of CO_2 to the C_2 symmetric *ansa*-zirconocene compound resulted in N-C bond formation with different regiochemistry than the hafnium compound. Thus, the symmetry imparted by the cyclopentadienyl ligand environment may be used to direct N_2 functionalization opposite the *tert*-butyl group. Treatment with four equivalents of Me_3SiI liberated the N, N'-dicarboxylated silylated hydrazine.



An alternative approach for N-C bond formation is direct addition of a carbon-based electrophile to coordinated dinitrogen. While well-known for group 6 transition metal dinitrogen complexes, such reactions remain rare in group 4 chemistry. Addition of MeOTf (OTf = triflate) to the hafnocene dinitrogen complex, **2-N₂** formed the hafnocene methyl diazenido compound in modest yield along with other fully characterized side products. Subsequent treatment of this product with a proton source, typically HCl or water, liberated free N, N'-dimethylhydrazine. Thus, a direct route from dinitrogen, independent of ammonia, has been discovered for the synthesis of various alkylated hydrazines.



Current efforts are aimed at exploring the reactivity of the dimethylated diazenido compound toward various electrophiles. Methods for the synthesis of hydrazones have recently been discovered and will be a cornerstone for future investigations. We have also recently synthesized a new C_2 symmetric, *ansa* hafnocene dinitrogen complex and are exploring its reactivity with electrophiles and CO_2.



DOE Interest

The synthesis of ammonia from its elements, N_2 and H_2, is one of the most energy-intensive processes practiced in the chemical industry. The impacts of this energy requirement are profound - crop fermentation products such as ethanol too energetically expensive to replace fossil fuels. Because many amines and other nitrogen-containing organic molecules are synthesized from industrial ammonia, it is beneficial to explore alternative, ammonia-free synthetic routes to this class of compounds. Our laboratory has recently discovered that many organic molecules can be synthesized from two inert atmospheric gases, N_2 and CO_2, along with appropriate electrophiles.

Future Plans

Our laboratory continues to focus our efforts in developing new bond-forming reactions with coordinated dinitrogen. Importantly, we have learned how to assemble N-C linkages via different mechanistic pathways: direct carbon-based electrophile addition, heterocummulene cycloaddition and insertion. Using these established paradigms, we will continue to explore synthetic methods for the selective construction of nitrogen-containing organic molecules using N_2 and (ideally) CO_2 as feedstocks.

Recent Publications Resulting from DOE Support

Pun, D.; Lobkovsky, E.; Chirik, P. J. “Indenyl zirconium dinitrogen chemistry: N_2 coordination to an isolated zirconium sandwich and synthesis of side-on, end-on dinitrogen compounds.” *J. Am. Chem. Soc.* **2008**, *130*, ASAP. (DOI: 10.1021/ja801021w)

Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. “Carboxylation of an *Ansa*-Zirconocene Dinitrogen Complex: Regiospecific Hydrazine Synthesis from N_2 and CO_2.” *J. Am. Chem. Soc.* **2008**, *130*, 4248-4249.

Toomey, H. E.; Pun, D.; Veiros, L. F.; Chirik, P. J. “1,2-Addition versus □-Bond Metathesis Reactions in Transient Bis(cyclopentadienyl)zirconium Imidos: Evidence for a d^0 Dihydrogen Complex.” *Organometallics* **2008**, *27*, 872-879.

Pun, D.; Lobkovsky, E.; Chirik, P. J. “Amineborane dehydrogenation promoted by isolable zirconium sandwich, titanium sandwich and N_2 complexes.” *Chem. Commun.* **2007**, 3297-3299.

Hanna, T. E.; Bernskoetter, W. H.; Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. “Bis(cyclopentadienyl) titanium dinitrogen chemistry: Synthesis and characterization of a side-on bound haptomer.” *Organometallics* **2007**, *26*, 2431-2438.

Hanna, T. E.; Keresztes, I.; Lobkovsky, E.; Chirik, P. J. “Diazene dehydrogenation follows H_2 addition to coordinated dinitrogen in an *ansa*-zirconocene complex.” *Inorg. Chem.* **2007**, *46*, 1675 - 1683.

Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. “Nitrogen-carbon bond formation from N_2 and CO_2 promoted by a hafnocene dinitrogen complex yields a substituted hydrazine.” *Angew. Chem. Int. Ed.* **2007**, 2858-2861. (Article Featured on Cover)

DE-FG02-07ER15844 **Malcolm H. Chisholm**

"Mechanistic and Synthetic Studies Aimed at the Development of Single-Site Metal Alkoxide Catalysts for the Generation of Polyesters and Polycarbonates"

Postdoctorals: Keith Quisenberry ('06, '07), Ruaraidh McIntosh ('07, '08).
Graduate Students: Hongfeng Yin ('06), Gulsah Yaman ('06, '07), Chandrani Chatterjee ('07, '08)
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Goal

To develop an understanding of the fundamental reactions involved in, and subsequently the design of new catalysts for the formation of polyoxygenates (polyethers, polyesters and polycarbonates) from renewable resources.

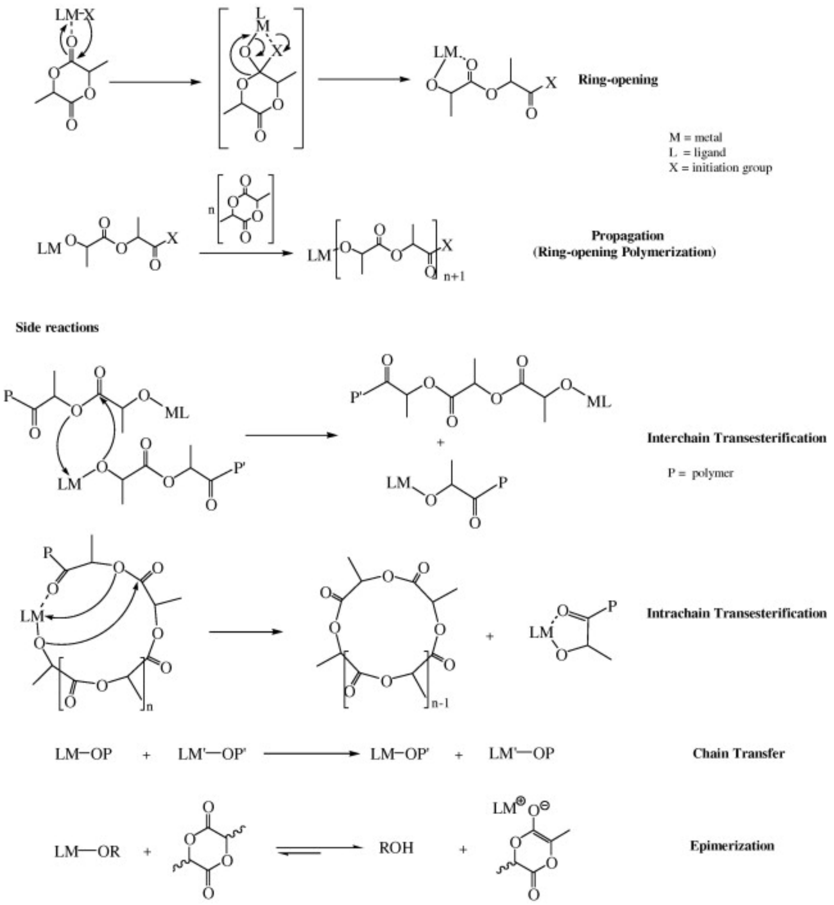
DOE Interest

Renewable resources will play an increasingly important role in the production of energy and chemical commodities. Currently 90% of the chemical industry is petroleum based but we can anticipate this will change significantly as new feedstocks and chemical processes are developed from biomass. The focus of this research program is on catalysis development for the production of "new generation polymers" from renewable resources such as carbon dioxide and lactide.

Recent Progress

The various reactions involved in the ring-opening polymerization of lactide are shown in Scheme 1. Related reactions are also operative in the ring-opening polymerization of other cyclic esters such as caprolactone and in trimethylene carbonate to give polyesters and polycarbonates, respectively. Our work has shown that the relative rates of polymerization are dependent on the polarity of the M-OR bonds so that for example we observe $M^{2+} > M^{3+} > M^{4+}$ as in $Mg^{2+} > Al^{3+} > Sn^{4+}$. Studies of the relative slow Al(3+) alkoxide polymerization reveal the relative rates of these reactions to be: reversible LA coordination > alcohol-alkoxide exchange > chain end exchange > ring-opening/enchainment of monomer > trans-esterification > epimerization. In the stereoselective ring opening of *rac*-LA, we have found that the importance of chain-end control and solvent to be equally important with enantiomorphic site control.

For M^{2+} ions the rate of ring-opening and propagation is dependent on both bond polarity and size of the metal ion leading to the order $Ca^{2+} > Mg^{2+} > Zn^{2+}$. The highly reactive catalysis achieved by Ca and Mg metal complexes is compromised by facile ligand exchange (Schlenk equilibria) and hydrolysis by deleterious water. In order to suppress these deleterious side reactions we have designed a tris-pyzolyl ligand having hemi-labile ether appendages. This has shown a most fascinating versatile coordination chemistry and has led to the isolation of a remarkably stable calcium complex (chemically persistent to air and moisture) that is an effective initiator for the ROP of lactides and related cyclic esters. The seven coordinate phenoxide is shown in Figure 1.



Scheme 1. Reactions involved in ring opening polymerization of lactide using a coordination catalyst.

(?6-Tp*)Ca-OC$_6$H$_4$-p-CH$_3$

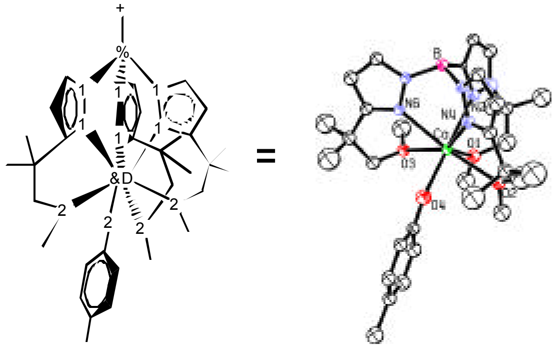


Figure 1.

As noted in Scheme 1, intrachain cyclization leads to cyclic esters and we have designed a supported catalyst system for the conversion of lactide to cyclic esters (MeCHC(O)O)$_n$. The catalyst system produced a dynamic combinatorial library of cycles and the introduction of NaBPh$_4$ provides a means of chemical application of the 18-membered rings by complexation and the formation of Na[MeCH(O)O]$_6$BPh$_4$. Treatment of this salt with TMEDA in CH$_3$CN frees the cycles which due to epimerization exist as two meso isomers (*RRRSSS*) and (*RSRSRS*) and six enantiomeric pairs each of which has been identified and characterized. The meso (*RSRSRS*) isomer and its complexation with Na$^+$ as determined by a single crystal structure are shown in Figure 2.

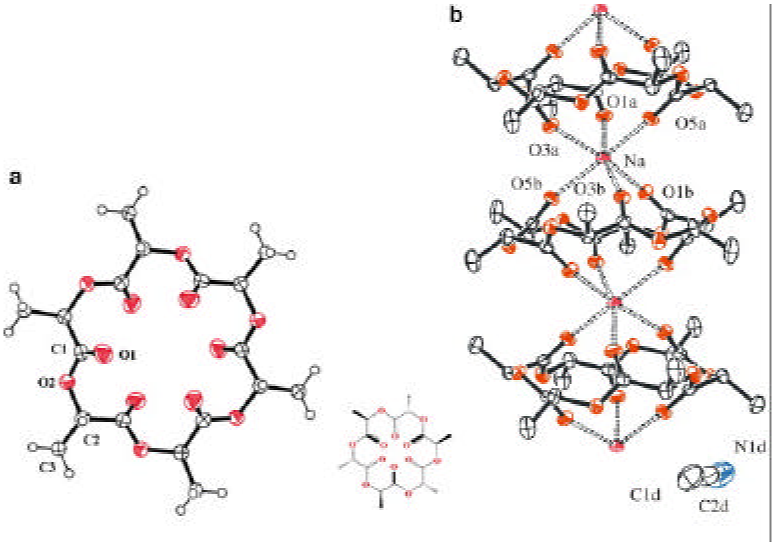
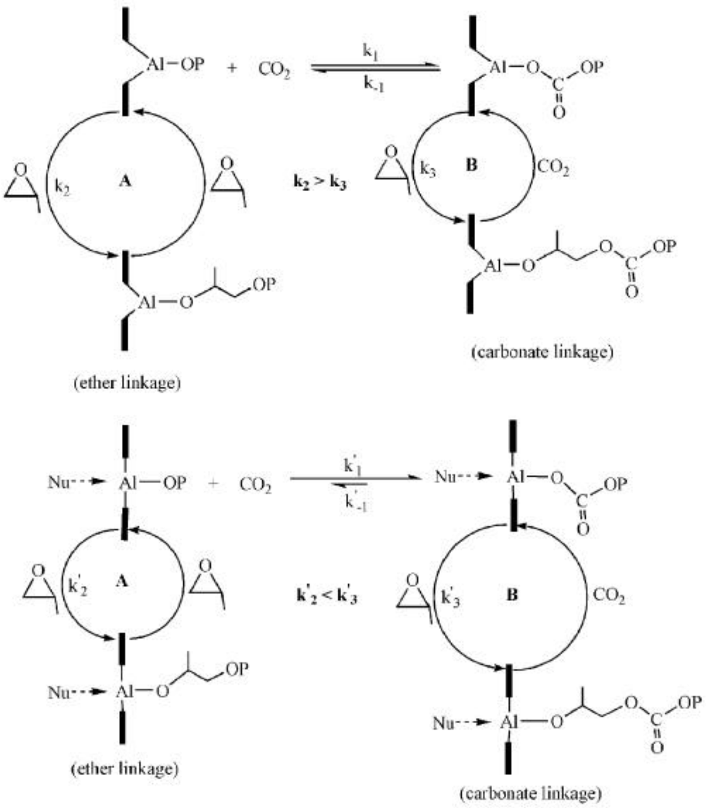


Figure 2.

Studies of the copolymerization of propyleneoxide, PO, and carbon dioxide to give polypropylenecarbonate, PPC, have elucidated the key reaction steps by which the PO molecule is enchained. See Scheme 2.



Scheme 2. Proposed mechanism for PO/CO_2 copolymerization by (TPP)AlX systems, where Nu represents the added Lewis base promoter.

Our initial work with (porphyrin)AlOR complexes is currently being extended to related (porphyrin)MOR initiators where the metal is chromium and cobalt. This is a particularly interesting study because all the metals have similar ionic radii but are d^0, d^3 and d^6 with differing coordination properties. Of particular note is the facility of the Cr(III) system to produce polyether carbonates under mild conditions $H(OCH_2CHMe)_n(CO_2)_m$-H where $n > m$.

Future Plans

1. Develop stereoselective calcium catalysts for the ROP of *rac*-LA, *meso*-LA and related cyclic esters.

2. Develop a method for the production of cyclic esters with other functional groups.

3. Develop an understanding of the electronic factors influencing the copolymerization of PO and CO_2 by the paramagnetic d^3-Cr^{3+} and d^6-Co^{3+} ions.

Publications (2006-2008)

1. Comments on the Ring-opening Polymerization of Morpholine-2, 5-Dione Derivatives by Various Metal Catalysts and Characterization of the Products Formed in the Reactions Involving R_2SnX_2, Where X = OPr^i and NMe$_2$ and R = Bu^n, Ph and *p*-Me$_2$NCH$_4$. Malcolm H. Chisholm, Judith C. Gallucci, Clemens Krempner, and David C. Wiggenhorn, *Dalton Trans.*, (6), 846-851 (2006).
2. A *tris*-pyrazolylborate ligand with hemilabile O-donor groups. Examples of $?^3$, $?^5$, $?^6$ and bridging modes of bonding to Li^+, Na^+, K^+, Tl^+ and Ca^{2+} ions. Malcolm H. Chisholm, Judith C. Gallucci, and Gulsah Yaman, *Chem. Commun.,* (17), 1872-1874 (2006).
3. Cyclic esters and cyclodepsipeptides derived from lactide and 2,5-morpholinediones. Malcolm H. Chisholm, Judith C. Gallucci, and Hongfeng Yin, *PNAS*, 103(42) 15315-15320 (2006).
4. Stereoselective Polymerization of Lactide. Malcolm H. Chisholm and Zhiping Zhou, “Catalysis for Stereoselective Polymerization”, L. S. Baugh and J. M. Cannich Eds., Taylor and Francis publishers; Ch. 25 (2007).
5. Ring-Opening Polymerization of L-Lactide by Organotin(IV)alkoxides: R$_2$SnOPr^i)$_2$: Estimation of the Activation Parameters. Malcolm H. Chisholm, Judith C. Gallucci, and Clemens Krempner, *Polyhedron*, 26(15), 4436-4444 (2007).
6. 18-Membered Cyclic Esters Derived from Glycolide and Lactide: Preparations, Structures and Coordination to Sodium Ions. Malcolm H. Chisholm, Judith C. Gallucci, and Hongfeng Yin, *Dalton Trans.*, (42), 4811-4821 (2007).
7. Catalysis Design for Ring-Opening Polymerization of Cyclic Esters. 1. Group 1 Metal and Thallium(I) Trispyrazolylborate Complexes with Hemilabile Ligands. Malcolm H. Chisholm, Judith C. Gallucci, and Gulsah Yaman, *Inorg. Chem.,* 46(21), 8676-8683 (2007).
8. Mechanistic insights gained from studies of lactide polymerization by slow (M = Al) and fast (M = Ca) metal coordinate catalysts. Malcolm H. Chisholm, Judith C. Gallucci, Keith T. Quisenberry, Gulsah Yaman, Zhiping Zhou, *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry), 48(2), 814-815, (2007).
9. Complexities in the Ring-Opening Polymerization of Lactide Chiral Salen Aluminum Initiators. Malcolm H. Chisholm, Judith C. Gallucci, Keith T. Quisenberry and Zhiping Zhou, Inorg. Chem., in press (2008).
10. Catalytic Formation of Cyclic-Esters and –Depsipeptides and Chemical Amplification by Complexation with Sodium Ions. Malcolm H. Chisholm, J. of Organomet. Chem., 693, 808-818 (2008).

Grant Number: DE-FG02-84ER13297 **Robert H Crabtree**

Bifunctional Ligands for Enhanced Selectivity in Organometallic Catalysis

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Contact: Yale University Chemistry Department, New Haven 06520-8107.
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Goal

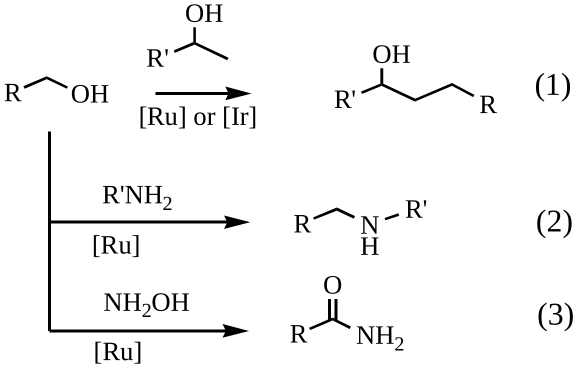
To design and construct ligands having additional functionality beyond simple ligation in order to obtain enhanced selectivity or activity in catalysis. To explore N-rich pincer ligands, a little-studied ligand class in organometallic catalysis but one for which construction of bifunctional ligands will be easier and which may allow less expensive metals to be used.

DOE interest

Catalysis of atom economic reactions that avoid coproduction of waste is a current topic in homogeneous catalysis. The very big recent price rise in Pd and Rh has made moving from these metals to the much cheaper Ru and Ir, and ultimately also to Fe, Co and Ni a goal of importance.

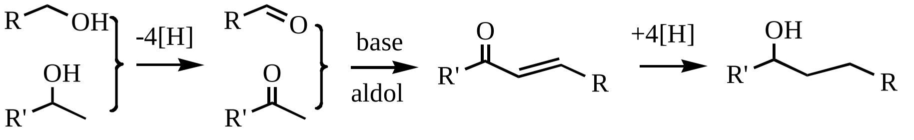
Recent Progress

N-rich pincer ligands are found to give the most active known catalysts for new classes of atom economic alcohol activation reactions. Ru and Ir catalysts are involved, meeting our goal of avoiding the most expensive Pt group metals.

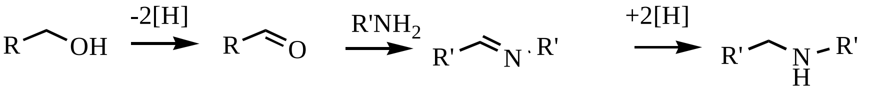


The catalysts chosen are rather unusual, containing terpyridine (terpy), a ligand we have found very useful in our coordination catalysis work. In this case we find that terpy has the additional advantage of making the catalytic mixtures air and moisture-stable, simplifying their application relative to known catalysts as well as giving much more active catalysts than previously reported. The best current catalysts are [Ru] = [(terpy)Ru(PPh$_3$)Cl$_2$] and [Ir] = [(terpy)IrCl$_3$] but optimization is far from complete.

The reactions appear to go by dehydrogenation of the alcohol to the aldehyde (or ketone). For eq. 1, this is followed by an aldol step that is remarkably selective for the cross coupled product where the secondary alcohol becomes the enolate nucleophile. The origin of this high selectivity is not yet clear. The final step (eq. 4) involves transfer of the hydrogen removed from the alcohols in the dehydrogenation step to the aldol product.


(4)

The reaction of eq. 2 may occur by dehydrogenation, imine formation, then hydrogenation (eq. 5).


(5)

The reaction of eq. 3 may go via oxime formation, followed by rearrangement of the oxime to the amide, a transformation we have independely observed with the [Ru] catalyst.

We have also developed a useful atom economic coupling of a carboxylic acid ArCOOH with an arene Ar'H via C-H activation to give Ar-Ar' and CO_2; the coproduced H_2 is oxidized by the oxidant also present to give $2H^+$. Coupling with Ar'I is also possible. The reaction is greatly enhanced in rate with microwave irradiation rather than the usual thermal activation. Palladium acts as the coupling catalyst and a number of oxidants are successful – Ag salts are the best but Cu salts and even organic oxidants also work. In favorable cases, conversions of 80% and yields of 60% are possible with 5 mol% catalyst. Intramoleular variants need to be tried and cheaper oxidants are sought.

Plans

The mechanistic aspects of these reactions need attention, particularly if we can gain insight into how to improve and extend them. The terpyridine area has been so productive that we intend to concentrate on this and on N-rich pincers in general, as well as seeing if the Pt metals can be avoided altogether in these and related catalytic reactions.

Publications (2006-8)

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DE-FG02-03ER15468 **Richard M. Crooks**

Understanding Multimetallic Catalysts using Dendrimer-Encapsulated Nanoparticles

Students:	Michael Weir & Emily Carino
Collaborators:	Douglas Buttrey (U. Delaware), Anatoly Frenkel (Yeshiva U. and the National Synchrotron Light Source), Graeme Henkelman (UT Austin), Valeri Petkov (Central Michigan U. and the Advanced Photon Source)
Contact:	Richard M. Crooks, Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712-0165

Goal

Synthesize and characterize structurally well-defined bimetallic nanoparticles using a dendrimer templating approach, and then evaluate their electrocatalytic properties as a function of size, composition, and structure. Compare results to theoretical calculations.

DOE Interest

The dendrimer templating approach is an effective route to the synthesis of chemically and structurally well-defined bimetallic catalytic nanoparticles. We envision that these materials will provide excellent experimental models for developing the next generation of catalytic materials. The partnerships with Graeme Henkelman at the University of Texas, Douglas Buttrey at the University of Delaware, Anatoly Frenkel at Yeshiva University (NSLS), and Valeri Petkov at Central Michigan University (APS) allows us to guide future development of highly selective bimetallic catalysts according to theoretical models and study their structural and catalytic properties in detail.

Recent Progress

There is much interest in the effect of catalyst size on rates of chemical reactions. One reaction of particular interest to the DOE is the oxygen reduction reaction (ORR), which is the cathode reaction in hydrogen/oxygen fuel cells. This reaction is particularly well-suited for quantitative study using dendrimer-encapsulated nanoparticles (DENs) for a number of reasons. First, in the size range of 1 – 2 nm, DENs have been found to be the most size-monodisperse catalytic nanoparticles available. Second DENs are prepared and characterized prior to surface immobilization, and this means that numerous high-resolution methods (TEM, EDS, EXAFS, high-energy XRD, XPS, and so forth) can be used to ensure that their degree of homogeneity is sufficient to make concrete statements regarding trends in catalytic activity. Third, electrochemical methods provide a means for making exceptionally accurate kinetic measurements.

Here, we utilized the dendrimer templating method to prepare 1-2 nm-diameter Pt nanoparticle catalysts consisting of an average of 55, 100, 147, 200, and 240 atoms having low (< ±0.3 nm) size polydispersity. Table 1 shows the measured (by TEM) and calculated particle sizes for these materials.

Table 1

Sample	Average Particle Size	Calculated Size[a]
G6-OH(Pt$_{240}$)	1.90 ± 0.29 nm	1.91 nm
G6-OH(Pt$_{200}$)	1.79 ± 0.26 nm	1.79 nm
G6-OH(Pt$_{147}$)	1.66 ± 0.25 nm	1.62 nm
G6-OH(Pt$_{100}$)	1.52 ± 0.27 nm	1.42 nm
G6-OH(Pt$_{55}$)	1.44 ± 0.26 nm	1.17 nm

These Pt DENs were linked to electrode surfaces using an electrochemical method that results in robust attachment. Next, two methods (CO oxidation and hydrogen desorption) were used to quantitatively determine the total area of exposed Pt on the electrode surface (Table 2).

Table 2

Catalyst	Charge from CO (μC)	Charge from H-des (μC)	Area from CO (cm^2)[b]	Area from H-des (cm^2)[b]	Ratio of Pt areas (H/CO)	Cacluated Area (cm^2)
Bulk Pt	131	66	0.31	0.31	1.0	0.196[c]
G6-OH(Pt$_{240}$)	360	126	0.86	0.60	0.70	0.15
G6-OH(Pt$_{200}$)	199	67	0.47	0.32	0.67	0.14
G6-OH(Pt$_{147}$)	97	31	0.23	0.15	0.64	0.11
G6-OH(Pt$_{100}$)[a]	27	7.5	0.064	0.036	0.56	0.085
G6-OH(Pt$_{55}$)[a]	14	3.2	0.033	0.015	0.46	0.058

Next, rotating disk voltammetry was carried out in aqueous O_2-saturated, 0.1 M $HClO_4$ to determine the kinetics of oxygen reduction for each of the five different sizes of Pt DENs. The results of this study are shown in Figure 1.

Figure 1

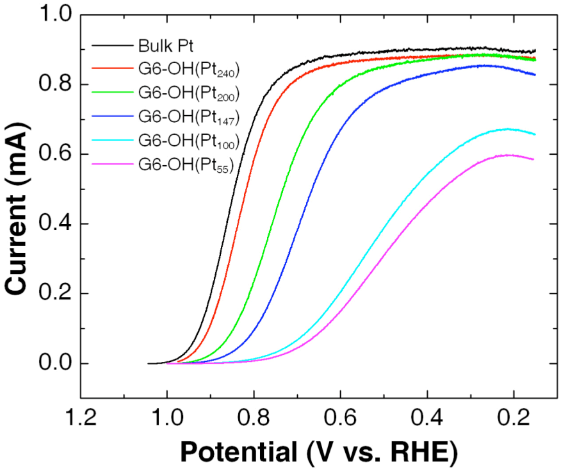
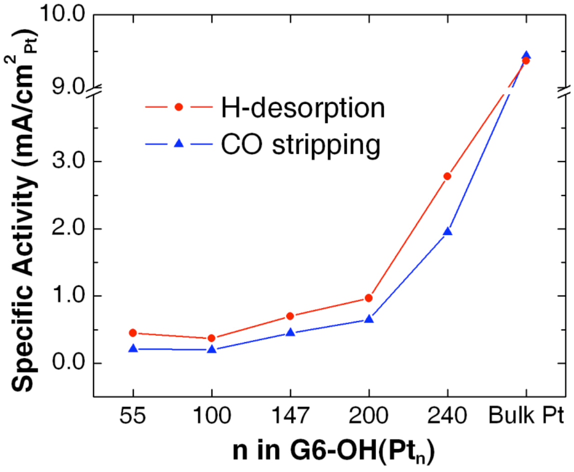


Figure 2



The specific activities (SAs) for the five DENs are determined by dividing the kinetic currents, determined from the voltammograms, by the experimentally measured surfaces areas (Table 2). This is an important step, because it provides a direct comparison of the kinetic properties of DENs having different sizes. Figure 2 compares the SA values determined at 0.80 V. Bulk Pt exhibits the highest SA value (9.4 mA/cm$^2_{Pt}$

at 0.80 V). The Pt DENs exhibit much lower SA values, and there is a clear monotonic decrease in SA as the particle size decreases. Because the dendrimers are the same for all the DENs, and because the number of dendrimers (and hence the number of DENs) should be the same, we conclude that these results establish a relationship between catalyst size (in the 1-2 nm size range) and activity. At present, we are working toward establishing a first-principles understanding of this relationship, but this will require detailed calculations and a better understanding of the structure of the nanoparticles.

Future Plans

We are currently focused on two primary objectives. First, we are working with our collaborator, Anatoly Frenkel, to carry out in-situ quick EXAFS studies of Pt DENs as a function of time during during the ORR. These studies will ensure that the nanoparticles are stable during reaction, and they will set the stage for more important stability studies of bimetallic catalysts. Second, guided by theoretical calculations carried out by our collaborator Graeme Henkelman, we are preparing core/shell Pd/Cu DENs. Calculations indicate that a Cu core should lower the d-band energy of the Pd shell and hence render it more Pt-like. We plan to vet the theory by comparing the activity of these bimetallic catalysts to Pt DENs containing the same number of atoms.

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DE-AC05-00OR22725 **Sheng Dai**

Colloidal Deposition Synthesis of Supported Gold Nanocatalysts Based on Au-Fe_3O_4 Dumbbell Nanoparticles for CO Oxidation

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Since Haruta's pioneering work in 1987 on the extraordinary catalytic activity of nanoscale gold particles for CO oxidation at low temperature,[1] synthetic methodologies for the preparation of gold nanoparticle catalysts have been extensively investigated. These include precipitation deposition,[2] co-precipitation,[3] ligand-assisted deposition,[4] ion exchange,[5,6] and colloidal deposition.[7,8] Among these synthetic methods, the colloidal deposition (CD) is relatively new and has recently gained an increased popularity due to the advancement in solution-phase syntheses of monodispersed Au nanoparticles and deposition of these nanoparticles on various supports without the constraint of support surface properties (e.g., isoelectric point). In this CD methodology, gold nanoparticles are pre-synthesized and subsequently deposited on supports via wet impregnation or incipient wetness.[7,8] The key drawback associated with the CD technique is that the pre-synthesized gold nanoparticles are only physically dispersed on oxide supports and the resultant gold catalysts lack direct metal-support interactions.[9] Furthermore, these catalytic systems have limited thermal stabilities and often sinter under high-temperature catalytic reaction conditions.[2,7] To overcome this intrinsic deficiency, we herein report a new CD methodology for the synthesis of sintering-resistant nanocomposite Au catalysts based on dumbbell-structured Au-Fe_3O_4 nanoparticles (Figure 1). Highly active gold catalysts for CO oxidation were prepared on carbon, silica, and titania.

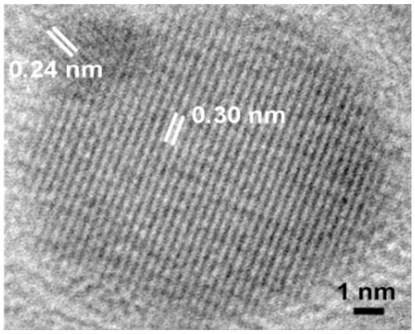

Figure 1. High-resolution TEM image of a single dumbbell-structured Au-Fe_3O_4 nanoparticle.

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DOE Grant No. DE-FG02-03ER15466 **W. Nicholas Delgass**

CATALYSIS SCIENCE INITIATIVE: Catalyst Design by Discovery Informatics – Olefin Polymerization over Single-Site Catalysts

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Goal

Develop and apply an informatics-intensive, model-based approach that extracts knowledge from data for the design of catalysts, focusing first on single-site olefin polymerization catalysts, water gas shift catalysts for the production of hydrogen, and metal-promoted zeolites for the alkane aromatization.

DOE Interest

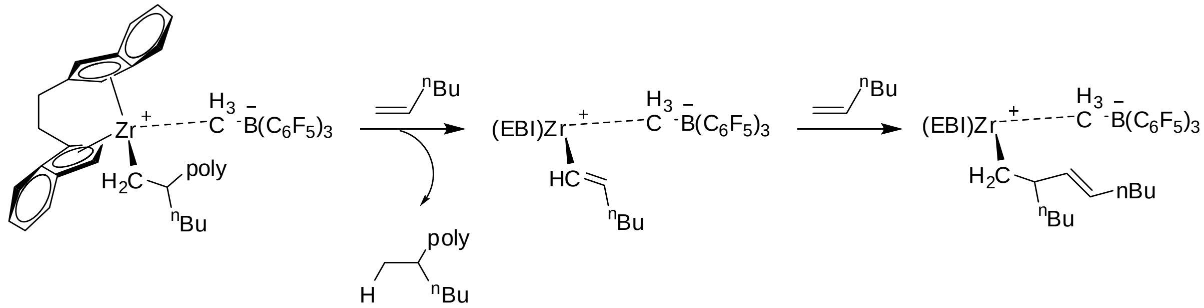
Validation of this new design concept has the potential to change the catalysis research landscape by dramatically shortening hypothesis testing and new discovery cycles for virtually any catalyst system, heterogeneous or homogeneous.

Recent Progress

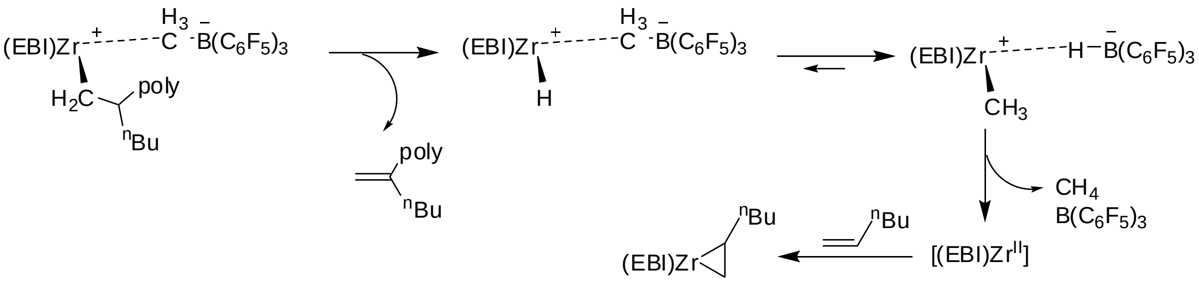
- ***Kinetics and Mechanism of 1-Hexene Polymerization Catalyzed by [rac-(C_2H_4(1-indenyl)$_2$)ZrMe$_2$], Britzinger's Catalyst.***

The kinetics of 1-hexene polymerization catalyzed by (EBI)Zr$(CH_3)_2$ activated with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ was investigated by following monomer consumption with NMR, as well as by GPC analysis of the resulting polymer taken at ca. 20, 30, and >95% conversion. The active site count was performed by quenching the reaction at 20-30% conversion with CH_3OD and analyzing the chain ends by ^{2}H-NMR. Two signals were observed at 1.0 and 1.5 ppm (integrals 3:1), corresponding to primary and secondary alkyl positions respectively. This observation is consistent with ¼ of the catalyst sites containing 2,1-misinsertion. The olefinic region of the polymer was analyzed for vinylene and vinylidene by ^{1}H-NMR at 30 and 96% conversion. Global kinetic modeling in the from of fitting the MW distribution of the resulting polymer with the kinetic data from NMR shows the data is consistent with the presence of dormant sites and a chain transfer pathway. Both processes require first order dependence on monomer concentration. We propose that 2,1-misinsertion creates dormant sites. This is supported by active site counting by ^{2}H-NMR. The chain transfer to monomer mechanism (Scheme 1) accounts for lower peak molecular weight at high monomer conversions and introduces additional vinylene groups. Another potential dormant site pathway is formation of the $[HB(C_6F_5)_3^-]$ ion pair (Scheme 2), which may occur at high conversions. We plan on quantifying the amount of CH_4 the system evolves.

Our study has provided insight on the chemical pathways that account for the molecular weight of polyhexene in this catalyst system while providing accurate rate constants for initiation, propagation, and chain transfer. The developed kinetic model is expected to be of tremendous value to us and others in evaluating other catalysts.



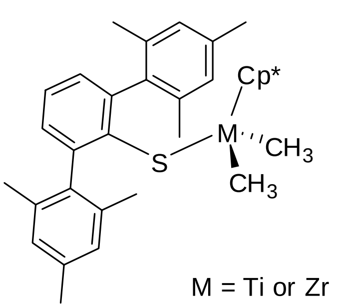
Scheme 1. Chain transfer to monomer.



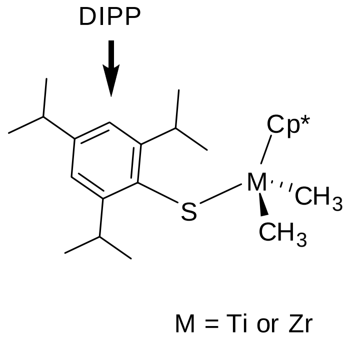
Scheme 2. Vinylidene formation at high conversion.

- ***Synthesis, Characterization and preliminary polymerization studies with new catalyst families featuring thiolato, amido, and imido ligands*.**

We have successfully prepared the sterically hindered thiolato complexes of Ti and Zr (see structures below). While neither complex with the $B(C_6F_5)$ activator catalyzes 1-hexene polymerization in a variety of solvents (toluene, bromobenzene, and dichlorobenzene), the Ti complex does catalyze ethylene polymerization readily under ambient temperature and pressure. DFT computational studies showed that the employed thiolato ligand is too hindered to allow sufficient ion-pair separation for 1-hexene docking and predicted the DIPP analog to be more favorable for 1-hexene polymerization (see structure below). We have prepared the (DIPP)SH ligand and are in the process of synthesizing the Ti and Zr complexes.

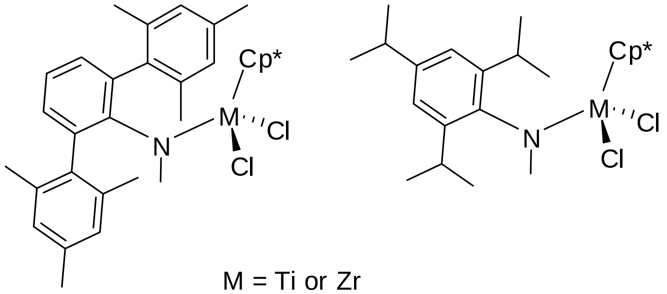


Synthesized



Target, ligand already prepared.

The synthesis of amido analogs of the thiolato precursors (see structures below) is under way. We have the chloride precursors in hand. However, the methylation reaction requires further optimization.



When Li[ArNH] ligands are employed, the reaction with Cp*MR$_3$ (where, M = Ti or Zr, and R = Cl or CH$_3$) proceeds to eliminate HCl or CH$_4$ and yields metal imido complexes. These are of interest because they may potentially act as catalysts without requiring an activator. We have prepared the chloride complexes with the bulky ligand shown above. However, the methylation reaction has eluded us so far and has not produced pure crystalline material. Nevertheless, we are pursuing alternate routes and hope to have the alkyl imido analogs in hand in the near future.

- ***Detailed Kinetic Analysis of 1-Hexene Polymerization by the Britzinger Catalyst***

Kinetic analysis of the (EBI)Zr(CH$_3$)$_2$ system showed that early in the reaction the molecular weight of the polymer was too high to be explained by the observed propagation rate while later in the reaction the peak molecular weight predicted was too high compared to the experiment. Thus, the data confirm that published models cannot fully account for the behavior of this important system. Formation of a dormant site accompanied by an additional chain transfer reaction (i.e. chain transfer over and above beta-hydride elimination) is capable of describing both the observed propagation rate and the molecular weight distribution (MWD) as given in Figure 1. An iterative process in which the kinetic modeling drives the design of experiments is currently being employed to find experimental evidence for the existence of a dormant site and an additional chain transfer reaction. This has been a time-intensive process as new experimental techniques have been incorporated into our arsenal of mechanism-probing methods. The additional experimental techniques have subsequently enriched the data set, further constraining the kinetic modeling effort as additional types of data, e.g. vinylene/vinylidene double bond concentration and ^{2}H-NMR end group analysis, are fit in conjunction with the originally considered monomer concentration versus time data and the time evolution of the MWD. Table 1 illustrates that although Figure 1 shows the monomer consumption and MWD data are predicted by the 'dormant + additional chain transfer' kinetic model, this particular kinetic model fails to predict the double bond concentration and thus is not an adequate model to describe the system. The discovery of the true kinetic mechanism presently remains elusive but significant progress has been made as a number of various kinetic models have been proposed and systematically discarded based on experimental evidence obtained during the iterative process.

Although this catalyst system has proven to be more challenging than initially anticipated, several positives have resulted. This system suffers from the special case of having a rich multi-response data

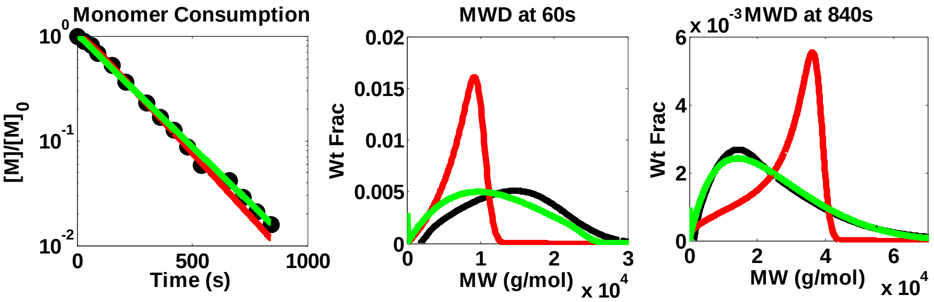


Figure 1. 1-hexene consumption and molecular weight distribution where **black** is data, **red** has no dormant sites, and **green** includes 'dormant sites + additional chain transfer mechanism'.

Table 1. Double Bond Concentration for 'Dormant + Additional Chain Transfer' Kinetic Model Given in Figure 1 (**green**)

Time (s)	Double Bond Concentration Experimental (mM)	Predicted (mM)
100	4.9	1.7
800	6.6	4.7

set that cannot be described by any presently proposed kinetic model, even those with higher numbers of parameters. The resulting good news is that, while a mechanism can never be proven correct, a high level of confidence can be placed in the mechanism that will ultimately be found to describe the (EBI)Zr(CH_3)$_2$ catalyst system. Our comprehensive approach of kinetic modeling with a rich multi-response data set aims to address this problem with each catalyst system examined, thus giving deserved confidence in the final kinetic model.

The (EBI)Zr(CH_3)$_2$ catalyst system has pushed the capabilities of our kinetic tools as a myriad of new kinetic mechanisms have been proposed, evaluated and discarded. Subsequently, the journey to find a kinetic model for this catalyst system has promoted vast improvements in the kinetic modeling tools in the form of enhanced usability, augmented functionality and increased robustness. In addition, the navigation tree to guide the researcher through the kinetic analysis based on discriminating features that can occur in the data as a result of different mechanisms has seen the growth of new branches and pruning of old branches. This improved navigation tree comes as a direct result of the incorporation of the new mechanisms considered, the additional types of experimental data used and the extensive knowledge gained from a year of (EBI)Zr(Me)$_2$ kinetic modeling. Finally, these improvements to the kinetic modeling tools have produced a kinetic modeling tool set expressly equipped to analyze each new catalyst introduced into our library.

- ***Effects of Ion Pairing and Sterics on Chain Propagation Kinetics***

Efforts this year have culminated in a complete analysis of the role and interplay of ion/counterion pairing and interaction in propagation kinetics. In all, a series of approximately 30 mixed Cp′/ArO catalyst systems were studied. The effects of changing cyclopentadienyl group (Cp, Ind, Cp*), aryloxide ligand (23 structures), counterion ($[MeB(C_6F_5)_3]^-$, $[B(C_6F_5)_4]^-$), metal (Ti, Zr), and solvent (toluene, bromobenzene, and 1,2-dichlorobenzene) were addressed. We predicted and synthesized several new catalysts that display higher activities due to opportunistic ligand coordination upon ion pair separation. Computed bond orders and geometric parameters unambiguously showed this opportunistic coordination of the metal center to an ortho substituent of the aryloxide in the separated ion pairs. Notable among this group of catalysts is Cp*Ti(OC_6H_4-2-Br)Me_2/$B(C_6F_5)_3$ which exhibits unusually high 1-hexene polymerization activity.

Increasing the solvent dielectric constant (K_S) increases the reaction rate by lowering the electronic energy (E_{IPS}) required for ion pair separation. An equation was developed that accurately predicts how E_{IPS} varies as a function of K_S. Experimentally, the chain propagation reaction order can also change from first-order to a combination of zero- and first-order as K_S increases. This behavior is explained in terms of a two-step chain propagation mechanism in which monomer first coordinates to the metal center to form a π-complex followed by insertion into the growing polymer chain. As K_S increases, the formation of the π-complex can become energetically favorable causing its concentration to saturate the ion pairs. Under these conditions, the reaction becomes zero-order in monomer.

- ***The Role of Steric Congestion in Chain Initiation/Propagation Kinetics***

We found that the rate of chain initiation compared to chain propagation is controlled by steric congestion at the metal center and the types of ion pairs formed during the reaction process. Geometries and energies of different ion pair types were computed using density functional theory. We can classify counterion behavior by noting that the counterion may be located in either the inner or the outer coordination sphere of the metal, and the outer sphere ion pair may or may not have opportunistic bonding from the ligand, growing chain, or initiating group. Using these results, a theory was developed to explain why some of the mixed cyclopentadienyl/aryloxide ligated catalysts exhibit slow chain initiation kinetics while others exhibit facile chain initiation kinetics. Predictions were compared to experimental data for about 25 catalysts and found to be in good agreement.

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Future plans

We will continue on the path toward our stated goal. The focus will be on the single site polymerization catalysts, where we think we are poised for significant breakthroughs. The new catalyst families under development will broaden our catalyst library. The population balance modeling tools along with molecular weight distributions and continuing DFT support will allow a rich and diverse data set spanning related rate constants over a broad range of chemistries. This system remains the ideal test bed for the *Discovery Informatics* methodology. The water gas shift reaction will be our heterogeneous catalyst test bed. We expect the new Bayesian kinetic data fitting tools to enhance our ability to discriminate models and obtain rate parameters. We also expect our speed of model building to be enhanced by the continuing evolution of the database and visualization tools. We will continue to explore the surprising support effects discovered in Pt and Pd systems and try to establish the upper limit of the WGS rate on group VIII metals. DRIFTS and EXAFS measurements will be used to help define descriptors of these catalyst systems.

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KC-03-04-01 **Jeffrey W. Elam (Argonne National Laboratory)**

Atomic Layer Deposition Synthesis of Nanostructured Membrane Catalysts

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Atomic layer deposition (ALD) is a thin film growth technique that uses alternating, self-limiting chemical reactions between gaseous precursors and a substrate to deposit material in an atomic layer-by-layer fashion. In contrast to conventional line-of-site coating technologies, ALD allows the precision coating of materials with complex geometries. Additionally, a wide variety of materials can be applied by ALD including most oxides, nitrides, and many metals. These attributes make ALD attractive for synthesizing nanostructured catalysts. In this project, we are applying ALD methods to prepare nanostructured catalysts built upon anodic aluminum oxide (AAO) membrane scaffolds. The AAO membranes consist of ordered arrays of nanopores with diameters of 40 nm and pore lengths of 70 microns. Using a series of deposition steps, we can apply ALD layers of different materials to perform specific functions. For instance, we can first deposit 10 nm Al_2O_3 to adjust the AAO pore diameter, followed by 1 nm TiO_2 to serve as a catalytic support material, followed by 0.2 nm V_2O_5 as the active catalyst. Typically these layers are deposited uniformly throughout the AAO nanopores, but recently we have developed a technique to deposit materials at specific depth locations within the AAO nanopores. This ALD method is based upon the passivating effect produced by one precursor to prevent the adsorption of a second precursor. For example, a surface exposed to trimethyl aluminum is not reactive towards diethyl zinc. This effect, combined with Knudsen diffusion in which the precursor exposure times dictate the depth of penetration of the deposited layer, enables spatially controlled “stripe coating” within AAO supports.

DE-FG03-86ER13514 **William J. Evans**

Advancing Chemistry with f Elements

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Goal

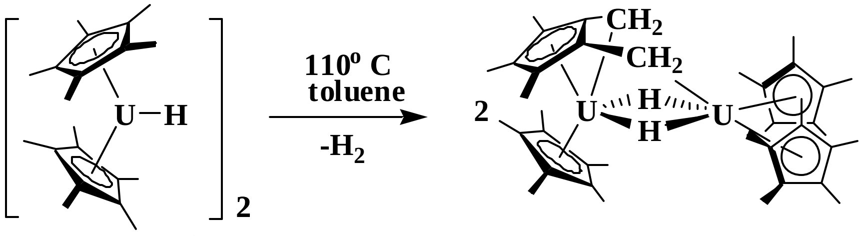
The objective of this research is to use the unique properties of the f elements to advance chemistry in energy related areas. This proposal is oriented to the discovery of reaction pathways that will provide the basis for new types of catalytic cycles and processes that at present are not under consideration as options to manipulate chemical feedstocks and waste streams because either the transformation or the requisite intermediates are unknown. The chemistry to be developed in this project should minimally show a stoichiometric vision of new possibilities in catalysis. Both new structural types and reaction pathways will be pursued.

DOE Interest

The large, electropositive, f orbital metals, the lanthanides and actinides, as well as the closely related yttrium, represent extremes in the periodic table in terms of chemical and physical properties that can be used to identify a broader set of alternatives for addressing problems in energy utilization, transmission, and generation. For example, studying the reactivity of f element M-C, M-N, and M-H bonds in coordination environments in which they can display a high degree of reactivity can lead to the identification of new types of reactions. Comparisons of 4f vs. 5f metal reactivity can provide fundamental insight useful in understanding the separation of lanthanides and actinides in radioactive waste streams as well as in the development of new alternatives for nuclear fuel synthesis. As the energy relevant chemistry of these heavy metals is advanced, Ph.D. students will be trained in the chemistry of the f elements.

Recent Progress (in two representative areas)

M-H Reaction Chemistry: Exploration of one of the simplest metal ligand linkages, the M-H bond, has led to substantial surprises with complexes known for decades. Simply heating the uranium hydride, $[(C_5Me_5)_2U(\mu\text{-}H)]_2$, first reported in 1981, to 110 °C in toluene leads to double C-H activation at one $(C_5Me_5)^{1-}$ group to make the first example of a $[m\text{-}h^5:h^1:h^1\text{-}C_5Me_3(CH_2)_2]^{3-}$ ligand in which one methylene group is "tucked-in" to bind to the metal of its ring and a second is "tucked-over" to the metal of another metallocene unit, eq 1.

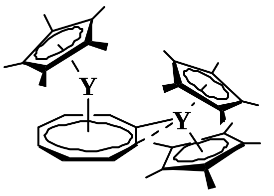


(1)

$(C_5Me_5)U[\mu\text{-}h^5:h^1:h^1\text{-}C_5Me_3(CH_2)_2](\mu\text{-}H)_2U(C_5Me_5)_2$ is the first crystallographically characterized example of a tuck-in complex of any f element and the first crystallographic evidence on uranium tuck-in and tuck-over structures. “Tuck-in” intermediates have played prominent roles in explaining the C-H activation reactivity of complexes such as $[(C_5Me_5)_2LuMe]_n$, $(C_5Me_5)_2ScMe$, and $(C_5Me_5)_2Th(CH_2CMe_3)_2$. However, despite the repeated use of tuck-in complexes in mechanistic schemes involving f elements, no spectroscopic or crystallographic evidence has ever been obtainable until now to support the existence of such an intermediate in a lanthanide or actinide complex.

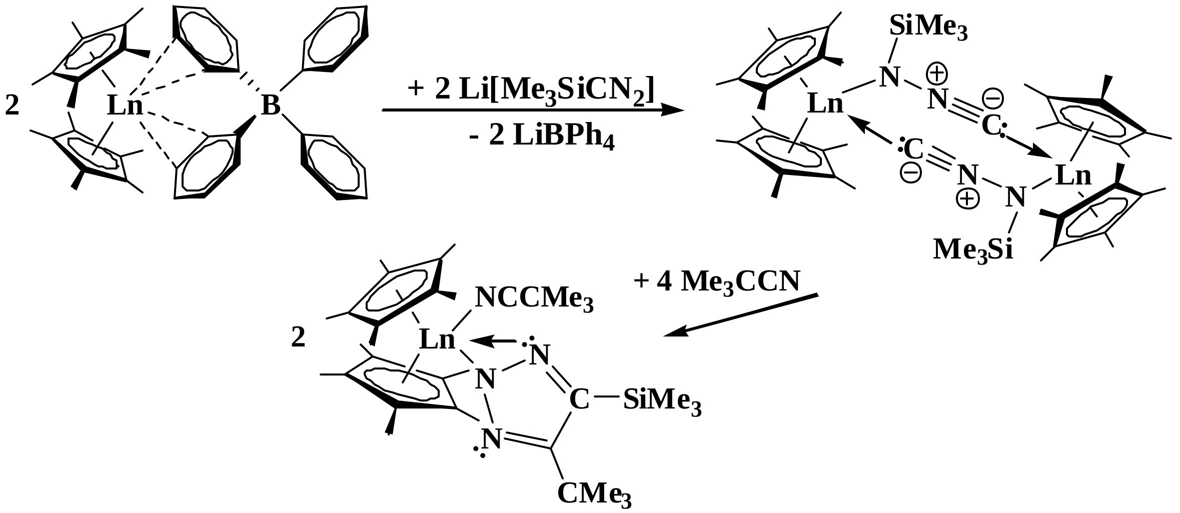
A

Exploration of Ln-H reaction chemistry using $[(C_5Me_5)_2YH]_2$ and 1,3,5,7-cyclooctatetraene in benzene led to another unusual ansa cyclopentadienyl complex, the ansa-allyl-cyclopentadienyl product, $(C_5Me_5)Y(h^5\text{-}C_5Me_4CH_2\text{-}C_5Me_4CH_2\text{-}h^3)$, **A**. The same reaction in cyclohexane provided the first example of a structurally characterized $(\mu\text{-}h^8\text{: }h^1\text{-}C_8H_7)^{3-}$ ligand in $(C_5Me_5)Y(\mu\text{-}h^8\text{: }h^1\text{-}C_8H_7)Y(C_5Me_5)_2$, **B**.



B

Diazoalkane Chemistry--Triazole Synthesis: In efforts to expand diazoalkane f element chemistry by taking advantage of the special reactivity of the cationic metallocene complexes of the tetraphenylborate anion, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, the latter complexes were treated with the salt obtained from ^{i}BuLi and Me_3SiCHN_2. The bimetallic isocyanotrimethylsilyl amide complexes, $\{(C_5Me_5)_2Ln[\mu\text{-}N(SiMe_3)NC]\}_2$ were isolated and subsequently found to react with nitriles to form 1,2,3-triazoles, eq 2. Initial studies with Sm and La have now been extended to smaller lanthanides as well as uranium to explore size and orbital effects on reactivity. In contrast to the lanthanide complexes, the uranium analogs are extremely soluble.



(2)

Future Plans

(1) The reaction chemistry of the tuck-in tuck-over complex, $(C_5Me_5)U[\mu\text{-}h^5\text{:}h^1\text{:}h^1\text{-}C_5Me_3(CH_2)_2](\mu\text{-}H)_2U(C_5Me_5)_2$, will be explored and compared with that of the lanthanide tuck-over hydrides, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}h^1\text{: }h^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)_2$. (2) Attempts to make the triazole synthesis catalytic in lanthanide will be attempted. Hydrogenolytic cleavage of the triazole and initiation of the catalytic cycle via a metallocene hydride would provide proof of

concept. (3) Expansion of M-C and M-N reaction chemistry of complexes of the f orbital metals in new and highly reactive environments will be pursued.

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KC-03-02-01-0 Project # 47319 **James A. Franz**

An Energy-Based Approach to Developing Interfacial Catalysts: Thermochemistry, Kinetics and Theory of Catalytic Transformations

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Goal

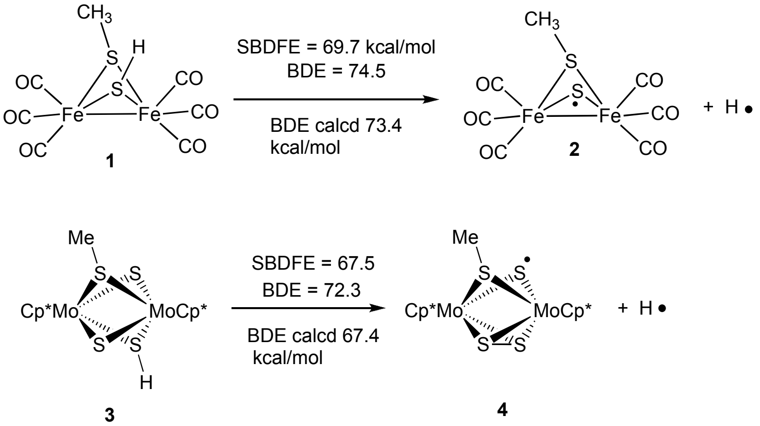
Our goal is discover and develop new reactions and catalytic cycles based on the thermodynamics of individual reactions involved. We seek an understanding of the thermodynamics of elementary reactions involving transfer of hydrogen atoms (H•), hydrides (H^-) and protons (H^+) from metal centers, carbon, sulfur or oxygen. Reactions of this type, in which "H" is transferred in one form or another, constitute critical steps in many types of catalytic reactions pertinent to energy usage and storage. Thermochemical values such as homolytic bond dissociation energies and hydricity are obtained through thermochemical cycles involving electrochemical measurements, pK_a values, etc. By systematically modifying steric and electronic properties of ligands and metals, and evaluating the resulting effect on thermochemical properties, we seek to determine the principles that govern the energetics of single steps, then utilize this knowledge to design catalytic reactions. Experimental studies are complemented by computational efforts. Experimental homolytic bond strengths, hydricities, and pK_a values provide key data for benchmarking theoretical approaches, such as application of DFT methods and basis set evaluation for metals and ligands. Computational and experimental data are used to rationally predict ligands and metals best suited for fast, long-lived catalysts. In our recent results, some of the first benchmark thermochemical data for H_2 activation and S-H/S-C activation are provided and compared to theory.

DOE Interest

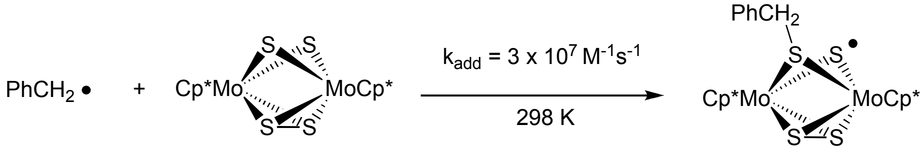
Fast, robust molecular catalysts (including electrocatalysts) are needed to address numerous problems pertinent to energy storage and delivery. Interconversion between fuels, or between fuels and electricity, requires catalysts for formation and cleavage of bonds to H. An improved understanding of the energetics of reactions that transfer hydrogen atoms, hydrides, or protons is essential to the effective utilization of these ubiquitous reactions in catalytic cycles. The specific knowledge gained in this project will help in the development of new catalytic reactions, but in a broader sense we suggest that this type of approach will be applicable to a wider range of catalytic reactions than the ones being examined by our group.

Recent Progress

New Bond Strengths for Prototype Catalyst Systems: Thermochemical and DFT Studies of the μ_2-SH bond. Understanding hydrogen activation, hydrogen transfer, and bond activation (e.g., S-C, S-H) pathways at the molecular level in catalysis requires a comprehensive knowledge of the underlying thermochemistry. We have employed thermochemical cycle methods to determine solution bond dissociation free energy (SBDFE) data for Fe(μ_2-SH)Fe and Mo(μ_2-SH)Mo systems in acetonitrile, as shown in the Figure. The availability of the bond strength data allows the evaluation of theoretical methods for prediction of bond strengths. DFT ECP calculations (ROB3LYP/(CEP-121G (Mo), 6-311++G(2d,2p)(CHS)// ROB3LYP/(CEP-121G (Mo), 6-31G(d)(CHS)) predict an S-H bond strength of **3** of 67.4 kcal/mol, deviating from experiment by -5 kcal/mol. For the FeSH system **1,** similar levels of theory yield a BDE for **1** of 73.4 kcal/mol, within 1.5 kcal/mol of experiment. These results, particularly for the MoS systems, show that further development of basis sets and methodology will be required to achieve thermochemical predictions approaching experiment. However, the BDE computation of **3** led to the discovery of three distinct geometric isomers of the product radical. The significance of the bond strengths is seen by comparison to S-H bonds of conventional molecules, which range from 79.1 (PhS-H) to 87.3 (CH_3S-H) to 91.2 (H_2S) kcal/mol. Thus, μ-complexation of the S-H bond results in a dramatic reduction in homolytic bond strength, to 74.5 kcal/mol (Fe) and 72.3 kcal/mol (Mo). In the context of heterogeneous catalysis of hydrogenation, reduction of the S-H bond by changing from H_2S to Mo(μ-SH)Mo yields greatly enhanced rates of H atom transfer to aromatic/olefinic acceptors, increasing by a factor of about 10^8 at 200 °C. The determination of these new bond strengths for FeSH and MoSH clusters provide the first standards for calibration of theoretical methods for the catalyst prototype systems.



C-S Bond-Making and Bond-Breaking at Mo(μ-S_2)Mo Clusters. To provide a quantitative understanding of the kinetics and thermochemistry of C-S bond making at MoS clusters, the first kinetics for addition of a carbon-centered radical to an MoS cluster have been determined. From the activation barrier for addition of benzyl radical to the MoS cluster (4 ± 2 kcal/mol), and the estimated enthalpy of addition of -25 kcal/mol, we arrive at a barrier for scission of benzyl radical from **5** of 29 ± 4 kcal/mol. By incorporation of $PhCH_2S$- into the cluster and formation of the radical **5**, the C-S bond strength of $PhCH_2SH$ has been reduced



5

from 61 to 29 kcal/mol, greatly enhancing the rate of C-S cleavage in a catalytic (e.g., hydrodesulfurization) system.

A New Weak Intercluster S-S Bond and the Persistent Radical Effect. We specifically designed radical **4** to be a stable radical. Bulky substituents render **4** nearly stable, but it reversibly forms a dimer through an S-S bond. ESR studies and NMR studies reveal an exceedingly week S-S bond in the dimer, and rapid, reversible dissociation to regenerate the monomeric radical **4**. The weak bond confers upon the radical the properties of a persistent radical: slow self-reaction and rapid reaction with reactive carbon-centered radicals, as shown by exclusive cross-termination of **4** with benzyl radical to give $(Cp^*Mo)_2(S)_2(S\text{-}CH_2Ph)(SCH_3)$.

Thermodynamic Studies of the M-H Bond and Their Use in Developing Catalysts for H_2 Oxidation, Production, and Storage. Understanding the thermodynamic properties of the M-H bond and the use of these properties in the design of new catalysts and catalytic reactions for important energy conversion reactions are long-term objectives of this program. For example, the heterolytic cleavage of H_2 is an important fundamental step in the oxidation and production of H_2 by hydrogenase enzymes. To avoid high energy intermediates in this catalytic process, it is important to match the hydride acceptor ability of a metal complex with the proton acceptor ability the base participating in the heterolytic cleavage reaction, so that $\Delta G \approx 0$ for this process. This principle guides the design of catalysts containing pendant bases that are highly active catalysts for H_2 oxidation and production. For example, the hydride acceptor ability of $[M(\text{diphosphine})_2]^{n+}$ complexes (n = 2 for Ni, Pd, and Pt and n = 1 for Co and Rh) is dependent on the nature of the metal and the natural bite angle (NBA) of the diphosphine ligand (or more accurately the dihedral angle between the two diphosphine ligands), and electronic and steric properties of the substituents on the diphosphine ligands. A particularly interesting and useful result is that the hydride donor ability of the corresponding $[HM(\text{diphosphine})_2]^{(n-1)+}$ complexes can be varied by 20 to 30 kcal/mol by varying only the NBA without any appreciable change in either the homolytic solution bond dissociation free energies (SBDFEs) or the pK_a values of these hydrides. Studies of $[Ni(\text{diphosphine})_2]^{2+}$ complexes have resulted in the development of new catalysts for H_2 oxidation and production. Fast catalytic production of H_2 is observed with $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$ ($P^{Ph}{}_2N^{Ph}{}_2$ = 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane) with catalytic rates approaching that of the NiFe hydrogenase enzyme with an over-potential of approximately 0.3 V. A related Ni complex, $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2]^{2+}$, is a catalyst for H_2 oxidation. Thermodynamic studies of the binding of H_2 and CO by this latter complex indicate that H_2 binds to this complex approximately 20 times more strongly than CO. As a result, this catalyst is uninhibited by the presence of 5% CO, a concentration that would poison Pt catalysts or hydrogenase enzymes. A comparison of the thermodynamic driving force for H_2 binding to these complexes suggests that the energy associated with this step is the dominant factor controlling the overall catalytic rate.

In addition to understanding the factors controlling the hydride acceptor ability of metal complexes, it is also important to understand the factors controlling the basicity of the pendant amines in these complexes. A series of studies have been performed to determine the pK_a values of the protonated amines for both iron and nickel complexes. These results indicate that the nature of the metal and its ligands strongly influence the basicity of the nitrogen atom in these complexes. How closely matched the pK_a values of these protonated amine ligands are to those of the corresponding hydride or dihydrogen complex resulting from proton transfer to the metal strongly affects the rate of proton/hydride exchange or heterolytic cleavage reactions in these complexes.

There are also many fundamental thermodynamic questions with respect to hydrogen activation and hydride transfer reactions that may be of importance to H_2 storage in the form of chemical hydrides. For example, ammonia borane (NH_3BH_3) and borohydride (BH_4^-) have been proposed for chemically storing H_2 because of their relatively high hydrogen content. However, regeneration of these materials from the so-called spent fuels will require a knowledge of those factors influencing the activation of H_2, the pK_a values of the transition metal dihydride or dihydrogen complexes resulting from H_2 activation, and the hydride donor abilities of the monohydrides resulting from heterolytic activation of H_2. Because of the strong hydride donors required, $[Rh(dmpe)_2]^+$ was selected as a candidate complex to demonstrate the activation of H_2 and subsequent transfer of the hydride ligand from $HRh(dmpe)_2$ to BEt_3 to form $[HBEt_3]^-$. These results demonstrate the feasibility of generating B-H bonds from H_2 gas, and the importance of understanding those structural features that control H_2 activation and hydride transfer reactions in designing potential systems for achieving the regeneration of proposed hydrogen storage materials.

Ionic Hydrogenations: Proton Transfer and Hydride Transfer Reactions from Metal Hydrides. N-heterocyclic carbene (NHC) ligands have been shown to have stronger binding to the metal than phosphine ligands, which would be expected to diminish dissociation of the ligand from the metal. Since our molybdenum and tungsten catalysts for ionic hydrogenation of ketones decomposed by loss of phosphine, new complexes were synthesized with an NHC ligand. $CpW(CO)_2(IMes)^+B(C_6F_5)_4^-$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) was crystallographically characterized using x-ray radiation at the National Synchrotron Light Source. The IMes is bonded as a bidentate ligand, with one C=C bond of the arene weakly bonding to the metal. The weakly bound C=C ligand is hemilabile, being readily displaced by H_2, THF, ketones or alcohols. The tungsten ketone complex $[CpW(CO)_2(IMes)(Et_2C{=}O)]^+[B(C_6F_5)_4]^-$ is a catalyst precursor for the hydrogenation of neat $Et_2C{=}O$, but activities are modest, and decomposition of the catalyst occurs. The product of the catalyst decomposition is $[H(IMes)]^+$, resulting from protonation of the NHC ligand, exposing a vulnerability of the NHC ligand in this catalytic reaction.

Future Plans

This project will continue to use thermochemical studies to enable the development of stepwise kinetic and thermodynamic descriptions of catalytic transformations. These transformations include pathways of activation of hydrogen, activation of C-heteroatom bonds, and key model bond-making and bond-breaking pathways essential to primary reaction pathways in heterogeneous catalysis.

Study of Thermochemistry, Kinetics and Theory of Metal-X Activation of C-X, C-H and Hydrogen. Accurate DFT prediction of thermochemical properties for transition metals is essential for establishing potential surfaces and for prediction of reactivity of catalyst systems. It will be essential to establish the limits of DFT and HF theory including complete basis set approaches, to determine basis set extrapolation approaches appropriate to transition metals with complex ligands and solvation. To benchmark these methods, accurate stepwise kinetics and thermochemistry for reaction of the C-H bond and H-H bonds at sulfur, oxygen and metals, and for reaction of reactive intermediates (radicals, ions) will be essential. Thus, new methods for measurement of thermochemistry for the stepwise reactive of the elements of

C-H and H$^-$H bonds with MoS, MoO, and other complexes with activated heteroatom ligands will be developed. The goal will be to achieve stepwise bond formation thermochemistry and kinetics, together with application of appropriately accurate DFT and HF computational predictions.

Study of New Metal Alkyl and Metal Formyl Systems. Transition metal alkyl complexes are important intermediates in a number of reactions including the hydrogenation and hydroformylation of olefins, C-H activation, and C-C bond formation and cleavage. However, systematic studies of M-C bond energies are lacking. The thermodynamic approaches discussed above for M-H bonds should be applicable for determining the features controlling both the heterolytic and homolytic solution bond dissociation free energies (SBDFEs) for M-CH_3 bonds. Quantitative information on the structural and electronic factors controlling M-C SBDFEs and models for predicting M-C bond SBDFEs would be of considerable use to researchers studying catalytic reactions involving C-H and C-C bond formation and cleavage reactions.

Similarly, transition metal formyl complexes are thought to be important intermediates in the reduction of CO_2 and CO. Previous work in our group has determined the hydride donor abilities and homolytic SBDFEs for a series of formyl complexes, but thermodynamic information for more reduced species such as hydroxymethyl and methyl complexes are completely lacking, as are pK_a values of protonated formyl complexes. Thermodynamic studies of these complexes could lead to significant advances in understanding the precise energetic requirements that need to be met to develop fast and energy efficient catalysts capable of the hydrogenation or electrochemical reduction of CO_2 and CO at low temperatures and pressures.

Ionic Hydrogenations: Proton Transfer and Hydride Transfer Reactions from Metal Hydrides. The thermodynamics of proton transfer reactions have a critical role in the ionic hydrogenation reactions we are studying. We will seek to determine the pK_a of cationic dihydrides such as $[CpW(CO)_2(IMes)(H)_2]^+$. Initial synthetic attempts are aimed at Cp ligands substituted with an electron-withdrawing group (C_6F_5), and we will determine how this ligand influences the acidity of the metal hydride. Our ionic hydrogenation catalysts involve displacemet of a bound ketone by hydrogen. To understand the thermochemistry of this reaction, equilibrium constants for displacement of ketone ligands by H_2 will be determined by high pressure NMR.

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Water Oxidation by a Ruthenium Complex with Non-Innocent Quinone Ligands: Possible Formation of an O–O Bond at a Low Oxidation State of the Metal

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A novel dinuclear Ru complex, $[Ru_2(OH)_2(3,6\text{-}Bu_2Q)_2(btpyan)](SbF_6)_2$ (3,6-Bu_2Q = 3,6-di-*tert*-butyl-1,2-benzoquinone, btpyan = 1,8-bis(2,2´:6´,2˝-terpyrid-4´-yl)anthracene), that contains redox active quinone ligands exhibits excellent electrocatalytic activity for water oxidation when immobilized on an indium-tin-oxide electrode.[1] The novel features of the dinuclear and related mononuclear Ru species with quinone ligands, and comparison of their properties to those of the Ru analogues with the bpy ligand (bpy = 2,2´-bipyridine) replacing quinone, are discussed together with new theoretical and experimental results that show striking features for both the dinuclear and mononuclear species.[2] The identity and oxidation state of key mononuclear species, including the previously reported oxyl radical, have been reassigned. Our gas-phase theoretical calculations indicate that the Tanaka Ru-dinuclear catalyst seems to maintain predominantly Ru(II) centers while the quinone ligands and water moiety are involved in redox reactions throughout the entire catalytic cycle for water oxidation. $[Ru_2(O_2^{-})(Q^{-1.5})_2(btpyan)]^0$ is a key intermediate and the most reduced catalyst species that is formed by removal of all four protons before four-electron oxidation takes place. While our study toward understanding the complicated electronic and geometric structures of possible intermediates in the catalytic cycle is still in progress, the current status and new directions for kinetic and mechanistic investigations, and key issues and challenges in water oxidation with the Tanaka catalyst (and its analogues with Cl- or NO_2-substituted quinones and a species with a xanthene bridge instead an antheracene) will be discussed.

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DE-FG02-05ER15630 **Michel R. Gagné**

Selective Approaches to the Activation of Carbohydrates

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Goal

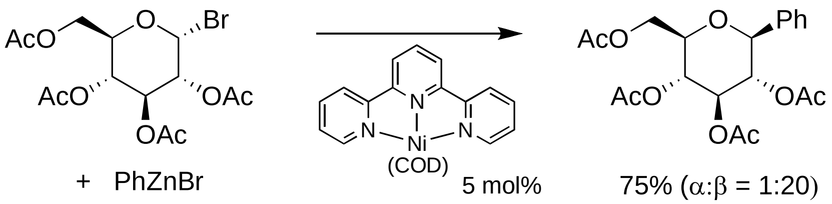
To develop new approaches to the selective activation of C-X (X= O, Br, Cl, etc) bonds in carbohydrates, and to subsequently manipulate those bonds to synthesize new value added compounds from an abundant feedstock.

DOE Interest

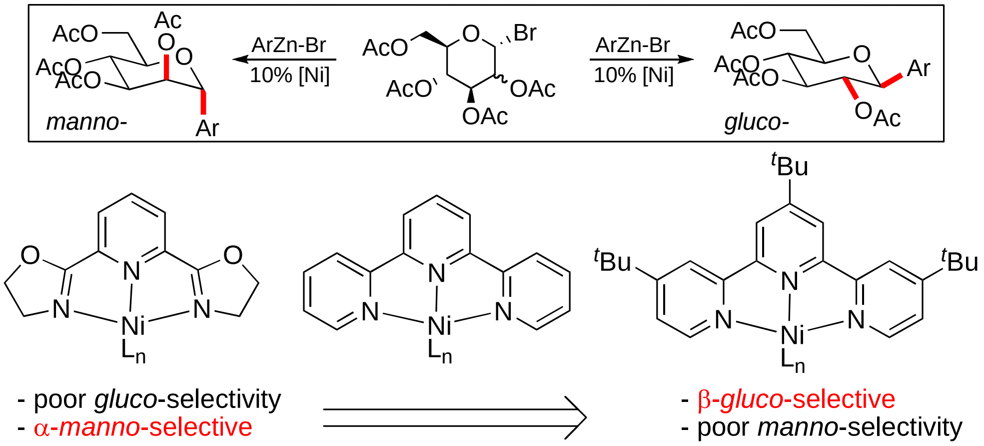
Carbohydrates are plentiful and renewable C6-sources, but they are notoriously difficult to convert into useful chemical stuffs, partially because of their already high oxidation states. If new methods could be developed to convert these materials into valuable chemical substances, the value and utility of these feedstocks (starch, cellulose, sugar, et) would grow and thus enable a shifting of our reliance on petroleum or coal resources towards one that was renewable. To enable progress to this goal we are investigating the fundamental reactivity of reactive carbohydrates towards transition metal complexes that are normally involved in a variety of transition metal catalyzed reactions.

Recent Progress

Ni-catalyzed cross coupling reactions. Our first efforts have focused on examining oxidative addition to glycosyl halides, and then trapping the resulting oxidative addition product by a cross coupling reaction. Since beta-elimination of C1-organometallics is a well-established problem in carbohydrate chemistry we have focused on pincer-ligated catalysts that block the cis-coordination sites on a putative organometallic species. Our first generation catalysts have focused on terpy or pybox coordinated Ni catalysts, since these were found (through a screening endeavor) to satisfactorily catalyze the coupling of alkyl or aryl zinc reagent and a glycosyl halides (the Negishi reaction) to yield biologically relevant *C*-glycosides. These structures are medicinally interesting since they are not readily hydrolyzed under physiological conditions like normal saccharides (see below for example).

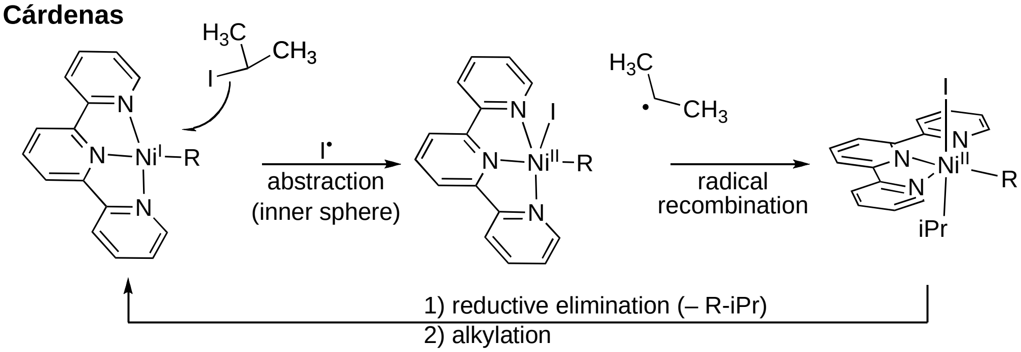


While several useful methods for the synthesis of these compounds have emerged from our experiments, these results were obtained in a rather Edisonian fashion with little knowledge of the mechanism of these reactions. Several fascinating observations dealing with the effect of the pincer ligand on the stereoselectivity of the reactions have emerged:

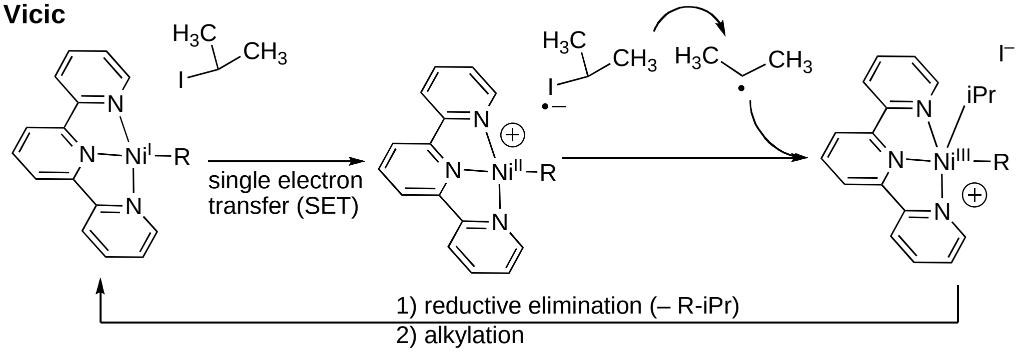


To summarize, it appears as though terpy-based catalysts have an inherent preference for synthesizing equatorially disposed alkylated or arylated products, while pybox catalysts apparently have no predisposition for equatorial or axial products and are subject to substrate control. While some of the evidence is contradictory, it appears as though radical pathways may provide the equatorial bias in the terpy catalysts. Two potential catalytic cycles, one forwarded by Vicic and the other by Cárdenas provide model radical-type mechanisms. The ultimate role of anomeric effects on the reactivity of these reactive species is of interest.

Cárdenas



Vicic



Future Plans

Ni catalysis. We plan to continue investigating the role of ligand structure on the reactivity and selectivity of glycosyl halides with the goal of discovering conditions wherein oxidative addition – and all of the subsequent reactions that could be achieved on the activated carbohydrate – can be made under catalyst control. Control over equatorial or axial products regardless of the identity of the sugar is desirable, as it will provide access to important structures.

New Oxidative Addition Systems. In the coming year we plan to initiate studies on the oxidative of glycosyl halides with other transition metal complexes with an eye to expanding the type of transformations that a carbohydrate can be coaxed to undergo. In particular we plan to extensively examine variants of Vaska's complex, which have been shown to undergo oxidative addition by a broad range of mechanisms (S_N2-like, SET-type, and atom abstraction) by changing the phosphine ligand and the substitution pattern on the alkyl halide.

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DE- FG02-93ER14353 **Alan S. Goldman**

Alkane Dehydrogenation and Tandem Dehydrogenation Systems Using Pincer-Ligated Iridium Complexes

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Goal

The program has several overlapping goals:

(1) To develop improved catalysts for the dehydrogenation of alkanes to give alkenes, particularly with regioselectivity for the terminal position (1° C-H bonds). Other substrates suitable for dehydrogenation include heteroatom-containing species (e.g. amines to give enamines), polymers, and hydrogen-storage materials.

(2) Development of tandem-catalyst systems in which dehydrogenated products are subject to secondary reactions, e.g. addition of arenes (to give alkylarenes) or cyclizations (to give aromatics from linear alkanes).

(3) Experimental determination of the thermodynamics and kinetics of substrate-catalyst interactions, and the concomitant development of improved computational methods, including the screening of existing DFT functionals for such systems. In particular, we find that a full accounting of steric effects is critical for the design of dehydrogenation catalysts. However, the ability of DFT methods to accurately predict steric effects in organometallic systems is still relatively untested. The development of such abilities will be of great value for the design of dehydrogenation catalysts and for many organometallic catalyst systems more generally.

DOE Interest

Development of efficient methods for the manipulation and conversion of hydrocarbon feedstock is of great importance with respect to energy security and environmental considerations. Alkane dehydrogenation offers energy-efficient routes to commodity chemicals, and has been shown to be applicable toward alkane metathesis which is of potential value in the upgrading of Fischer-Tropsch product mixtures. The development and testing of improved computational methods will be applicable toward the development of organometallic catalysts in general.

Recent Progress

Rational steric-based design of new dehydrogenation catalysts.

Pincer-ligated iridium complexes have shown great promise as catalysts for the dehydrogenation of alkanes. The complex (^{tBu}PCP)IrH$_n$ was first reported by Kaska and Jensen to catalyze the transfer-dehydrogenation of alkanes. Subsequent work in our lab in collaboration with the Kaska and Jensen groups led to the discovery that the kinetic product of dehydrogenation of *n*-alkanes is the α-olefin, and to the development of systems for "acceptorless" dehydrogenation (in which hydrogen is evolved as H_2, rather than transferred to a sacrificial acceptor). Other substrates that we have shown can be efficiently and usefully dehydrogenated include poly-α-olefins and tertiary amines. In most cases, the sterically less-hindered complex (^{iPr}PCP)IrH$_n$ was found to give much greater rates; however, the isopropyl groups are found to be susceptible to dehydrogenation-induced decomposition.

In an attempt to reduce steric crowding while maintaining the robust nature of t-butyl groups, we considered the use of methyl groups on the ligating phosphorus atoms. Preliminary experiments indicated that the all-methylated analog was too unencumbered and would undergo dimerization or cluster formation. Further consideration led to the hypothesis that steric bulk would be best distributed in an unsymmetrical fashion so as to offer minimal resistance to C-H addition or β-H-elimination, while still preventing cluster dimerization.

Toward this end ($^{Me/tBu3}$PCP)IrH$_4$ has been synthesized, isolated and characterized (Fig. 1). In accord with our hypothesis that an alkane-matched steric environment would yield more favorable catalytic rates, ($^{Me/tBu3}$PCP)IrH$_4$ has been found to catalyze dehydrogenation significantly faster than (^{iPr}PCP)IrH$_n$. Even more importantly, it is found to yield higher turnover numbers for transfer-dehydrogenation and appears to remarkably stable. It has likewise proven highly effective as a co-catalyst for alkane metathesis.

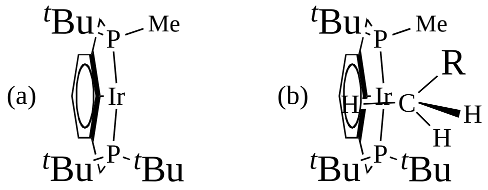


Fig. 1. ($^{Me/tBu3}$PCP)Ir (a) alone, and (b) illustrating the potentially large affect of a single methyl-for-t-butyl substitution on a P atom on the steric congestion in an alkane C-H addition reaction.

We also have reason to believe that ($^{Me/tBu3}$PCP)Ir, and perhaps other less bulky catalysts, will effectively promote C-C coupling reaction with sp^2-carbons. In other work, we have found that sp^2-C-C coupling is strongly dependent on the ability of the vinyl or aryl group to rotate so as to "face" an attacking group. Thus, this system offers the potential for new C-C coupling catalysts, which ideally, but not necessarily, use C-H bonds as the initial point of attack.

Tandem catalysis.

During the course of the dehydrogenation reactions the pincer-iridium catalysts initially show excellent rates, which fall off steeply as olefin is produced, largely due to inhibition by product. An intriguing approach to this problem is to couple dehydrogenation with a secondary reaction that prevents the build-up of olefin; ideally, the secondary reaction would be useful in its own right.

One of the most important uses of olefins industrially is the "alkylation" of arenes (ca. 50 x 10^9 lb-olefin/year). Use of the corresponding alkanes, in place of olefins, would be quite attractive.

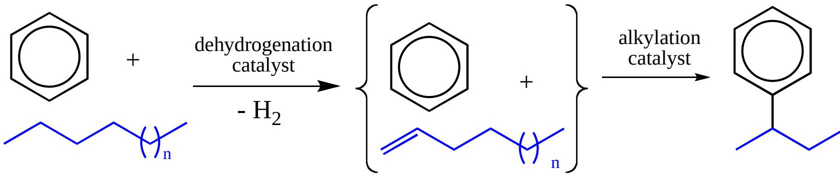
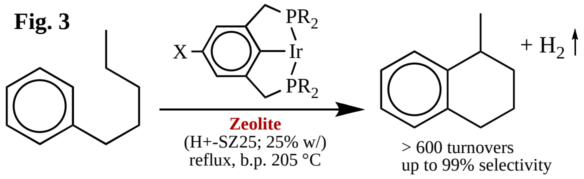


Fig. 2

Thus far we have been very successful in effecting this reaction type *intra*molecularly. With the use of zeolites as alkylation catalysts in tandem with (PCP)Ir-based catalysts, we have successfully effected, for example, the ring-closing of 1-pentylbenzene (Fig.3).

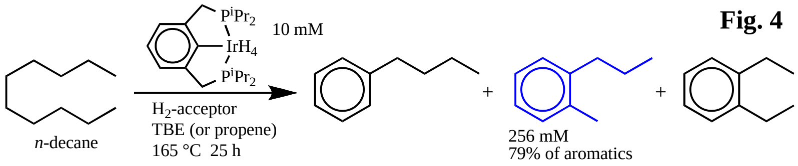
Another example of successful tandem dehydrogenation catalysis has been the aromatization of *n*-alkanes (Fig. 3). Using a sacrificial hydrogen acceptor such as t-butyl-ethylene (TBE) or even propene, *n*-alkanes can be extensively dehydrogenated to give aromatics. Somewhat coincidentally, this could potentially give long-

Fig. 3



chain alkylated aromatics similar to those targeted above (Fig. 2), but from an alkane-only feedstock. The reaction in Fig. 4, however, gives unbranched alkyl groups on the aromatic ring; in many cases this would be desirable but impossible to obtain with conventional alkylation catalysts. Quite surprisingly, the major product is specifically the corresponding ortho-alkyl-toluene (e.g. *n*-propyltoluene from *n*-decane). The mechanism of this reaction is under study but is believed to proceed via dehydrogenation to give conjugated triene, followed by Cope cyclization to give cyclohexadiene derivatives, followed by further dehydrogenation to give the ultimate aromatic product.

Fig. 4



Thermodynamics and kinetics of substrate-catalyst interactions; experimental determination and the development of improved computational (DFT) methods.

The potential power of computational chemistry in the design of catalysts has long been recognized, yet has proven to be quite elusive. This failure to date is perhaps attributable to a lack of attention paid to steric factors, in favor of the more "interesting" electronic effects. Steric effects, however, often (usually) play a critical role in determining the energetics of a real-world catalyst. While our experience to date with current DFT-based technology has indeed allowed us to gain significant understanding of the role of electronic factors in our catalytic systems, we have been forced to examine the failure to obtain "chemical accuracy" with full, non-truncated, organometallic species such as (^{tBu4}PCP)Ir-based catalysts. In this context we have determined the thermodynamics of a broad and diverse range of pincer-ligated iridium reactions and have attempted to reproduce the results computationally. Our key finding is that, with the use of basis sets of moderate size, the PBE functionals produce significantly better results than the B3LYP functionals most commonly used by computational organometallic chemists.

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DE-FG02-03ER15490 **T. Brent Gunnoe**

Transition Metal Catalyzed Hydroarylation of Multiple Bonds: Exploration of Second Generation Ruthenium Catalysts and Extension to Copper Systems

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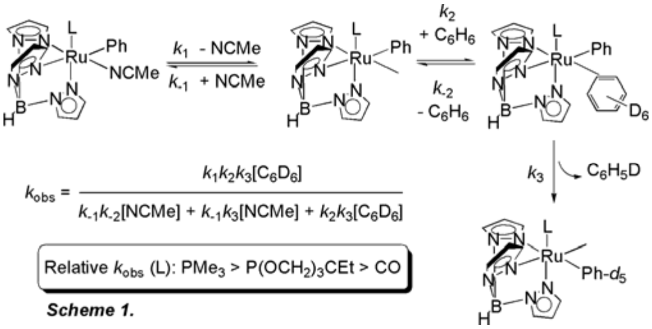
Goal

The goal of this project is to increase understanding of fundamental aspects surrounding homogeneous catalysts for the addition of carbon-hydrogen bonds across carbon-carbon multiple bonds. These studies will facilitate the rational design of future catalysts for the hydroarylation and hydroalkylaton of carbon-carbon multiple bonds.

DOE Interest

The conversion of hydrocarbons derived from fossil resources into higher value materials is a foundation of the chemical industry. Processes for primary carbon-carbon bond forming steps using basic hydrocarbon building blocks are often inefficient and energy intensive, and the development of more efficient routes for the conversion of hydrocarbons could result in cleaner chemical processes, reduced energy consumption and conservation of valuable chemical resources. Access to catalyst technologies for selective conversion of C-H bonds into functionalized materials is of potential value to commodity and fine chemical markets as well as for the production of fuels.



$$k_{obs} = \frac{k_1k_2k_3[C_6D_6]}{k_{-1}k_{-2}[NCMe] + k_{-1}k_3[NCMe] + k_2k_3[C_6D_6]}$$

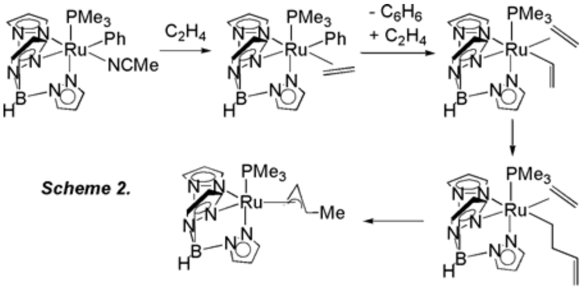
Relative k_{obs} (L): $PMe_3 > P(OCH_2)_3CEt > CO$

Scheme 1.

Recent Progress

In 2003 we reported that TpRu(CO)(NCMe)R {R = alkyl, phenyl, 2-thienyl or 2-furyl; Tp = hydridotris(pyrazolyl)borate} complexes serve as catalyst precursors for the addition of aromatic C-H bonds across C=C bonds. For example, TpRu(CO)(NCMe)Ph catalyzes the addition of benzene C-H bonds across the double bonds of ethylene and α-olefins. Mechanistic studies have revealed that the Ru(II) metal center serves to directly mediate both C-H activation and C-C coupling steps. In the past year, we have been working to: 1) develop a detailed understanding of the impact of ancillary ligand identity on the catalytic cycle (using TpRu(L)(NCMe)R systems as a foundation), 2) prepare and study catalysis with cationic Ru(II) variants, 3) extend catalysis toward new coordination geometries (e.g., four-coordinate catalyst precursors) and electronic structures, and 4) extend our studies of C-H activation to sp^3 hybrid bonds.

For TpRu(L)(NCMe)Ph {L = CO, PMe_3, $P(pyr)_3$ (pyr = *N*-pyrrolyl), and $P(OCH_2)_3CEt$} systems, we have pursued detailed studies focused on the impact of the steric profile and donating ability of ligand "L" on both stoichiometric benzene C-H activation and catalytic hydrophenylation of olefins. Relative rates of stoichiometric benzene activation have been determined by comparing the overall rate of TpRu(L)(NCMe)Ph reaction with C_6D_6. Increased donating ability of L results in more facile C-D activation of C_6D_6 (Scheme 1).



Scheme 2.

Despite evidence that the benzene C-H activation step is the rate determining step in the catalytic hydrophenylation of ethylene, using TpRu(PMe_3)(NCMe)Ph as catalyst results in nominal production of alkylbenzene. Combined experimental and computational studies suggest that the more donating PMe_3 ligand (compared with CO) results in substantial inhibition of ethylene insertion. As a result, ethylene C-H activation is competitive with catalytic ethylene hydrophenylation, and catalyst decomposition via formation of TpRu(PMe_3)(η^3-C_3H_4Me) becomes problematic (Scheme 2). Extension of these studies to TpRu{$P(OCH_2)_3CEt$}(NCMe)Ph, with the bicyclic phosphite exhibiting donor properties intermediate between PMe_3 and CO ligands, suggests that metal electron density may provide a benchmark for predicting affinity toward catalytic hydrophenylation of olefins. In contrast to the more electron rich PMe_3 complex {Ru(III/II) 0.29 V vs. NHE}, the phosphite system {Ru(III/II) 0.55 V vs. NHE} catalyzes the hydrophenylation of ethylene; however, unlike the less electron rich CO system {Ru(III/II) 1.02 V vs. NHE), ethylene C-H activation to ultimately produce TpRu{$P(OCH_2)_3CEt$}(η^3-C_3H_4Me) is competitive with catalysis. These results suggest that although the activation barriers for C-H activation are influenced, the modulation of metal electron density most dramatically impacts the rate of olefin insertion for the TpRu(L)(NCMe)Ph systems, which has become a primary consideration for future catalyst development. Most recently, we have demonstrated that TpRu(L)(NCMe)R systems can activate sp^3 hybrid C-H bonds in addition to C-C bond forming steps, but such reactions are currently limited to substrates that compete with NCMe for coordination to the Ru metal center.

Recently, we have extended studies of C-H/H-H activation to four-coordinate complexes. It is anticipated that such systems might more readily undergo β-hydride elimination with subsequent olefin dissociation, thus providing an opportunity to develop catalysts for the oxidative hydroarylation of olefins. Our initial efforts have focused on the putative four-coordinate d^6 cation $[(IMes)_2Ru(CO)(H)]^+$ {IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene} and four-coordinate d^8 systems. The Ru complex is an efficient catalyst for hydrogenation of multiple bonds in addition to catalyzing the oxidative hydrophenylation of ethylene; however, under conditions explored to date, the latter reaction proceeds in low yields. We have also discovered a robust d^8 complex that catalyzes the hydroarylation of olefins.

Future Plans

Our studies of TpRu systems suggest that six-coordinate/d^6 precursors that mimic the electronics of the TpRu(CO)(NCMe)Ph system should be active catalysts while potentially providing flexibility with ligand steric parameters to control selectivity. For example, we have prepared precursors to TpRu(PF_3)(NCMe)Ph and $[EpRu(L)(NCMe)Ph]^+$ systems {Ep = tris(pyrazolyl)ethane}, and we predict that Ep-Ru systems with L = phosphite or alkylphosphine will behave similar to the TpRu(CO)(NCMe)R systems while providing more robust catalysts. We are also exploring catalyst development with octahedral d^6 systems based on metals other than Ru with fundamental interest focused on whether catalysis with such systems will respond to electronic modulation similar to our TpRu(II) systems (i.e., can we develop a set of general predictors for catalyst efficacy for octahedral/d^6 catalyst precursors?). In addition, our preliminary results with four-coordinate d^6 and d^8 systems are promising, and in the next year we plan to expand the scope of our studies with these complexes.

Publications (2006 – 2008)

1. "Reactions of TpRu(CO)(NCMe)(Ph) (Tp = hydridotris(pyrazolyl)borate) with Electron-Rich Olefins: Examples of Stoichiometric C-S and C-H Bond Cleavage" Goj, L. A., Lail, M., Pittard, K. A., Riley, K. C., Gunnoe, T. B.*, Petersen, J. L. *Chem. Commun.* **2006**, 982-984.
2. "Reactions of a Ru(II) Phenyl Complex with Substrates that Possess C-N or C-O Multiple Bonds: C-C Bond Formation, N-H Bond Cleavage and Decarbonylation Reactions" Lee, J. P., Pittard, K. A., Cundari, T. R., Gunnoe, T. B.*, Petersen, J. L. *Organometallics* **2006**, *25*, 1500-1510.
3. "Hydrogen-Deuterium Exchange between TpRu(PMe_3)(L)X (Tp = hydridotris(pyrazolyl)borate; L = PMe_3 and X = OH, OPh, Me, Ph, or NHPh; L = NCMe and X = Ph) and Deuterated Arene Solvents: Evidence for Metal-Mediated Processes" Feng, Y., Lail, M., Foley, N. A., Gunnoe, T. B.*, Barakat, K. A., Cundari, T. R., Petersen, J. L. *J. Am. Chem. Soc.* **2006**, *128,* 7982-7994.
4. "Single-Electron Oxidation of Monomeric Copper (I) Alkyl Complexes: Evidence for Reductive Elimination through Bimolecular Formation of Alkanes" Goj, L. A., Blue, E. D., Delp, S. A. Gunnoe, T. B.*, Petersen, J. L. *Organometallics* **2006**, *25,* 4097-4104.
5. "Chemistry Surrounding Monomeric Cu(I) Methyl, Phenyl, Anilido, Ethoxide and Phenoxide Complexes Supported by *N*-Heterocyclic Carbene Ligands: Reactivity Consistent with both Early and Late Transition Metal Systems" Goj, L. A., Blue, E. D., Delp, S. A., Gunnoe, T. B.*, Cundari, T. R., Pierpont, A. W., Petersen, J. L., *Inorg. Chem.* **2006**, *45*, 9032-9045.
6. "Reactivity of Ruthenium (II) and Copper (I) Complexes that Possess Anionic Heteroatomic Ligands: Synthetic Exploitation of Nucleophilicity and Basicity of Amido, Hydroxo, Alkoxo and Aryloxo Ligands for the Activation of Substrates that Possess Polar Bonds as Well as Non-Polar C-H and H-H Bonds" Gunnoe, T. B.* *Eur. J. Inorg. Chem.* **2007**, 1185-1203.
7. "Reactivity of TpRu(L)(NCMe)R (L = CO, PMe_3; R = Me, Ph) Systems with Isonitriles: Experimental and Computational Studies Toward the Intra- and Intermolecular Hydroarylation of Isonitriles" Lee, J. P., Jimenez-Halla, J. O. C., Cundari, T. R.*, Gunnoe T. B.* *J. Organomet. Chem.* **2007**, *692*, 2175-2186.
8. "Comparative Reactivity of TpRu(L)(NCMe)Ph (L = CO or PMe_3): Impact of Ancillary Ligand L on Activation of Carbon-Hydrogen Bonds including Catalytic Hydroarylation and Hydrovinylation/Oligomerization of Ethylene" Foley, N. A., Lail, M., Gunnoe, T. B.*, Cundari, T. R., Petersen, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 6765-6781.
9. "Combined Experimental and Computational Study of TpRu{P(pyr)$_3$}(NCMe)Me (pyr = *N*-pyrrolyl): Inter- and Intramolecular Activation of C-H Bonds and the Impact of Sterics on Catalytic Hydroarylation of Olefins" Foley, N. A., Lail, M., Gunnoe, T. B.*, Cundari, T. R.*, Boyle, P. D., Petersen, J. L. *Organometallics* **2007**, *26*, 5507-5516.
10. "Combined Experimental and Computational Studies on the Nature of Aromatic C-H Activation by Octahedral Ru(II) Complexes: Evidence for σ-Bond Metathesis from Hammett Studies" DeYonker, N. J., Foley, N. A., Cundari, T. R.*, Gunnoe, T. B.* *Organometallics* **2007**, *26*, 6604-6611.
11. "Activation of sp^3 Carbon-Hydrogen Bonds by a Ru(II) Complex and Subsequent Metal-Mediated C-C and C-N Bond Formation" Foley, N. A., Gunnoe, T. B.*, Cundari, T. R.*, Boyle, P. D., Petersen, J. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 726-730 (selected as an *Angew. Chem.* "hot" paper)

DE-FG-02-96ER14678 **John F. Hartwig**

Chemistry of Complexes with Transition Metal-Heteroatom Bonds: Novel Insertion Chemistry and Macromolecule Synthesis

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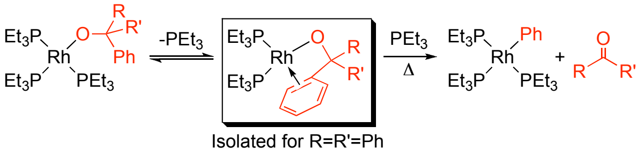
Goal

We are seeking to discover new elementary reactions from which to build catalytic processes and to gain information on the electronic properties of new arylamine materials. Most of these projects reflect our continued interest in the development and understanding of transition metal-catalyzed reactions that proceed through alkoxide or amide intermediates. We have been studying the chemistry for aminations of olefins and related catalytic transformations of amines and alcohols. In the past two years, we have been studying factors that control (a) β-aryl eliminations from metal alkoxide complexes; (b) metal-alkoxide insertion into olefins; and (c) N-H oxidative additions of alkylamines and ammonia equivalents to iridium complexes we showed previously to add ammonia and aniline.

DOE Interest

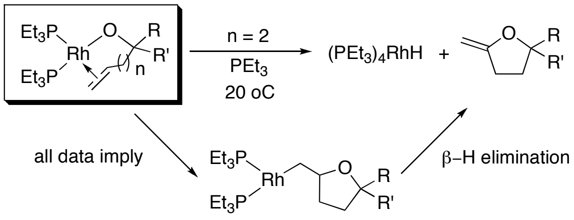
Homogeneous catalysis has been used to prepare polyolefins, carboxylic acids, and aldehydes from olefins in quantities of billions of pounds per year. Much of these materials are ultimately converted to amines and alcohols. Thus, much energy, waste, and capital construction cost would be reduced if amines and other nitrogen-containing feedstocks, as well as alcohols and ethers, could be directly prepared from olefins. Unfortunately, water, alcohols, amines and ammonia are often poisons to transition metal catalysts. In addition, cleavage of the N-H bond of an amine is challenging under neutral catalytic conditions, because in most cases N-H bonds are only weakly acidic, and the Lewis acid/base adducts with amines are more stable than the N-H activation complexes. Thus, our studies to understand the organometallic chemistry of N-H bond cleavage and insertion reactions of amido and alkoxo complexes with olefins will lead to an ability to form amines and alcohols directly from olefin feedstocks.

Recent Progress



β-Aryl Eliminations from Rh(I) Alkoxides: Under DOE support, we had observed β-aryl elimination from rhodium(I)-iminyl complexes (*J. Am. Chem. Soc.* **2005**, *127*, 11618-11619). This study led us to examine if similar β-aryl eliminations occur from rhodium alkoxide complexes. Rhodium alkoxides containing β-aryl groups [Rh(PEt$_3$)$_n$(OCPhRR')] (n=2,3) were prepared by addition of the benzyl alcohols to the silylamide [Rh(PEt$_3$)$_3$(N(SiMe$_3$)$_2$)]. In one case, the alkoxo complex containing an interaction of the β-aryl group with rhodium was formed and characterized by X-ray diffraction.

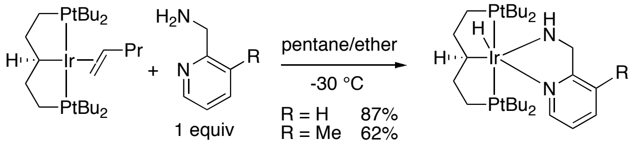
Heating of the alkoxide complexes in the presence of added PEt$_3$ generated the rhodium phenyl complex, (PEt$_3$)$_3$RhPh, and the corresponding ketones in good to high yields. Kinetic results are most consistent with irreversible β-phenyl elimination from bisphosphine-ligated rhodium alkoxide complexes, which result from ligand dissociation from the corresponding trisphosphine complexes. The crystal structure contained a Rh-aryl interaction and provided a view into the interactions that precede the C-C bond cleavage.



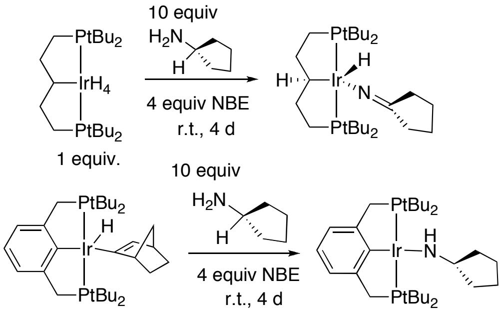
Olefin Insertion into a Rhodium Alkoxide: Our previous observation of the insertion of alkenes into the M-N bond of rhodium amido complexes (*J. Am. Chem. Soc.* **2005,** *127*, 12066-12073) prompted us to investigate analogous reactivity of rhodium alkoxides. We have been unable to prepare rhodium alkoxides that undergo intermolecular insertions of alkenes, but we did prepare a perhaps more illustrative example of the insertions of olefins into alkoxides by preparing alkoxides containing tethered, coordinated olefins.

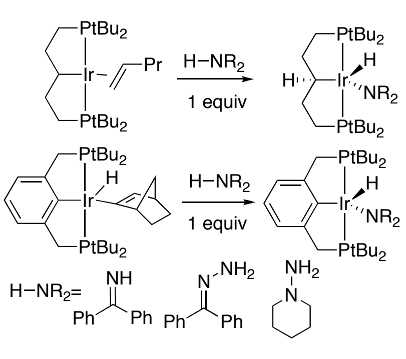
The alkoxide complex {Rh(PEt$_3$)$_2$[κ^1:η^2-OCRR'(CH$_2$)$_2$CH=CH$_2$]} was *in situ* generated from protonolysis of the silylamide of {Rh(PEt$_3$)$_2$[N(SiMe$_3$)$_2$} with enols. The resulting complex was unstable at room temperature, but was easily characterized at low temperatures. The olefin group was clearly bound to rhodium, as determined by ^{103}Rh-^{1}H and ^{103}Rh-^{13}C coupling to the olefinic protons and carbons. At room temperature this complex underwent an intramolecular process in the presence of added PEt$_3$ to afford 2,2-disubstituted-5-methylenetetrahydrofurans and (PEt$_3$)$_4$Rh-H in good yields.

Kinetic and a stereochemical assessment of the insertion process by using a specifically deuterium-labeled trans olefin of the enol supported a *syn* addition of the rhodium and alkoxo unit across the olefin. This result is consistent with a direct olefin insertion into the Rh-O bond, followed by rapid β-hydride elimination. In contrast, {Rh(PEt$_3$)$_2$[κ^1:η^2-OCRR'CH$_2$CH=CH$_2$]}, having one less methylene linker, was isolated as a stable solid, and its X-ray structure confirmed the Rh-olefin interactions deduced by NMR spectroscopy. Heating of this complex resulted in β-allyl elimination.

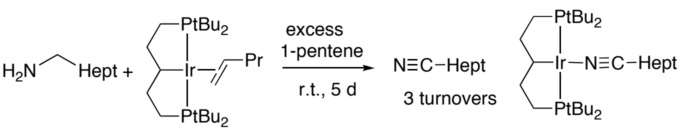


N-H Activation of Aliphatic Amines Possessing β-Hydrogens: Previously, we reported the oxidative addition of the N-H bonds in aniline and ammonia by PCP-pincer ligated iridium(I) complexes, leading to the terminal hydridoiridium(III) amides (*J. Am. Chem. Soc.* **2003**, *125*, 13644; *Science* **2005**, *307*, 1080). Recently, we extended these N-H oxidative addition processes to the N-H bonds of alkylamines containing β-hydrogens. In order to suppress undesired β-hydride elimination from the alkylamido products, we employed pyridyl-tethered amines, so that the pyridyl group can occupy the vacant site required for the subsequent β-hydrogen elimination process. The strategy allowed isolation of the first iridium(III) alkylamido complexes containing β-hydrogens and the first oxidative additions of alkylamines to form stable monomeric products.





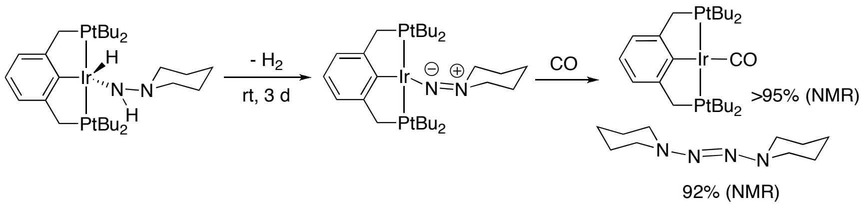
We have also isolated the product from N-H activation of an imine that was generated *in situ* from the reaction of an aliphatic amine containing one β-hydrogen. In the presence of a hydrogen acceptor, the PCP-IrH$_2$ complex containing an aliphatic backbone reacted with cyclopentylamine to form an iminyl hydride complex. In contrast, reaction of the analogous PCP-IrH_2 complex containing an aromatic backbone gave only a σ-adduct of the amine.



Primary aliphatic amines underwent two successive N-H activations and *β*-hydride elimination sequences to form nitriles in the presence of a hydrogen acceptor. For example, the reaction of 1-octylamine with the PCP iridium complex containing the aliphatic backbone gave an octane nitrile complex. X-ray crystallography showed that the nitrile was bound end-on through nitrogen.

N-H Activation of Imines, Hydrazones and Hydrazines using Pincer Iridium Complexes: Fre studies on the oxidative addition of the N-H bonds in imines, hydrazones and hydrazines have been reported, although these reagents are often used as ammonia surrogates in synthetic chemistry. Considering their synthetic potential, we have undertaken studies of N-H activation of benzophenone imine, benzophenone hydrazone, and *N*-aminopiperidine. We have shown that all of these reagents readily undergo N-H oxidative addition to iridium(I) species ligated by PCP pincer lignads containing both aliphatic and aromatic backbones. With one exception, all of oxidative adducts are stable and have been crystallographically characterized.

A Pincer Iridium Complex of an Aminonitrene: In one case, the addition process led to formation of an aminonitrene complex. The PCP-Ir complex containing an aromatic backbone underwent a double N-H activation process with *N*-aminopiperidine. The initial product of N-H activation was observed directly and was shown to slowly eliminate one equivalent of H_2 in the presence or absence of a hydrogen acceptor to give the aminonitrene complex shown in the graphic. The identity of this complex was confirmed by X-ray diffraction. In the presence of excess CO this complex generated the corresponding tetrazine product, perhaps from release of the 1,1-diazene.



Future Plans

Olefin Insertion of Rhodium Amides and Alkoxides Containing Chelating Bisphosphines. Our studies have established that bis(monophosphine)rhodium amides and alkoxides undergo insertions of olefins. In the future, we will synthesize and isolated related complexes containing chelating bisphosphines and study their intermolecular and intramolecular reactivity towards olefins. Specifically, we will examine steric and electronic effects of the ancillary dative ligands and the reactive anionic ligands. In addition, we will explore related reactions with isoelectronic palladium complexes.

Pincer Iridium Complexes of Nitrenes. Nitrene complexes of low-valent late metals are important intermediates in nitrene transfer chemistry. However, the rarity of these complexes has hampered detailed studies of their reactivity. Thus, the chemistry of the aminonitrene complex and synthesis of related complexes will be a new focal point for future studies.

Publications (2006-2008)

1. Zhao, P.; Incarvito, C.D.; Hartwig, J. F. "Direct Observation of β-Aryl Eliminations from Rh(I) Alkoxides" *J. Am. Chem. Soc.* **2006**, *128*, 3124-3125.
2. Zhao, P.; Incarvito, C.D.; Hartwig, J. F. "Carbon-Oxygen Bond Formation between a Terminal Alkoxo Ligand and a Coordinated Olefin. Evidence for Olefin Insertion into a Rhodium-Alkoxide" *J. Am. Chem. Soc.* **2006**, *128*, 9642-9643

DE-FG02-86ER13569 **William D. Jones**

Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds

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Contact:	Dept. of Chemistry, University of Rochester, Rochester, NY 14627 phone: (585)275-5493; Email: jones@chem.rochester.edu webpage: http://chem.rochester.edu/Faculty/Jones.html group webpage: http://chem.rochester.edu/~wdjgrp

Goals and Objectives

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 focused on the following general goals: (1) fundamental studies of C-H bond cleavage reactions of trispyrazolylboraterhodium 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 halfnium. We have made progress in each of these areas, as described below.

Significant Recent Achievements and Results

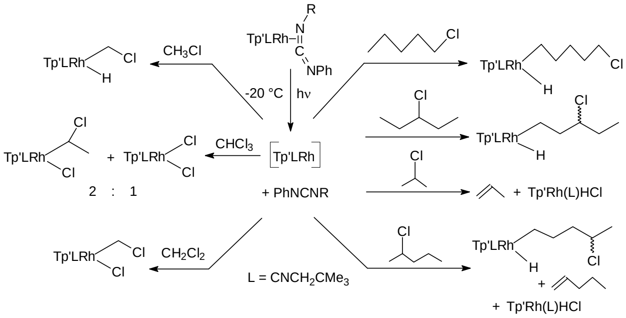
The accomplishments of the current year include: (1) measurement and quantitatively modeling of the processes available to metal alkyl hydride complexes in a trispyrazolylborate-rhodium complex, including both linear and cyclic hydrocarbons; (2) measurement *for the first time* of the selectivity for a metal fragment binding to methyl vs methylene groups in a linear hydrocarbon; (3) measurement of C-H activation selectivities in aliphatic nitriles, showing a kinetic preference for activation of the terminal methyl groups; (4) measurement of 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) cleavage of C-C bonds in aryl-acetylenes, aryl-nitriles, and alkyl-nitriles, expanding substantially the breadth of C-C cleavage; (6) investigation of 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) discovery of 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.

Our poster will focus on two of our current areas of research:

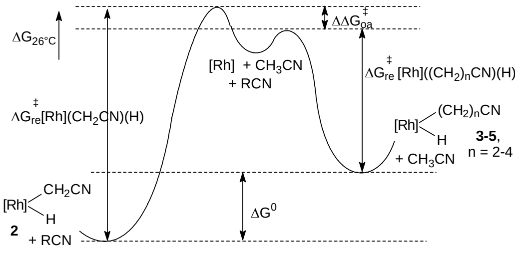
C–H Bond Activation: With our trispyrazolylborate rhodium system, we have been able to determine the relative rates at which C-H bond of an alkane first binds to the Tp'RhL fragment. The execution of this experiment is not completely obvious, as reaction of the fragment with any linear hydrocarbon only gives a single product, the n-alkyl hydride. One cannot determine how the alkane initially bound if a single product is observed. We have performed competition experiments with pentane and propane that allow one to determine alkane binding selectivities. This analysis shows that *a methylene group binds 1.5× faster than a methyl group*.

We have also examined activation of several chloroalkanes (Scheme I). *A 100% preference for C–H activation of a terminal methyl group over a C–Cl bond is observed.* With chloromethane, only C–H cleavage is seen. A competition between chloromethane and methane shows a 2.5× preference for C–H activation of chloromethane. We have also examined activation of several cyanoalkanes (Scheme II). *A 100% preference for C–H activation of a terminal methyl group is observed.* Curiously, these adducts show remarkable stability towards reductive elimination, an effect that appears to be attributable to the inductive electron-withdrawing power of the cyano group.

Scheme I:

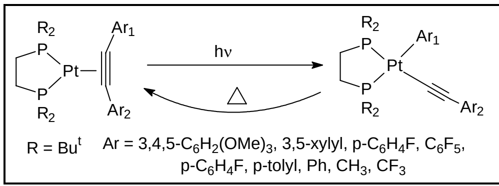


Scheme II:



Complex	RCN	$\Delta G^{\ddagger}_{re}$	$\Delta\Delta G^{\ddagger}_{oa}$	$\Delta G°$
2	CH_3CN	31.36	0	0
3	C_2H_5CN	25.47	0.22	5.67
4	C_3H_7CN	23.64	0.31	7.41
5	C_4H_9CN	22.88	0.44	8.04

C–C Bond Activation: We have investigated a series of P-P and P-N chelates of group 10 metals for activity in C-C bond activation. 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-P 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. 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 comparative reaction studies of this system showed that the phenyl-alkyne C-C triple bond can be made to undergo oxidative addition (eq 1)! This reaction has now been examined for a wide variety of aryl and alkyl alkynes.



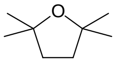
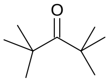
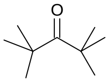
(1)

In addition, we are studying the C-CN cleavage in 2-methyl-3-butenenitrile, an isomerization that is key to the DuPont adiponitrile process. The selectivity is found to have strong temperature and solvent effect (Table I). We are also engaged in DFT calculations of C-CN bond cleavage reactions of benzonitrile at the Ni(dippe) fragment. These show a remarkable feature in the transition state for C-CN cleavage in which the C–CN bond has rotated by 90° relative to the NiP_2 plane (Scheme III).

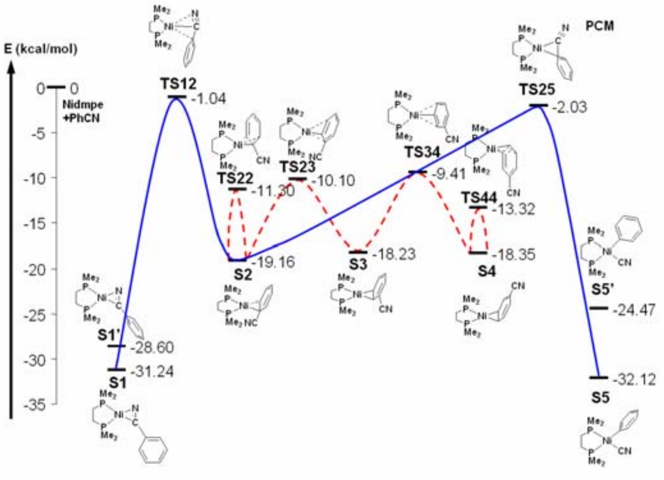
Extended Impact on Science, Technology, and Society

The work done here demonstrates that homogeneous transition metal compounds can break a variety of *strong* carbon-element bonds, including C-H, C-C, and C-F. These studies show that *direct processes* for conversion of hydrocarbons to value-added products are feasible, and that the scope for these new processes can include the strongest of bonds to carbon. The ability to manipulate C-C bonds in hydrocarbons offers the advantage of being able to become independent of a single hydrocarbon source for the production of our organic specialty chemicals and fuels.

Table 1. Isomerization of 2M3BN by $[Ni(dippe)H]_2$ at 100 °C.

solvent	linear:branched ratio	dielectric constant
decane	12.4 : 1	2
benzene	6.7 : 1	2.3
THF	3.9 : 1	7.5
trifluorotoluene	1.6:1	9.2
acetone	1 : 12	21
acetonitrile	1 : 27.3	36.6
	7.3:1	5
	1:1.5	10
	1.5:1	21.1

Scheme III:



Future Plans

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 functionalized hydrocarbons by trispyrazolylboraterhodium complexes, (3) C-C cleavage in nitriles.

Publications for 2006-2008:

1. "The Synthesis and Structural Properties of $[M(dippe)(\eta^2\text{-}C_4H_4S)]$ 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)
2. "Activation of Aromatic, Aliphatic, and Olefinic Carbon-Fluorine Bonds Using $Cp^*{}_2HfH_2$," Ryan D. Rieth, William W. Brennessel, and William D. Jones, *European Journal of Inorganic Chemistry*, **2007**, *18*, 2839-2847. (DOE)
3. "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)
4. "Structural and Dynamic Properties of Propane Coordinated to TpRh(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)
5. "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)
6. "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**, *129*, 8729-8736. (DOE)
7. "Polymorph of (1,2-bis(di-tert-butylphosphino)ethane)(dichloride)platinum(II)," A. Gunay, W.W. Brennessel and W.D. Jones, *Acta Cryst. E*, **2008**, *64*, m454. (DOE)
8. "P-C bond scission at the TRIPHOS ligand and C-CN bond cleavage in 2-methyl-3-butenenitrile using $[Ni(COD)_2]$," Alberto Acosta-Ramírez, Marcos Flores-Álamo, William D. Jones and Juventino J. García, *Organometallics*, **2008**, *27*, in press. (DOE)

DE-FG02-05ER15696 **Alexander Katz**

Controlling Heterogeneous Lewis Acid Catalysis via Surface Organometallic Approaches

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Goal

Inspired by metal atom isolation within the chiral environment of metalloenzymes such as vanadium bromoperoxidase, the goal of this program is the design and synthesis of a family of calixarene-based surface organometallic catalysts, in which the calixarene is used as a molecular scaffold having substituents in dative contact with the metal center, which enhance catalyst activity and selectivity. This requires deconvoluting inner-sphere effects of coordination and active site Lewis acidity, characterized here using ^{13}C CP/MAS NMR spectroscopy of *ipso* carbons on the calixarene skeleton in anchored V(V)-calixarenes, from support acidity and environment effects on heterogeneous catalysis. The long term goal is the synthesis of precise environments surrounding a metal center on a surface such as that shown in Figure 1 below. To this end, we have synthesized a broad class of calixarene ligands with asymmetric centers directly attached to the lower rim (published in *New J. Chem* 2008).

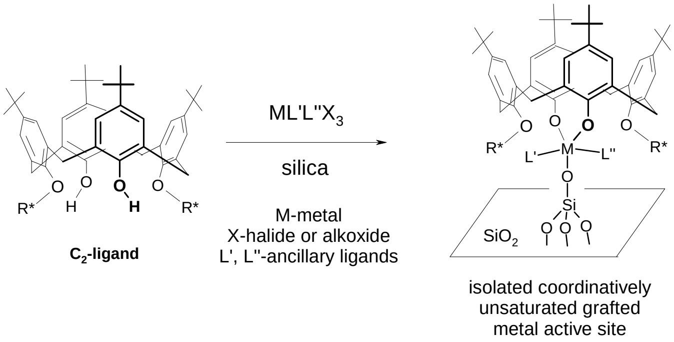
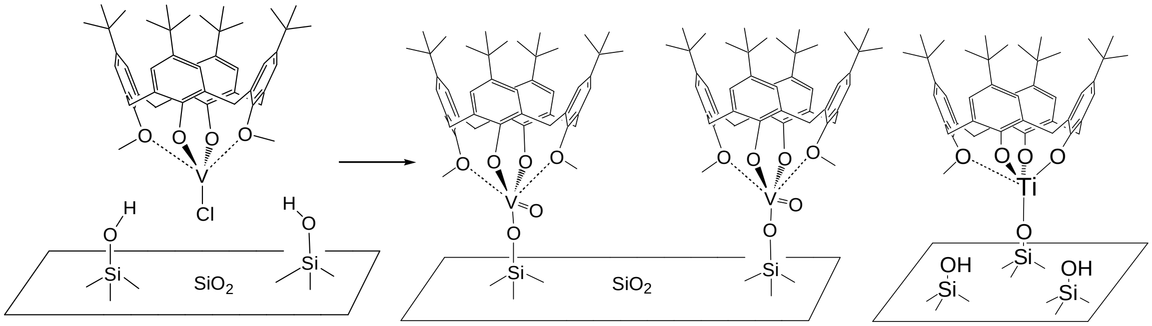


Figure 1: Envisioned surface organometallic materials based on chiral (asymmetric center identified by R*) C_2 symmetric calixarene ligands.

Recent Progress

Grafted Vanadocalixarenes on Silica:

The recently reported V(III)-calixarene precursor shown in Figure 2 was grafted to the surface of silica and oxidized to the corresponding V(V) surface organometallic complex. Diffuse reflectance UV-Vis spectroscopy indicates the presence of highly isolated vanadium centers in calcined **1c** with an edge energy of 3.1 eV, which remains unchanged independent of degree of hydration. ^{13}C CP/MAS NMR spectroscopy of **1c** demonstrates the presence of both methoxy groups present intact (64 ppm), when control materials with a single methoxy group per calixarene are analyzed side-by-side, such as **2c**. The two methoxy dative ligands in **1c** create a mildly Lewis-acidic V(V) center relative to the analogous, previously reported anchored Ti(IV)-calixarene materials, which exhibit an *ipso* carbon resonance at ~161 ppm in the ^{13}C CP/MAS NMR spectrum; indeed, there is no such resonance above 153 ppm for **1c**. This is consistent with unusually strong dative coordination observed in the structure of the homogeneous chloride precursor via single-crystal X-ray diffraction and leads to catalytic activities for epoxidation and sulfoxidation reactions for **1c** that make it on par with previously reported Ti-homooxacalix[3]arenes – about 20-fold lower than for **2c**, despite the higher formal charge on the metal center in **1c**.



1c

2c

Outer-Sphere Ligand Effects:

Building on our observation of the importance of outer-sphere acidity in Ti-surface organometallic catalyst **2c**, we have successfully decreased the silica surface acidity via silanol treatments. This has led to further enhance the catalytic activity of **2c** in the epoxidation of cyclohexene by *tert*-butyl hydroperoxide by a factor of three-fold over previous versions of **2c** having unmodified and more acidic silanol populations. There are potentially two independent explanations for this behavior. Either outer-sphere acidity or decreased d-orbital occupancy at the Ti metal center is responsible for this effect, and future Ti K-edge XANES and ^{13}C CP/MAS NMR spectroscopy studies of these materials are planned to elucidate the mechanism behind this rate enhancement.

Future Plans

The results above demonstrate that it is possible to control heterogeneous catalysis using a surface organometallic approach in which the ligand remains bound to the metal center and modifies its catalytic properties by virtue of these interactions. We are currently applying the above-mentioned concepts towards the discovery of oxidation catalysts having a permanent chiral ligand coordination sphere around the metal center, and an optimized outer-sphere for high catalytic activity. This necessitates investigating metals in higher oxidation states in combination with our surface organometallic approach to catalyst synthesis, in which the metals can still retain significant catalytic activity despite the presence of donor ligands that act to “program” the metal center.

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"The Role of Outer-Sphere Surface Acidity in Alkene Epoxidation Catalyzed by Calixarene-Ti(IV) Complexes" J. M. Notestein, A. Soloyvov, L. R. Andrini, F. G. Requejo, A. Katz*, and E. Iglesia*, *J. Am. Chem. Soc.* **2007**, *129*, 1122-1131.

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DE-FG02-06ER15765 **Richard A. Kemp**

Direct Epoxidations Using Molecular Oxygen

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Goal

Our goal is to develop homogeneous catalysts for the selective transfer of oxygen atoms from molecular oxygen to organic or inorganic substrates. In particular, we are interested in learning how to promote epoxidation reactions that cannot be catalyzed by known heterogeneous systems. While attractive, efficient routes to these organic epoxides or oxygenated substrates will be the major overall focus, the fundamental mechanistic understanding of oxidation chemistry gained in our studies will be of significant value to DOE's interest in using molecular oxygen in partial oxidation catalysis. More specifically, the understanding gained from each of the individual steps in our proposed cycle should impact other ongoing projects within the interests of DOE. Finally, examination of the fundamental steps via theoretical chemistry in order to impact the experimental program is also underway.

DOE Interest

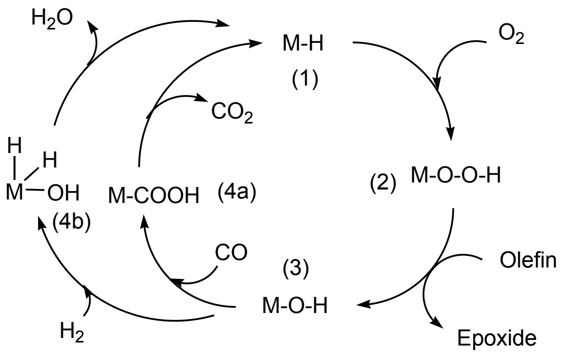
Significant reduction of energy usage in industrial-scale catalytic processes goes to the heart of the interests of DOE. As well, elimination of reaction steps in multi-step routes in order to prepare functionalized products directly is also of importance. More effective atom-efficient reaction chemistry providing less waste is also desired, particularly when combined with these other interests. Using molecular O_2 as the oxidation source can impact both the economic and environmental issues in a positive manner. Our ongoing research program meets all of these challenges. In addition fundamental knowledge is generated from this project and that understanding can also be applied to other important DOE-sponsored project areas. This knowledge and understanding is the key product to emerge from our studies. Recent "DOE Workshops on Catalysis" have emphasized the overwhelming importance of improved partial oxidation processes.

Recent Progress

Synthetic Chemistry

Modifications to (PCP)-Pd System: Our proposed catalytic cycle is shown in **Figure 1**. During this year we have expanded both the range of ligands and metals from our initially-studied $(PCP)^{t\text{-}Bu}$Pd-H system by altering the sterics and electronics on the substituents on the P atoms.

Figure 1. Proposed Catalytic Cycles for Making Epoxides



We have prepared PCP-Pd analogs with less bulk around P, including cyclohexyl and i-Pr derivatives, and converted their halide salts into the (PCP)^{R}Pd-H complexes. The smaller complexes smoothly insert O_2 to form crystallographically-characterized dimers of (PCP)^{R}Pd-OOH. We also prepared electron-deficient PCP-Pd complexes by replacing either one or both alkyl groups on the P atom with -C_6F_5 groups, resulting in the (PCP)^{C6F5}Pd-Cl and the mixed (PCP)$^{C6F5/Ph}$Pd-Cl precursors. We have not been able to successfully reduce these compounds to the hydrides. We were also interested in whether use of a larger group on P might produce a purely monomeric, and thus more reactive, Pd-OOH species rather than the dimeric species that we have seen in the solid-state crystal structures. Towards this goal we have recently prepared and isolated (PCP)^{Ad}Pd-Cl (Ad = adamantyl). Initial attempts at conversion to the Pd-H have not been successful; however, a variety of reducing agents for this reaction have not yet been tried. A Pd-H complex containing the more sterically-rigid anthracene backbone has also been prepared and characterized. The reduction and conversion into the Pd-H required Super Hydride™ rather than $NaBH_4$. A Pd-H species from a PNP-ligand system initially studied and developed by Ozerov has also been prepared. The insertion of O_2 into the Pd-H species of the anthracene backbone ligand and the PNP ligand occurs cleanly over time to give exclusively the Pd-OOH in each case. Interestingly, even in solution the hydroperoxides are the only species seen after several days at room temperature. This indicates that our hypothesis about these alternative ligand backbones providing additional stability appears to be valid.

We have also prepared (PCP)$^{t\text{-}Bu}$Ni-Cl, and have converted it to (PCP)$^{t\text{-}Bu}$Ni-H using $NaBH_4$. Reaction of the Ni-H compound with O_2 is slow and unfortunately gives a mixture of products as shown by ^{31}P NMR spectroscopy, and we are as yet unable to tell whether the desired Ni-OOH species is among the products.

(Bis)carbene Ligands with Late Transition Metals: Additionally, we have prepared Group 10 compounds containing multidentate carbene ligands rather than the phosphine-based ligands shown above. Unfortunately as was found with many of the PCP compounds investigated in this project, the reduction of the M-X species to M-H has been problematic. Changing the reducing ability of the reductant over a wide range led to either no reactivity, or complete dissociation of the ligand from the metal. These N-bis(carbene) ligands lead to highly charged species when using Group 10 metals, and solubility has also been an issue. We are preparing C-(bis)carbene ligands for these Group 10 metals which should aid in solubility and reactivity. The extra anionic charge on the ligand will obviate the need for the external Br^- anion. Novel chelating, multi-dentate carbene ligands based on the cyclic alkyl(amino) carbenes (CAAC) framework of Bertrand are currently being developed and synthesized. These new CAAC chelates should be more stable and have more tunable steric and electronic properties than do NHC ligands.

Reaction and Mechanistic Chemistry

Reactivity of M-OOH with Organic Species. The M-OOH species that we have prepared are effective at transferring an O atom to inorganic substrates, such as R_3P. However, our goal is to transfer the O atom selectively to organic substrates, and as yet we have been unsuccessful at transferring the O atom of Group 10 hydroperoxides to organic species such as olefins or isonitriles. The difficulty in losing O is interesting as other complexes containing Pd-OOR or Pt-OOH (prepared from H_2O_2) can transfer an O atom, and we have shown that $(PCP)^{t\text{-}Bu}$Pd-OOH will lose an O atom to form $(PCP)^{t\text{-}Bu}$Pd-OH. Rather than discouraging us, however, this lack of reactivity has challenged us to begin looking at a new H-assisted mechanistic route to lose the O atom, and we are preparing compounds that should operate by this different route. Computationally, this new reaction pathway is energetically-favorable.

Regeneration of M-H. $(PCP)^{t\text{-}Bu}$Pd-OH can be converted to $(PCP)^{t\text{-}Bu}$Pd-H using H_2 or CO. Recent studies have concentrated on using H_2. We have shown that the rate of conversion of $(PCP)^{t\text{-}Bu}$Pd-OH to $(PCP)^{t\text{-}Bu}$Pd-H proceeds by a second-order rate law (first-order in palladium and first-order in H_2). Though no intermediate has been observed for this reaction, insight into the intimate mechanism of the reaction was gained via computational methods. The theoretical calculations suggest a four-center intramolecular proton transfer as the lower energy pathway as compared to an oxidative addition/reductive elimination mechanism.

Future Plans

- Demonstrate the O-transfer reaction to organic substrates, leading to a greater level of understanding and *control* of this transfer reaction;
- Determine the structure/property relationship between the ligands attached to the metal and the reactivity to a) form a hydroperoxide, and b) transfer an O-atom;
- Prepare new Pd complexes with particular ligand modifications in order to evaluate a new, alternative H-assisted mechanistic pathway to transfer O-atoms to organic substrates;
- Prepare the chelating CAAC ligands and metal complexes, and examine in partial oxidation catalysis; and
- Expand into early metal chemistry by computationally and experimentally by examining early metal hydrides (especially Ti) and compare results with known heterogeneous catalysts.

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Novel Ligand Platforms for Transition Metal Catalyzed C-H Oxidation Reactions

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Highly modular, C_3-symmetric ligand platforms that enable geometric control or shape recognition of incoming ligands or substrates have been synthesized.[1] The syntheses and coordination properties of the tripodal tetraamine ligand tris(2-aminophenyl)amine, $N(o\text{-}PhNH_2)_3$, and its triamidoamine derivatives, $[N(o\text{-}PhNHC(O)R)_3]$ (R = alkyl or aryl) will be discussed. X-ray diffraction (XRD), electrochemistry, and DFT studies have been used to investigate the correlation between the amide ligand substituents and the ground-state electronic properties and reactivity of the resulting transition metal complexes. XRD studies have also shown that ligand orientation may be controlled by electrostatic interactions between electron deficient perfluorophenyl amide substituents and coordinated anionic (or polar) exogenous ligands. The correlation between catalyst architecture and C-H bond oxidation reactions will be described.

References

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DE-FG02-06ER15792 **Helena C. Malinakova**

Mechanistic Studies and Design of Cyclopalladated Catalysts for Three-Component Coupling Reactions Exploiting Allylpalladium(II) Umpolung

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Goal

Develop detailed mechanistic understanding of novel palladium(II)-catalyzed three-component coupling reactions, presumed to involve nucleophilic (umpolung) allylpalladium(II) complexes as catalytic intermediates, and design new types of palladium(II) catalysts capable of realizing asymmetric induction in the three-component coupling process.

DOE Interest

The research will expand our fundamental understanding of the relationship between the structure and reactivity of new types of nucleophilic allylpalladium(II) complexes enhancing our capabilities in palladium catalysis. As a result of these studies, new avenues for the design of more energy efficient, environmentally friendly and atom economical processes for the synthesis of small organic molecules desired by the pharmaceutical and chemical industries will become available.

Recent Progress

Synthetic scope of the Pd(II) catalyzed three-component coupling reaction: We have successfully applied the $Pd(OAc)_2/PR_3$-catalyzed protocol [1] to the synthesis of both acyclic and cyclic unnatural amino acid derivatives, the representative examples of which are shown in Table 1 and Scheme 1[2]. We have shown for the first time, that allenes ($RCH=C=CH_2$) featuring branched alkyl substituents, as well as substituents possessing an oxygen heteroatom can be used in the coupling reaction (Table 1).

Scheme 1

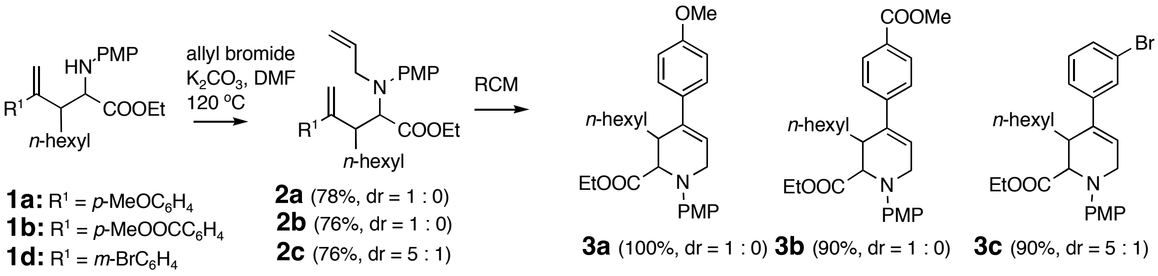
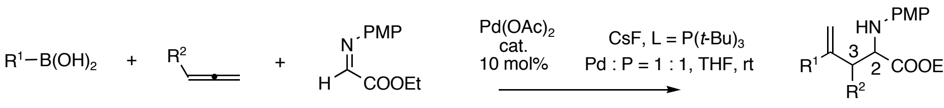
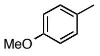
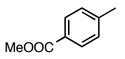
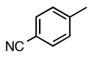
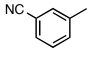
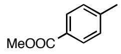
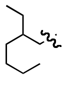
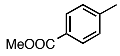
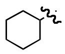
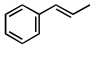
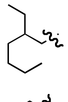
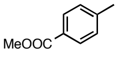
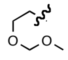


Table 1



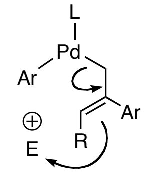
1a-1h

entry	R^1	prdt R^2 = *n*-hexyl	yield[a] (%)	dr[b]
1		**1a**	54	10 : 1
2		**1b**	74	21 : 1
3		**1c**	63	14 : 1
4		**1d**	82	5 : 1

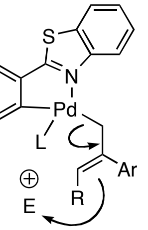
entry	R^1	R^2	prdt	yield[a] (%)	dr[b]
5			**1e**	81	25 : 1[c]
6			**1f**	69	25 : 1
7			**1g**	76	7 : 1[c]
8			**1h**	51	7 : 1

[a] Isolated yield. [b] Determined by ^{1}H NMR. [c] Dr for C2 and C3 stereocenters as determined by ^{1}H NMR. The presence of the additional stereocenter at C2' (1 : 1 ratio) in the side chain was only detected by ^{13}C NMR spectra for **1e** and **1g**.

New catalyst development and control of absolute stereochemistry: Allyl(aryl)palladium(II) complex **A** has been proposed to operate as a catalytic nucleophilic allyl transfer reagent in the reactions catalyzed by Pd(OAc)$_2$/PR$_3$ system [1]. Conceivably, a cyclopalladated complex **B** could operate as an analogous more stable catalytic intermediate, capable of an efficient asymmetry transfer if chiral nonracemic cyclopalladated auxiliary ligands were employed. Indeed, we have shown that an achiral cyclopalladated complex **C** was a *more effective* catalyst than Pd(OAc)$_2$ in the synthesis of homoallylic amines **4**. Furthermore, commercially available chiral nonracemic catalyst **D** afforded amine **4d** in 20% ee (Scheme 2)[3].

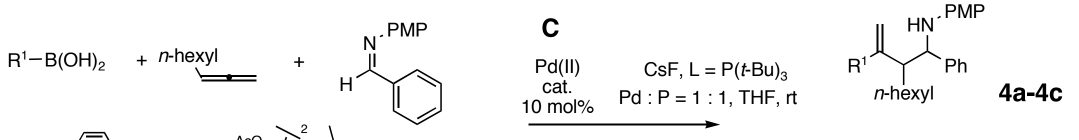


A

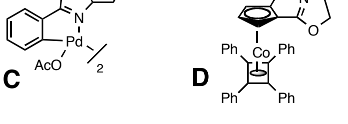


B

Scheme 2



4a-4c



C

D

4a: R^1 = *p*-MeOC$_6$H$_4$; Yield: 64% with **C**, 48% wiht Pd(OAc)$_2$)

4b: R^1 = *p*-CNOCC$_6$H$_4$; Yield: 54% with **C**, 30% wiht Pd(OAc)$_2$)

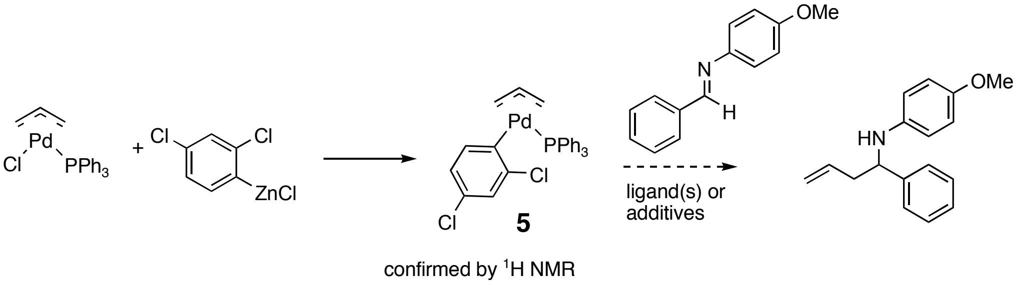
4c: R^1 = *p*-Me(C=O)C$_6$H$_4$; Yield: 77% with **C**, 43% with Pd(OAc)$_2$

4d: R^1 = *p*-(MeOOC)C$_6$H$_4$; Yield: 76% with **C**, 61% with Pd(OAc)$_2$

Structure-activity studies with stoichiometric nucleophilic allylpalladium(II) complexes: In recent studies, we have focused on in situ generation of stoichiometric allylpalladium(II) complexes analogous to the intermediates **A** and **B** (vide supra). To date, we have generated in situ complex **5**, which represents a model for the intermediate

A (Scheme 3). The formation of complex **5** was confirmed by ^{1}H NMR analysis[4]. The reactivity of complex **5** with electrophiles (imines) is currently being investigated, aiming to explore the kinetics of the nucleophilic allyl transfer (Scheme 3).

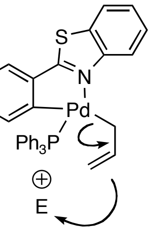
Scheme 3



Future Plans

(1) To optimize the structure of the chiral auxiliary cyclopalladated ligand in the palladacyclic catalysts related to complexes **C** and **D** to maximize the stereoinduction in the synthesis of amines **4**. Screening of diverse palladacycles will be followed by rational optimization of the most efficient catalysts, aiming to propose a general model for the mechanism of stereoinduction.

(2) To investigate the kinetics of the reactions between new types of stoichiometric allylpalladium(II) complexes represented by model compounds **5** and **6** and electrophiles (e.g. imines), aiming to elucidate the nature of the transition state and explore the structure-reactivity relationships for the key nucleophilic allyl-transfer event.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Publications (2006-2007) and References:

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2. C. D. Hopkins and H. C. Malinakova "Synthesis of Unnatural □-Amino Acid Derivatives via Three-Component Coupling Method Utilizing an Allylpalladium Umpolung" *Synthesis.* **22** (2007) 3558-3566.

3. A. Shiota and H. C. Malinakova, Unpublished results

4. R. Guo and H. C. Malinakova, Unpublished results

DE-FG02-86ER13511 **Tobin J. Marks**

Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis and Homogeneous Models

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Graduate students:	Neng Guo, John Roberts, Linda Williams, Staci Wegener
Collaborators:	Tim Wenzel, Peter Nickias (Dow Chemical Co.), Ignazio Fragala (U. Catania), Alceo Macchioni (U. Perugia), Scott Collins (U. Akron), Jeremy Kropf, Chris Marshall (Argonne National Laboratory).
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Goal

Elucidate, model, expand, and exploit pathways by which organometallic molecules undergo chemisorptive activation and dramatic reactivity enhancements on oxide surfaces. These processes connect directly to the efficiency of real-world, large-scale industrial processes and the capability to produce cleaner, greener, more environmentally acceptable products, including those from renewal resources. Research combines organometallic synthesis, surface chemistry and catalysis with computational modeling, and involves collaboration with industrial scientists. Specific objectives in the past year were: 1) Understand organometallic molecule chemisorption on "super Brønsted acid" oxides and nanoparticles, 2) Synthesize/characterize mononuclear and polynuclear homogeneous models for the chemisorbed catalytic species and counteranions, 3) Characterize the thermochemistry, structures, molecular dynamics, and mechanisms of these species, 4) Computationally model the catalyst properties.

DOE Interest

The catalyst syntheses, mechanistic studies, and product characterization activities that are the central part of this project relate directly to the efficiency, selectivity, and "greenness" of real-world industrial catalytic processes that are practiced on a huge scale and to the ability of these processes to produce cleaner, more environmentally acceptable products. This includes catalytic processes that use renewable, bio-feedstocks. These multifaceted, highly interdisciplinary projects provide ideal training for young scientists needed as part of a highly skilled U.S. technical workforce.

Recent Progress

Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces: Electrophilic zirconium surface alkyls are created in very high coverages by chemisorptive protonolysis of group 4-alkyl bonds and these species exhibit very high activity for arene and olefin hydrogenation as well as olefin polymerization. Benzene hydrogenation rates exceed that of any catalyst yet discovered. The kinetics and mechanism were characterized in detail, revealing that ~ 97% of the surface Zr species are catalytically significant--unusual for any heterogeneous catalyst. We expanded this investigation to other sulfated metal oxides and to other mononuclear and binuclear organometallic precursors. The sulfated metal oxides (SMOs) sulfated stannia (SnS), sulfated iron oxide (FeS), and sulfated titanium dioxide (TiS) were used as support materials/cocatalysts for olefin polymerization and hydrogenation catalysis. CPMAS NMR spectroscopy of

$Cp_2Zr(^{13}CH_3)_2$/SMO shows that cationic zirconocenium species are formed. Ethylene polymerization data with these catalysts show that polymerization activity dependent on both precursor ((ZrR_4 > Cp*$ZrMe_3$) and support (SnS > FeS > TiS); binuclear catalysts invariably give higher molecular weight polyolefins. As slurries, these catalysts are active for benzene hydrogenation and separable from liquid phase products by physical or, for FeS, by magnetic techniques. SnS nanoparticles can also be used as supports to create cationic "homogeneous" zirconium hydrocarbyl polymerization and hydrogenation catalysts. EXAFS studies are underway in collaboration with Drs. Jeremy Kropf and Chris Marshall (Argonne Nat. Lab.); for Cp*$ZrMe_3$/AlS, in which ~ 95% of the Zr sites are catalytically active, the Cp*$ZrMe_2^+$ cation essentially "floats" above the AlS^- anion with *very weak* ion pairing.

Ion-Pairing Effects on Single-Site Polymerization Catalyst Structure, Activity, and Selectivity: For electrophilic cation-anion ion-paired catalsyst systems, cocatalyst effects on enchainment rates, chain transfer processes, and catalyst stability/longevity can be significant, reflecting subtle non-covalent, cation-anion interaction/-molecular recognition effects. To investigate anion effects, a C_s-symmetic catalyst was activated with a series of cocatalysts of varying nuclearlity and "stickiness" over a broad range of concentrations, temperatures, propylene pressures, and solvent dielectric constanst. From these data it is possible to extract rate constants for the various competing selectivity processes. We learn that maxmimum selectivities are achieved in either of two very different ways: 1) depress site epimerization (chain swinging) with a weakly-coordinating cocatalyst at the expense of the propagation rate, 2) maximize the propagation rate to "outrun" competing stereoerror generation processes with minimally coordinating $B(C_6F_5)_4^-$.

In complementary work, a detailed cocatalyst/solvent/temperature/monomer concentration dependence study of propylene polymerization mediated by *both* C_s-symmetric and C_1-symmetric catalysts, paired with the charge-delocalizing cocatalysts, was carried out. Polymer stereoregularity, stereo-defect abundances, molar mass, and polymerization activity are all found to be strongly dependent on catalyst-cocatalyst ion pairing strength, with catalyst systems derived from the polynuclear perfluoroaryl cocatalysts in general exhibiting greater stereoregulation and polymerization activities than earlier systems employing their neutral analogs. With more polar 1,3-dichlorobenzene as the solvent, product polymer molar mass, stereoregularity, and activity are found to converge, indicating that ion pairing again plays an important role in determining the relative rates of termination and stereodefect production processes vs termination. Catalyst species observed by *ex-situ* spectroscopy to lack a cation - anion μ-Me or μ-F linkage exhibit the greatest polymerization activities and also a heightened tendency for stereodefect-introducing structural reorganization, with the former effect being dramatically stronger in cases of highly charged-delocalized counteranions. In these cases, a high degree of stereocontrol is observed together with very high polymerization activity, constituting a significant advance in catalysts for stereoselective olefin polymerization. In the most dramatic examples, syndioselectivities (and catalyst thermal stabilities) are on par with highly stereoregulating but much less active catalyst systems, and polymerization activities similar to very active (and thermally unstable) but poorly stereoregulating catalyst systems.

Studies with a second C_1-symmetric precatalyst and the same cocatalysts support the hypothesis that the presence or absence of a cation-anion bridging moiety (μ-F or μ-Me) significantly affects the relative rates of insertion as well as competing stereodefect production and termination processes. Enhanced termination via β-hydrogen elimination is observed in systems with no cation-anion bridging, and attenuated β-hydrogen elimination in systems in which a kinetically inert cation-anion contact exists. We can thereby differentiate between the contrasting origins for observed similarities in [propylene]-independent stereodefect production rates in these systems: in the bridged/strongly ion paired $Zr^{+}\cdots X^{-}$ systems, suppression of site epimerization between insertions (backskip failure) and suppression of insertion lead to formation of *rr* stereodefects, whereas in the unbridged systems, chain epimerization (involving a β-hydrogen elimination step) is likely the dominant [propylene]-independent *rr* stereodefect production process.

Theoretical Studies: Stereoinduction in olefin polymerization mediated by C_1-symmetric catalyst $H_2Si(ind)(^{t}BuN)TiCH_3^{+}$ was analyzed using DFT (collaboration: Prof. I. Fragala, U. Catania), including cocatalyst/counteranion effects. The catalyst activation energetics by $B(C_6F_5)_3$ were first analyzed and agree well with calorimetry. Next, the heterolytic ion pair separation energetics were scrutinized, and solvation effects assessed. Computed thermodynamic profiles for ethylene insertion at $H_2Si(ind)(^{t}BuN)TiCH_3^{+}$ indicate that insertion kinetics can be analyzed via SCF potential energies. Next, propylene insertion energetics at "naked" $H_2Si(ind)(^{t}BuN)TiCH_3^{+}$ were compared with those at $H_2Si(ind)(^{t}BuN)TiCH_3^{+}H_3CB(C_6F_5)_3^{-}$ to understand counteranion effects. We find that the counteranion, although affecting overall activity, does not significantly influence enchainment stereochemistry. The second ethylene insertion at $H_2Si(ind)(^{t}BuN)Ti(^{n}C_3H_7)^{+}H_3CB(C_6F_5)_3^{-}$ was analyzed to evaluate counteranion influence on propagation. We find that the ethylene enchainment transition state is energetically comparable to the first insertion transition state and that solvation has negligible effects on the energetic profile. These findings justify analysis of propylene insertion using a less computationally demanding "naked cation" model. Finally, enchainment at $H_2Si(ind)(^{t}BuN)TiR^{+}$ was analyzed for $H_2Si(ind)(^{t}BuN)TiCH_3^{+}$ + propylene (1st insertion) and for $H_2Si(ind)(^{t}BuN)Ti(^{i}C_4H_6)^{+}$ + propylene (2nd insertion). The first insertion is sterically-dominated with activation energies indicating predominant 1,2-olefin regiochemistry, while the second insertion reflects steric effects introduced by the growing chain, favoring isotacticity-enriching insertion pathways, in agreement with experiment.

Future Plans

In the area of novel supports for molecule-based catalysts, we will investigate supports claimed to be even more Brønsted acidic than the sulfated metal oxides, while EXAFS studies on adsorbate structure will continue at ANL. Systems with virtually 100% active sites present a unique opportunity. We also plan to use polymerization reactivity probes of the ion-pairing "tightness," and to explore binuclear and tandem supported catalytic processes in which cascade processes are turned on by virtue of the close proximity of the catalytic sites on the surface. This will be compared with results in solution on homogeneous model structures. In the area of ion-pairing studies, we plan to investigate cocatalyst-selectivity effects in other systems where ion-pairing might be intimately connected with enchainment selectivity. In the theoretical arena, we will explore whether double-layer effects at oxide surfaces may loosen ion-pairing, hence produce the enhanced reactivities observed, and investigate cooperative effects involving binuclear catalysts.

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4. Motta, A.; Fragala, I.L.; Marks, T.J. Stereochemical Control Mechanisms in Propylene Polymerization Mediated by C_1-Symmetric CGC Titanium Catalyst Centers, *J. Amer. Chem. Soc.* **2007**, *129*, 7327-7338.

5. Guo, N.; Stern, C.L.; Marks, T.J. Bimetallic Effects in the Homopolymerization of Styrene and Copolymerization of Ethylene and Styrenic Comonomers. Scope, Kinetics, and Mechanism, *J. Am. Chem. Soc.* **2008**, *130*, 2246-2261.

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8. Rodriguez, B.A.; Delferro, M.; Marks, T.J. Neutral Bimetallic Ni(II) Phenoxyiminato Catalysts for Highly Branched Polyethylenes and Ethylene-Norbornene Copolymerizations, *Organometallics*, in press.

9. Motta, A.; Fragala, I.L.; Marks, T.J. Proximity and Cooperativity Effects in Binuclear d^0 Olefin Polymerization Catalysts. Theoretical Analysis of Structure and Mechanism, submitted.

10. Rodriguez, B.A.; Delferro, M.; Marks, T.J. Neutral Binuclear Nickel Catalysts for Ethylene Polymerization in Polar Media and Ethylene Copolymerization with Functionalized Polar Comonomers, submitted.

DE-FG02-07ER15893 **Daniel J. Mindiola**

Catalytic Prospects Involving the Carboamination and Hydrophosphination of Alkynes.

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Goal

Develop reactive titanium reagents that can perform catalytic N−C, C−C, and P−C bond formatting reactions and under mild conditions. We want to develop facile entries to reactive catalysts that can be prepared with minimal costs or which are commercially available.

DOE Interest

Catalysts increment reaction rates by reducing the activation barrier of the reaction, yet remain unchanged upon completion of one catalytic cycle. Depending of the efficacy of the catalyst, energy expenditures can be ultimately reduced and the amount of product can be conveniently produced for subsequent research such as the synthesis of fine chemicals or just simply for use as a commodity product. In some cases however, the nature of the reaction or catalyst allow for "atom-efficient systems", where waste (mostly by-products) are minimized with much cleaner, catalytic alternatives. The latter parameter is important for obvious environmental concerns, but this factor becomes a critical feature when the product is needed in large demand. For this reason, we turn our attention to catalytic C−N, C−C and C−P forming reactions, since the products derived from these types of transformations offer the opportunity to study these systems from both an applied and fundamental point of view. Specifically, we are interested in α,β-unsaturated imine frameworks since this is a new class of highly arylated, organic archetypes. These types of frameworks are interesting given the highly conjugated nature surrounding the ene-imine functionality as well as the mechanism to their formation, since C=C and C=N bonds are catalytically formed while C−N bonds are catalytically broken.

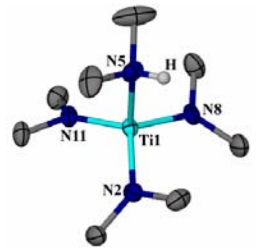
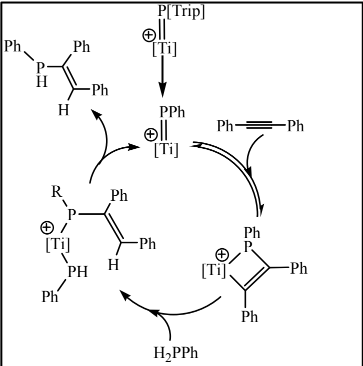


Fig 1. Molecular structure of the carboamination precatalyst. The anion $B(C_6F_5)_4$ has been omitted for clarity.

Recent Progress

Carboamination can be defined as the insertion of an alkyne into an aldimine C=N bond to form an α,β-unsaturated imine. Over the past two years our research group has developed carboamination catalysts to perform such a reaction using lower mol% than the metallocene-based systems originally developed by Bergman and co-workers. These precatalysts also perform carboamination reactions in shorter time frames and with greater yield of product, and can be conveniently prepared in a one pot reaction by using commercially available $Ti(NMe_2)_4$ and $[NHMe_2Ph][B(C_6F_5)_s]$. The crystallized salt generated from this acid-base reaction is shown in fig. 1. We have also discovered a titanium-based catalyst that can perform carboamination/cyclization reactions involving aldimines and internal alkynes to produce substituted quinolines. In addition to scope of substrate functional group tolerance, we are also currently investigating the active species responsible in the catalytic carboamination cycle as well as the role of the dimethylamino group, the electrophile, and the anion in such a process. Likewise, we are currently exploring titanium phosphindenes are hydrophosphination catalysts of alkynes and primary phosphines to generate secondary vinyl phosphines (Scheme 1). The latter product is potentially a good precursor to phosphalkenes. Synthetic, structural, and catalytic studies aimed at N−C, C−C and C−P bond forming reactions will be presented and discussed.



Scheme 1. Catalytic Hydrophosphination of Alkynes

Future Plans

Catalyst Development: Synthesize and characterize titanium based reagents for catalytic carboamination and hydrphosphination of alkynes. Ideally, we would like to prepare catalysts from commercially available precursors and facile to manipulate (e.g., $[Ti(NMe_2)_3(NHMe_2)]^+$, etc).

Addressing the Mechanism and the Nature of the Active Species: The role of the proton, the anion, and the titanium center will be investigated as well as the nature of the active catalyst. We are particularly intrigued in how titanium catalyzes the cyclization of α,β-unsaturated imines to substituted quinolines.

Explore the Reactivity and Physical Properties of the Conjugated Imine and Vinyl Phosphine: In addition to studying the catalyst, we also want to exploit the reactivity and physical properties of the highly unsaturated imine. We are particularly interested in the emissive properties and how these systems react towards nucleophiles. Likewise, we want to generate phosphaalkenes, catalytically, from the tautomerization of vinylphosphines since these reagents are an attractive feedstock used in the assembly of inorganic polymers bearing phosphorus as the heteroatom.

DE-FG02-97ER14807 **Jack R. Norton**

Catalytic Applications of H• Transfer from Transition-Metal Hydride Complexes

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DOE Interest

Chain transfer catalysis is an effective way of controlling chain length in radical polymerizations. Radical cyclizations have many synthetic applications, but are traditionally carried out by the stoichiometric use of Bu_3SnH — and its toxicity has limited the industrial use of this chemistry. Making weaker M–H bonds will not only improve the efficiency of these two catalytic reactions but be useful in designing methods for hydrogen storage.

I. Obtaining True Chain Transfer Constants from Apparent Chain Transfer Constants.

The efficiency of a chain transfer catalyst has traditionally been measured by its chain transfer constant (C_S), which is the ratio of the rate constant for chain transfer (k_{tr}) to that for propagation (k_p). Values of C_S are generally determined from the slope of a plot of $1/DP_n$ vs. [CTA]/[M], in which DP_n is the degree of polymerization, CTA is chain transfer agent, and M is monomer. When we calculate the efficiency of a chain transfer catalyst from such a plot we assume that all of the "catalyst" added remains active. This assumption is, however, not always true. It seems appropriate to call a chain transfer rate constant derived from the Mayo method an *apparent* value (k_{tr}(app)) if a significant fraction of the added catalyst is not in the active form. When we add a large concentration of our Cr chain transfer catalyst $(C_5Ph_5)Cr(CO)_3$• to a solution of MMA and AIBN, [Cr•] approaches a steady-state in which about 80% of the original Cr• has been converted to CrH and only about 20% of the original Cr• remains.

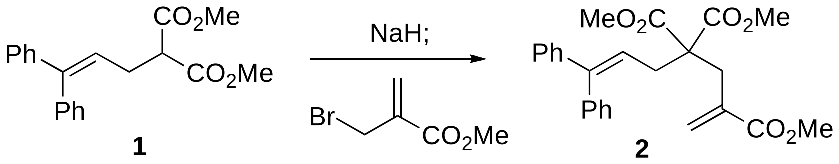
The balance between metalloradicals and hydrides in chain transfer catalysis is determined by the balance between H• transfer to the catalyst M• from chain-carrying radicals and reinitiation (transfer from M–H to monomer). For Cr hydrides, e.g., $(C_5Ph_5)Cr(CO)_3$•, with their relatively strong Cr–H bonds, this balance lies slightly on the side of H• transfer to Cr•, so [M–H] > [M•], and C_S(true) > C_S(app). For traditional Co(II) chain transfer catalysts, the balance lies completely on the side of the Co(II) "metalloradical", and C_S(true) is equal to C_S(app).

II. Measurement of the Rate Constant for H• Abstraction from Methyl Isobutyryl Radical by $(C_5Ph_5)Cr(CO)_3$•.

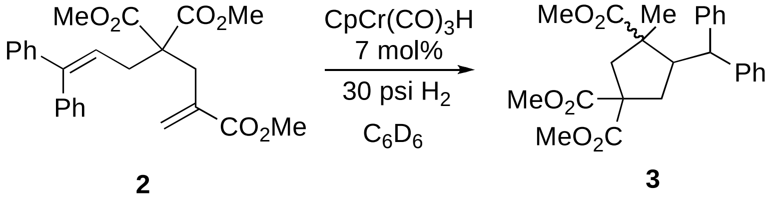
By maintaining a high concentration of $(C_5Ph_5)Cr(CO)_3$• during the AIBMe-initiated polymerization of MMA we have been able to measure this rate constant, k_{tr}(monomer), as 5.2×10^5 $M^{-1}s^{-1}$ at 70 °C. This value is smaller than that for the chain-carrying radical in an MMA polymerization ($k_{tr} = 1.4 \times 10^6$ $M^{-1}s^{-1}$), i.e., k_{tr} decreases significantly as we go from a monomeric radical to a polymer-chain-carrying radical.

III. Tin-Free and Catalytic Radical Cyclizations

We have extended our previous work on the radical cyclization (by H• transfer) of 1,6 dienes to the diene **2**, which upon H• transfer should give a radical that cyclizes relatively rapidly as a result of the Thorpe-Ingold effect. We have prepared **2** straightforwardly from the substituted malonate **1**.



Treatment of diene **2** with $CpCr(CO)_3H$ at 50 °C for 10 days afforded the cyclization product **3** exclusively; higher concentrations of **2** and $CpCr(CO)_3H$ led to clean cyclization after 1.5 days. The quantitative yield may result from a decrease in the rate of the competing hydrogenation and isomerization reactions as well as from an increase in the rate of cyclization. The decrease in the overall rate of the reaction is probably the result of a decrease in the rate of the initial H• transfer.



IV. The M–H Bonds in Vanadium Hydrides are Unusually Weak.

It should be possible to increase the rate of metal-to-olefin H• transfer by decreasing the strength of the M–H bond. We felt that V–H bonds were likely to be unusually weak, and thus determined (from their pK_a and the potential of the corresponding anion) the strength of those in $HV(CO)_4(P–P)$. To our knowledge the results in Table 1 are the first *solution* measurements of V–H bond strengths, and imply that the bonds in **4** are significantly weaker than the M–H bonds in other neutral hydride complexes — particularly the Cr–H bond in $CpCr(CO)_3H$.

Table 1. Values of pK_a, BDE, and $\Delta G°(H•)$ for $HV(CO)_4(P–P)$ and $CpCr(CO)_3H$. Relative Rate Constant for H• Transfer from **4a**–**d** to Styrene at 285 K in C_6D_6.

	E^o (V)	pK_a	M–H BDE (kcal/mol)	Relative k_H
$HV(CO)_4$(dppm) (**4a**)	–1.18 (1)	18.7(1)	57.9	20.0
$HV(CO)_4$(dppe) (**4b**)	–1.12 (1)	17.4(1)	57.5	10.6
$HV(CO)_4$(dppp) (**4c**)	–1.17 (1)	17.1(1)	56.0	8.2
$HV(CO)_4$(dppb) (**4d**)	–1.19 (1)	16.7(1)	54.9	6.7
$(\eta^5-C_5H_5)Cr(CO)_3H$			62.2[a]	1

These BDE values are low enough to call into question the *thermodynamic* stability of the hydrides **4** with regard to loss of H_2. The stability of the hydrides **4** at room temperature is probably the result of a *kinetic* barrier to hydrogen evolution.

$$2\ \mathrm{HV(CO)_4P\text{-}P} \rightleftharpoons \mathrm{H_2} + 2\ \bullet\mathrm{V(CO)_4P\text{-}P}$$

The V–H bonds in **4** do transfer H• *more rapidly* than does $\mathrm{CpCr(CO)_3H}$. We have determined the rate constants k_H for H• transfer to styrene from the vanadium hydrides **4** by observing the rate at which styrene is hydrogenated by **4**. (We have shown that the extent of back transfer is small by treating styrene with **4**-d_1.) The resulting k_H for **4** (Table 1) is 7 to 20 times faster than k_H for $\mathrm{CpCr(CO)_3H}$. These ratios, however, are considerably smaller than the ones we would expect if the differences in k_H were entirely the result of the differences in BDE between V– and Cr–H.

The relative value of the rate constants *within the vanadium series* in Table 1 is *opposite* that predicted from the V–H bond strengths, i.e., k_H *decreases* in the order **4a**>**4b**>**4c**> **4d**. The increasing size of the chelate ligands (from dppm through dppb) is presumably responsible.

When used in *stoichiometric* amounts the vanadium hydrides **4** effect the radical cyclization of dienes more rapidly, and under milder conditions, than does $\mathrm{CpCr(CO)_3H}$. The hydrides **4**, however, are not *catalytic* under an H_2 atmosphere.

Future Plans.

We will attempt to extend our radical cyclization chemistry to 1,6 dienes with other substituents. We will see if mixtures of Co and V carbonyls can effect such cyclizations catalytically. We will try to increase the rate of these H• transfer reactions by generating even weaker M–H bonds in the presence of diene substrates.

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2. Measurement of the Rate Constant for H• Abstraction from Methyl Isobutyryl Radical by $\mathrm{(C_5Ph_5)Cr(CO)_3}\bullet$, L.-H. Tang and J. R. Norton*, *Macromolecules* **2006**, *39*, 8236-8240.
3. Kinetics of Hydrogen Atom Transfer from $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cr(CO)_3H}$ to Various Olefins: Influence of Olefin Structure, J. W. Choi, L.-H. Tang and J. R. Norton*, *J. Am. Chem. Soc.* **2007**, *129*, 234-240.
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6. Chain-Transfer Catalysis by Vanadium Complexes during Methyl Methacrylate Polymerization, J. W. Choi, J. R. Norton*, *Inorg. Chim. Acta* **2008**, in press.

DE-FG-01ER15264 **Colin Nuckolls**

Catalytic Growth of Molecular-Scale Wiring

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Goal

The goal of this project is to develop catalytic methods to grow molecular wires from active metal-molecule linkages.

DOE Interest

The importance to the Department of Energy and its mission is three-fold. First, the science will develop new methodology that will expand the tool kit of catalytic processes and will apply what is learned to problems in Materials Science. Second, this approach will afford tailorable materials useful in nanoscale charge-transport applications such as highly efficient solar cells and light emitting diodes. Third, because many of these types of explicit metal molecule linkages are unknown, there is potential to discover previously unknown physical phenomena that could have broad impact.

Recent Progress

We detail two different systems. In one, we study methods to activate metal surfaces with carbenes to initiate olefin metathesis as a means to grow oligomeric, molecular-scale wires (Figure 1A) that are both structurally and electronically in contact with a metal surface (Figure 1B). In the other system, we study where a chemical seed in the form of a molecular hemisphere is able to encode the catalytic growth of a particular single walled carbon nanotube (Figure 1C).

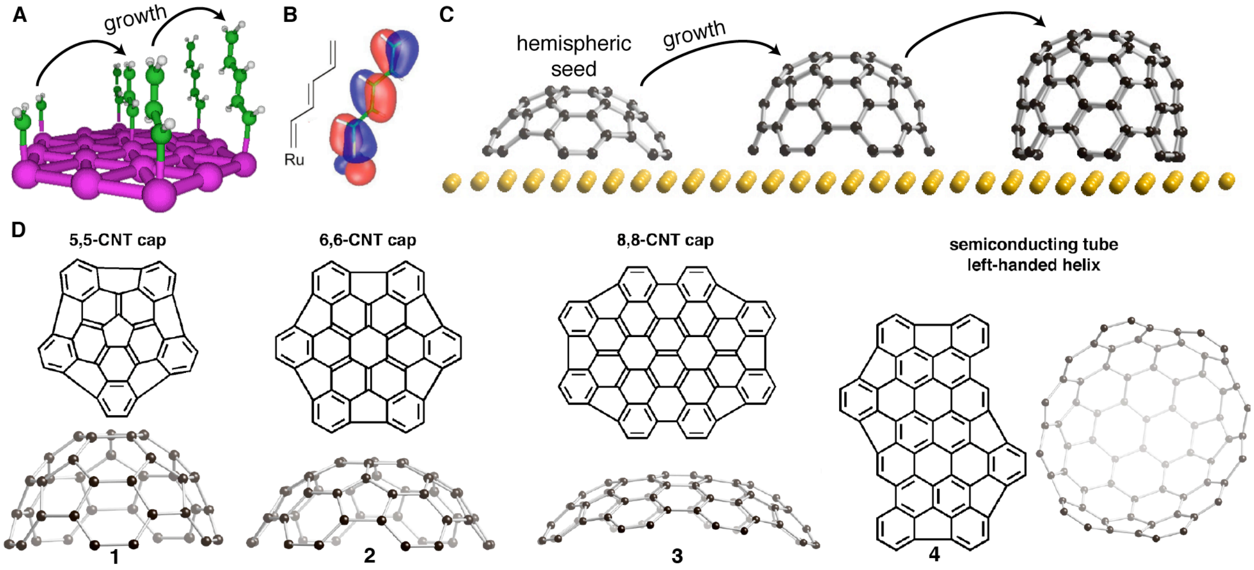

Figure 1. Specific aims (A) The catalytic growth of wires using metathesis from carbene functionalized surfaces is developed. (B) The conjugation of the wire should extend into the metal through the d-p π-bond. (C) A hemispheric seed is used as a template for the growth of SWNTs

with a defined diameter and chirality. (D) Hemispheric molecular seeds (**1**-**4**) for the growth of SWNTs with different diameters, chiral twist angles, and therefore different electronic band structures.

We investigate carbene/metal linkages as method to activate metal surfaces. The π-bonding in this metal-molecule linkage extends the conjugation into the metal providing an efficient conduit to get charge from the metal and into the molecule and vice-versa. We recently found a new monomer for the growth of conjugated wires from homogeneous and heterogeneous metathesis catalysts. It is a new type of strained [8]-annulenes, where one of its double bonds is kinked into a *trans*-configuration, is found to wind into helical conformation and is spring-loaded with ~18kcal/mol strain energy to act as an active monomer for ROMP. The polymerization produces a living phenylene vinylene with all ortho-linkages. The polymer has equal number of *cis* and *trans* double bonds.

Future Plans

We will develop nanoscale test beds to evaluate the efficiency of the polymerization process. The long-term goal is to investigate the utility of catalytic reactions *in situ,* in miniaturized electrical devices.

We will also study methods to catalytically synthesize single walled carbon nanotubes. In particular, we aim to utilize the molecular hemispheres described above by attaching them to surface of transition metals, and to use this attachment as a method to encode the growth of a particular single walled carbon nanotubes (Figure 1D). We hypothesize that the hemisphere is capable of controlling the diameter and chirality of the growing nanotube. We aim to synthesize molecular precursors and to develop methods both in solution and on surfaces to form them into hemispheres.

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DE-FG02-06er15815 **Oleg V. Ozerov**

Catalysis of C-F activation by Highly Electrophilic Si Compounds

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Goal

Develop a novel approach to activation and functionalization of C-F bonds using electron deficient main group catalysts.

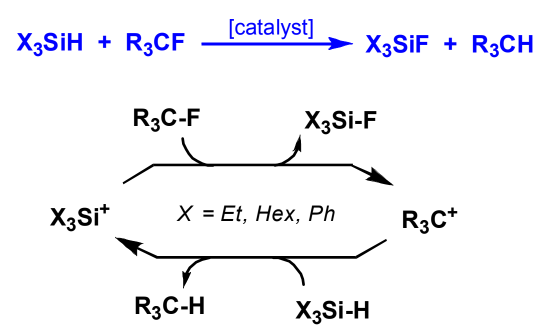
DOE interest

Carbon-fluorine bonds are the strongest single bonds involving carbon and are among the strongest and most inert bonds in all of chemistry. The ability to functionalize C-F bonds would be of great utility. Frequently cited benefits of such ability are the transformations of freons and CF_4 to environmentally benign substances. However, other novel applications are easily foreseen: 1) modification of the surfaces of fluoropolymers changing their adhesion properties; 2) functionalization of perfluoroalkyl monomers may lead to novel semifluorinated polymeric materials; 3) rational introduction of perfluoroalkyl substituents into fluorous phase catalysts; 4) improved understanding of the underlying C-F chemistry and applications in organic chemistry.

Recent Progress

Silylium-mediated hydrodefluorination (HDF) reactions. A few years ago, we described a novel approach to C-F activation (Scheme 1) that relies on a highly electrophilic silylium in the critical fluoride abstraction step. This approach allowed for HDF of substrates with C(sp^3)-F bonds at ambient conditions. We initially used the

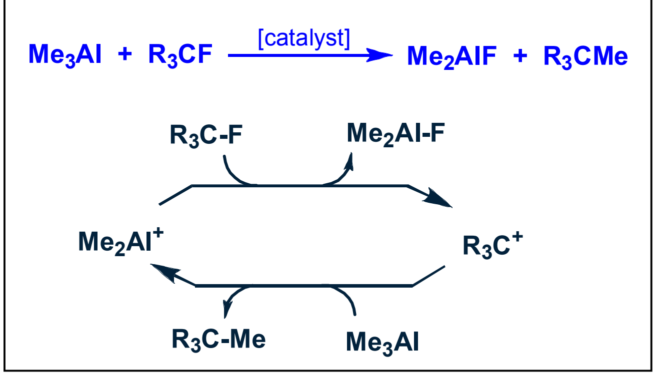
Scheme 1: Hydrodefluorination using Si catalyst



$[B(C_6F_5)_4]^-$ anion to sustain the highly electrophilic species generated in solution, however, it quickly became obvious that it is insufficiently robust. Halogenated carborane anions $[HCB_{11}X_{11}]^-$ have proven to be far superior to $[B(C_6F_5)_4]^-$. Whereas $[B(C_6F_5)_4]^-$ supports HDF reactions only with the less demanding substrates and low turnover numbers (<100) because of anion decomposition, carboranes support turnover numbers in excess of 1000 without decomposition. For instance, $[HCB_{11}H_5Cl_6]^-$ supports conversion of $C_6F_5CF_3$ to $C_6F_5CH_3$ at room temperature and complete defluorinaton of $CF_3(CF_2)_3CH_2CH_3$ at 75 ºC.

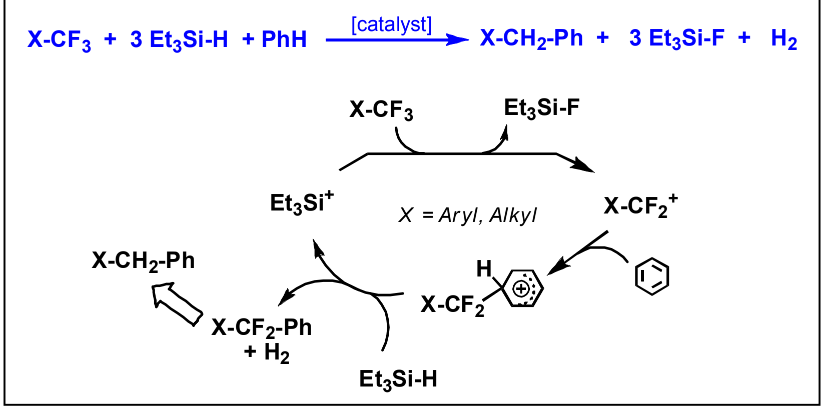
Alumenium-mediated defluorination reactions. Aluminum, like Si, is also highly fluorophilic and a similar catalytic cycle (Scheme 2) can be envisioned for alumenium-catalyzed replacement of F with an alkyl. Our studies show that catalytic conversion of C(sp^3)-F bonds to C-Me bonds is indeed possible with $R_2Al[CB_{11}H_6Br_6]$ as catalyst and Me_3Al as the Me source. For instance, the CF_3 groups of various benzotrifluorides ($Ar-CF_3$) can be cleanly converted into CMe_3 groups under ambient conditions. Other alkylaluminum reagents can similarly be used. However, with β-H-containing alkylaluminum reagents (e.g., Et_3Al) both an alkyl and a hydride transfer from Al to C is observed.

Scheme 2: C-F to C-C using Al catalyst



Friedel-Crafts chemistry. The silylium- or alumenium-mediated reactions described above give rise to highly reactive carbocations in due course. In the presence of aromatic substrates, products, and solvents, we have observed catalytic Friedel-Crafts chemistry. Scheme 3 demonstrates a generic example where X-CF_3 in benzene is catalytically converted into X-CH_2-Ph. Even unreactive arenes (e.g., $C_6H_4Cl_2$ or $C_6H_3F_3$) can be involved in this transformation. While this is often a side-reaction in the HDF catalysis, it is possible to optimize the conditions to favor the Friedel-Crafts product.

Scheme 3: Friedel-Crafts coupled C-F activation



For instance, 1,3-diphenylpropane is the major product in the HDF reaction of $PhCH_2CH_2CF_3$ in benzene. The Friedel-Crafts chemistry represents a different approach to conversion of C-F to C-C bonds.

Future Plans

C-F activation of perfluoroalkanes. While we have achieved C-F activation of perfluoroalkyl groups, activation of perfluoroalkanes remains a challenge. We see potential for solving this problem in the variation of the silane source and the solvent system.

Kinetic and mechanistic studies of the HDF reaction. We will use kinetic studies by multinuclear NMR techniques to probe the mechanism of our C-F activation reactions and isolate key intermediates. The robustness of carborane anions makes both components possible.

Explore the scope of the C-F activation applicability. We will explore the degree of compatibility of our C-F activation protocols with functional groups in the substrate.

Involvement of computational techniques. Computational approaches will allow us to better design future improvements to the process and understand the mechanism. We will engage collaborators and target bringing this expertise to our group as well.

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DE-FG02-93ER14339 **Gerard Parkin**

Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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Goals

The specific objectives and research goals of the research performed have been to obtain information that is relevant to transition metal mediated transformations of organic substrates. Such studies are of importance due to the fact that vast quantities of organic materials are available from natural resources but their full potential is yet to be realized because of synthetic difficulties. Specific issues that were addressed during the course of this research included: *(i)* establishing the coordination mode preferences of *N*–heteroaromatic molecules towards molybdenum relevant to hydrodenitrogenation, *(ii)* factors influencing coordination *versus* oxidative addition of C–H Bonds to molybdenum and tungsten, and *(iii)* a new type of precatalyst for olefin polymerization.

DOE Interest

The mission of the Catalysis and Chemical Transformations program of the Department of Energy is to support basic research to understand the chemical aspects of catalysis because “Catalysts are crucial to energy conservation in creating new, less-energy-demanding routes for the production of basic chemical feedstocks and value-added chemicals. Catalysts are also indispensable for processing and manufacturing fuels that are a primary means of energy storage.” Our research focuses on several issues pertaining to catalysis that belong to the above mission, such as hydrodenitrogenation and olefin polymerization.

Recent Progress

1. Coordination Mode Preferences of Molybdenum Towards N–Heteroaromatic Compounds and Their Catalytic Hydrogenation

We previously reported that $Mo(PMe_3)_6$ reacts with quinoline (QH) to give $(\eta^6\text{–}C_5N\text{-QH})Mo(PMe_3)_3$, the first example of a complex in which quinoline coordinates *via* its heterocyclic ring. At higher temperatures, however, $(\eta^6\text{–}C_5N\text{-QH})Mo(PMe_3)_3$ undergoes a haptotropic shift of the quinoline ligand to give the isomer $(\eta^6\text{–}C_6\text{-QH})Mo(PMe_3)_3$ in which the ligand coordinates *via* its carbocyclic ring. In an effort to define further the coordination chemistry of molybdenum relevant to hydrodenitrogenation, we have investigated the reactivity of $Mo(PMe_3)_6$ towards other heterocyclic nitrogen compounds with two fused six-membered rings that are related to quinoline, namely isoquinoline (iQH), quinoxaline (QoxH) and quinazoline (QazH). Significantly, the reactivity observed for these molecules is quite distinct from that of quinoline.

For example, in marked contrast to the reaction between $Mo(PMe_3)_6$ and quinoline, which requires heating at 80˚C to give $(\eta^6\text{–}C_5N\text{-QH})Mo(PMe_3)_3$, the corresponding reaction of isoquinoline proceeds rapidly at room temperature to yield $(\eta^2\text{–}N,C\text{–iQ})Mo(PMe_3)_4H$, as a result of cleavage of a C−H bond adjacent to nitrogen. While $(\eta^2\text{–}N,C\text{–iQ})Mo(PMe_3)_4H$ is the kinetic product of the reaction, $(\eta^2\text{–}N,C\text{–iQ})Mo(PMe_3)_4H$ dissociates PMe_3 and converts sequentially to $(\eta^6\text{–}C_5N\text{–iQ})Mo(PMe_3)_3$ and $(\eta^6\text{–}C_6\text{–iQ})Mo(PMe_3)_3$ upon heating. The adoption of these three coordination modes is significant because isoquinoline otherwise displays the $\kappa^1\text{–}N$–coordination mode. Likewise, quinoxaline and quinazoline, derivatives of quinoline that feature two nitrogen atoms, also react with $Mo(PMe_3)_6$ at room temperature to undergo oxidative addition of an adjacent C−H bond to give $(\eta^2\text{–}N,C\text{–Qox})Mo(PMe_3)_4H$

and (η^2–*N,C*–Qaz)-Mo(PMe_3)$_4$H, respectively. At elevated temperatures, (η^2–*N,C*–Qox)Mo(PMe_3)$_4$H converts sequentially to (η^6–C_4N_2–QoxH)Mo(PMe_3)$_3$ and (η^6–C_6–QoxH)Mo(PMe_3)$_3$.

Hydrogenation of the heterocyclic ring is generally considered to be a prerequisite for HDN of *N*–heteroaromatic compounds because the N–C bonds of saturated cyclic amines are typically weaker than those of their unsaturated counterparts. For this reason, we have examined the reactivity of the various (η^6–NHetH)Mo(PMe_3)$_3$ compounds towards H_2. Significantly, both (η^6–C_5N–iQH)Mo(PMe_3)$_3$ and (η^6–C_4N_2–QoxH)Mo(PMe_3)$_3$ react with H_2 at 90°C to give Mo(PMe_3)$_4$$H_4$ and release 1,2,3,4–tetrahydroisoquinoline and 1,2,3,4–tetrahydroquinoxaline, respectively. Together with the fact that (η^6–C_5N–QH)Mo(PMe_3)$_3$ reacts with H_2 to liberate 1,2,3,4–tetrahydroquinoline, it is evident that the molybdenum center is capable of selectively hydrogenating the heterocyclic ring of a variety of fused derivatives, a consequence of the fact that η^6–coordination of the heterocyclic ring is kinetically favored in this system. The selective hydrogenation of the heterocyclic ring is important because a considerable saving of hydrogen and energy during HDN would be achieved if *only* the heterocyclic ring of polyaromatic nitrogen compounds were to be selectively hydrogenated.

The stoichiometric hydrogenation of the heterocyclic rings of quinoline, isoquinoline and quinoxaline is of considerable interest since such reactions have not been reported for other molybdenum systems. In order to develop further this finding, we sought to obtain a catalytic system for hydrogenation using molybdenum and discovered that Mo(PMe_3)$_4$$H_4$ is a catalyst for the hydrogenation of quinoline, isoquinoline, and quinoxaline to 1,2,3,4–tetrahydroquinoline, 1,2,3,4–tetrahydroisoquinoline, and 1,2,3,4–tetrahydro-quinoxaline, respectively.

2. Factors Influencing Coordination versus Oxidative Addition of C–H Bonds to Molybdenum and Tungsten: The Calixarene Framework Promotes C–H Bond Activation.

We have demonstrated that *p*-t-butylcalix[4]arene, [Calix$^{Bu^t}$(OH)$_4$], reacts with Mo(PMe_3)$_6$ and W(PMe_3)$_4$(η^2–CH_2PMe_2)H to yield compounds of composition {[Calix$^{Bu^t}$(OH)$_2$(O)$_2$]M(PMe_3)$_3$$H_2$}, resulting from the oxidative addition of two adjacent phenolic O–H bonds to the metal center. Despite the common composition, however, X–ray diffraction studies indicate that there is a significant difference in the solid state structures pertaining to the manner by which one of the calixarene methylene groups interacts with the metal center. Specifically, the molybdenum complex exists as an agostic derivative [Calix$^{Bu^t}$(OH)$_2$(O)$_2$]Mo(PMe_3)$_3$$H_2$, whereas the tungsten derivative exists as a metallated trihydride, [Calix-H$^{Bu^t}$(OH)$_2$(O)$_2$]W(PMe_3)$_3$$H_3$. In order to determine whether the calixarene framework is responsible for the differences between the molybdenum and tungsten compounds, we sought related compounds derived from non-macrocyclic phenols. Therefore, we examined the reactivity of the simple diphenol CH_2(Ar^{Me2}OH)$_2$ [2,2'-methylenebis(4,6-dimethylphenol)] towards Mo(PMe_3)$_6$ and W(PMe_3)$_4$(η^2–CH_2PMe_2)H, giving [κ^2,η^2–CH_2(Ar^{Me2}O)$_2$]Mo(PMe_3)$_3$$H_2$ and [κ^2,η^2–CH_2(Ar^{Me2}O)$_2$]W(PMe_3)$_3$$H_2$, respectively. NMR spectroscopic studies demonstrate that the tungsten complex [κ^2,η^2–CH_2(Ar^{Me2}O)$_2$]W(PMe_3)$_3$$H_2$ exists in facile equilibrium with the metallated trihydride [κ^3–CH(Ar^{Me2}O)$_2$]W(PMe_3)$_3$$H_3$, whereas the molybdenum counterpart [κ^3–CH(Ar^{Me2}O)$_2$]Mo(PMe_3)$_3$$H_3$ is not readily accessible. Structural comparisons with the related calixarene compounds demonstrate that the methylene group of the calixarene ligand shows a greater propensity to undergo oxidative addition than does the methylene-bridged diphenoxide ligand.

3. Cp[Tm^{Me}]ZrCl$_2$, a Tris(2-mercapto-1-methylimidazolyl)hydroborato Complex of Zirconium and a New Type of Precatalyst for Olefin Polymerization

Cp[Tm^{Me}]ZrCl_2, the first *tris*(2-mercapto-1-methylimidazolyl)hydroborato complex of zirconium, is obtained by reaction of CpZrCl_3 with [Tm^{Me}]K. The molecular structure of Cp[Tm^{Me}]ZrCl_2 has been determined by X–ray diffraction and the geometry closely resembles the bent metallocene motif of

Cp_2ZrCl_2. An important distinction, however, is that $Cp[Tm^{Me}]ZrCl_2$ is chiral, with C_1 symmetry. In combination with methylalumoxane, $Cp[Tm^{Me}]ZrCl_2$ produces an active catalyst for ethylene polymerization.

Future Plans

The principal objectives of the research to be performed in the next budget period will be to extend the application of calixarene ligands to synthesize dinuclear molybdenum and tungsten compounds that include metals such as nickel. Since nickel is a promoter for HDS and HDN, these complexes are intended to mimic aspects of heterogenous HDS and HDN catalysts.

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5. "$Cp[Tm^{Me}]ZrCl_2$, a *Tris*(2-mercapto-1-methylimidazolyl)hydroborato Complex of Zirconium and a New Type of Precatalyst for Olefin Polymerization" by Daniela Buccella, Abraham Shultz, Jonathan G. Melnick, Felicia Konopka, and Gerard Parkin, *Organometallics* **2006**, *25*, 5496-5499.
6. "*p*-tert-Butylcalix[4]arene Complexes of Molybdenum and Tungsten: Reactivity of the Calixarene Methylene C–H Bond and the Facile Migration of the Metal around the Phenolic Rim of the Calixarene" by Daniela Buccella and Gerard Parkin, *J. Am. Chem. Soc. J. Am. Chem. Soc.* **2006**, *128*, 16358-16364.
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Transition metal complexes as artificial NADH analogs: towards photochemical reduction of carbon dioxide

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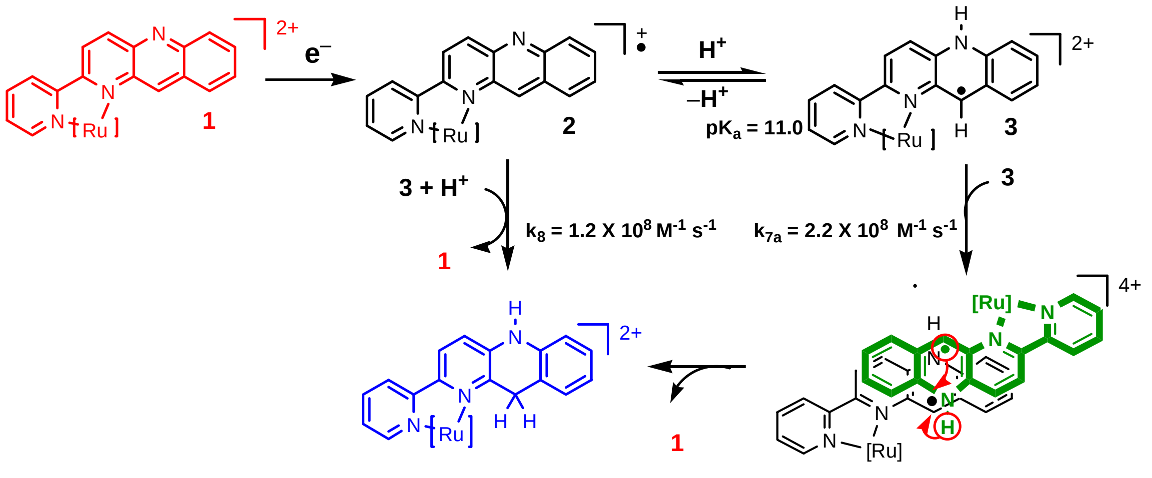
Artificial photosynthetic systems have received increased attention in the last several years in the light of global problems of rapid depletion of fossil fuels and increased greenhouse gas emissions. Nature elegantly utilizes photocatalytic reactions to store solar energy in the form of chemical equivalents as well as converting carbon dioxide into hydrocarbons. One of the key components of the part of Photosystem I that is responsible for CO_2 reduction is the NADPH co-enzyme, which serves as a hydride donor. As has been shown previously $[Ru(bpy)_2(pbnHH)]^{2+}$ (pbnHH = 1,5-dihydro-2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) can be used as an electrocatalyst to reduce acetone to isopropanol.[1] In the current work we have studied the photochemical formation and hydride donor abilities of the artificial NADH analog $[Ru(bpy)_2(pbnHH)]^{2+}$. The detailed mechanism of photochemical formation of $[Ru(bpy)_2(pbnHH)]^{2+}$ in water was described based on a combination of experimental and theoretical investigations including radiation chemistry and photochemical techniques.[2,3]



The hydride donor formation proceeds through non-protonated and protonated one-electron reduced intermediates with the pK_a of the protonated species being about 11. The one-electron reduced species disproportionates to produce one molecule of the hydride donor and one molecule of starting material. The reaction between two protonated one-electron reduced species proceeds through the formation of a π-stacking dimeric intermediate based on the electron density of the SOMO in the naphthyridine ligand, as evidenced by the analysis of spin densities obtained from DFT studies. The absence of a significant kinetic isotope effect in the disproportionation reaction is also consistent with dimer formation. We believe that the lack of a KIE for the cross reaction between protonated and non-protonated one-electron reduced species indicates that the disproportionation reaction involves a stepwise pathway of electron transfer followed by proton transfer.

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[1] Koizumi, T.; Tanaka, K., *Angew. Chem. Int. Ed.* **2005,** *44*, 5891-5894.

[2] Polyansky, D.; Cabelli, D.; Muckerman, J. T.; Fujita, E.; Koizumi, T.; Fukushima, T.; Wada, T.; Tanaka, K., *Angew. Chem. Int. Ed.* **2007,** *46*, 4169-4172.

[3] Polyansky, D.; Cabelli, D.; Muckerman, J. T.; Koizumi, T.; Fukushima, T.; Tanaka, K.; Fujita, E. *Inorg. Chem.* **2008,** *47*, in press.

DE-FG02-03ER15455 **Lawrence Que, Jr.**

Bio-inspired Iron Catalysts for Hydrocarbon Oxidations: April 2008 report

Project initiated September 1, 2006; 2007-08 budget: $143,000 total costs
Postdoctoral associates: Ruben Mas-Balleste, Iweta Przjomska-Ray
Graduate students: Paul Oldenburg, Yan Feng, Partha Das

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, Minnesota 55455
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Goal

To develop iron catalysts for hydrocarbon oxidations inspired by nonheme iron oxygenases and to understand their mechanisms of action.

Motivation

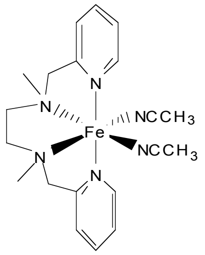
Stereoselective oxidation processes of C-H and C=C bonds catalyzed by nonheme iron enzymes are very common in the biological world. Inspired by these bioinorganic systems, our group has explored the oxidation of olefins using H_2O_2 as terminal oxidant that is catalyzed by [Fe^{II}(BPMEN)(CH$_3$CN)$_2$]$^{2+}$ (BPMEN = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane), [Fe^{II}(TPA)(CH$_3$CN)$_2$]$^{2+}$ (TPA = tris(2-pyridylmethyl)amine), and related complexes.

Recent Progress

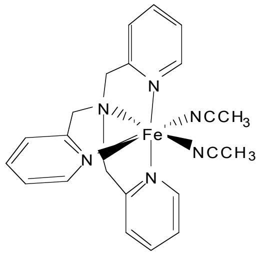
We report three important developments in our work during the past year.

1. Towards synthetically useful iron-catalyzed olefin epoxidation; Evidence for an Fe^{V}=O epoxidizing agent.

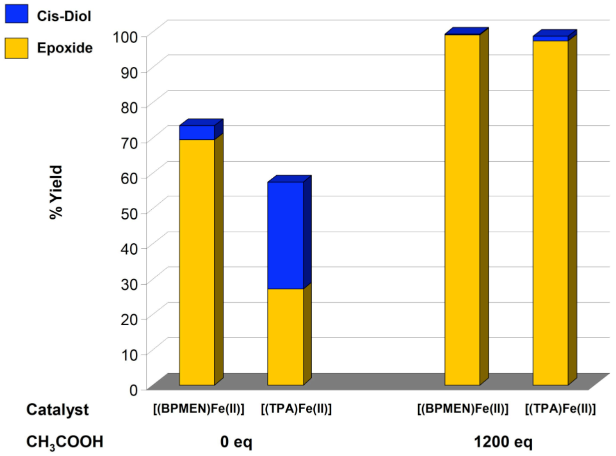
We have found that the addition of acetic acid to our Fe(BPMEN) and Fe(TPA) (Figure below) reaction mixtures greatly enhances their epoxidation abilities, such that cyclooctene epoxidation occurs with >99% conversion efficiency by 0.5 mol% catalyst within one minute of reaction time in a 1:2 MeCN/HOAc solvent mixture at 0 °C.



[(BPMEN)Fe^{II}(CH$_3$CN)$_2$]$^{2+}$



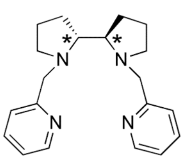
[(TPA)Fe^{II}(CH$_3$CN)$_2$]$^{2+}$



At lower temperature, a [(TPA)Fe^{III}(OOH)(HOAc)]$^{2+}$ intermediate can be trapped. Although this species decays to [(TPA)Fe^{IV}(O)]$^{2+}$, the latter is clearly not the oxidant, since it reacts more slowly with olefins than the catalytic system and does not carry out oxo transfer. It is thus formed as a side reaction. These observations have led us to propose that the active species is in fact [(TPA)Fe^{V}(O)(acetate)]$^{2+}$. This hypothesis is corroborated by the observed formation of a monoacetylated *cis*-diol minor product that would result from *syn*-addition of the Fe^V oxidant to an olefin.

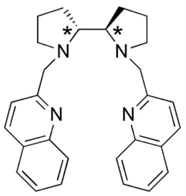
2. An asymmetric catalyst that carries out olefin cis-dihydroxylation with 97% ee.

We have synthesized a tetradentate ligand with a bipyrrolidine backbone in place of ethylenediamine in 6-Me_2-BPMEN to obtain a new chiral ligand 6-Me_2-BPBP. The iron complex catalyzes the *cis*-dihydroxylation of *trans*-2-heptene to afford a *cis*-diol product with 97% enantiomeric excess. The Fe(6-Me_2-BPBP) catalyst is only the second example of an asymmetric iron *cis*-dihydroxylation catalyst. Its enantioselectivity tops that of the first example, 97% vs 80%. A communication of this work recently appeared in *Angewandte Chemie*.



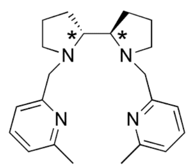
BPBP

1: *α*-[Fe^{II}(BPBP)]$^{2+}$



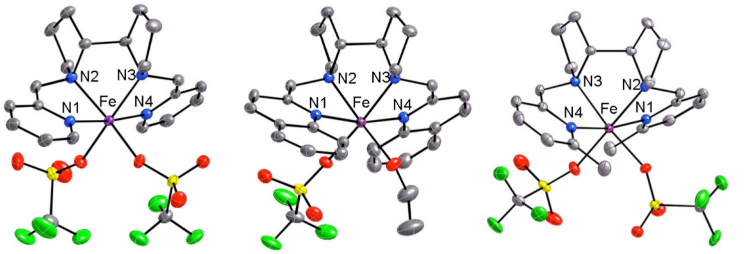
BQBP

2: *α*-[Fe^{II}(BQBP)]$^{2+}$



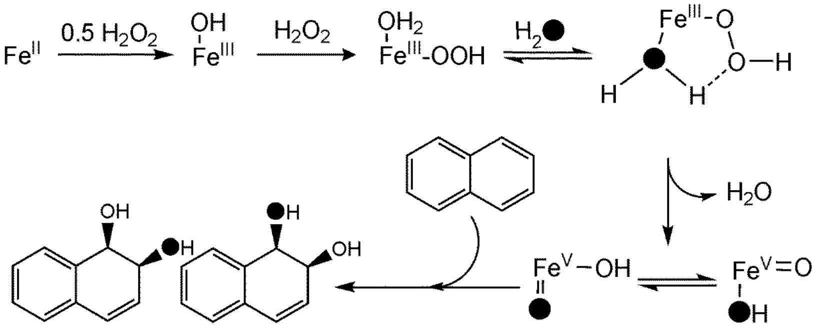
6-Me_2-BPBP

3: *α*-[Fe^{II}(6-Me_2-BPBP)]$^{2+}$



***3. First example of biomimetic cis-dihydroxylation of naphthalene*.** We have found in recent experiments that some of the olefin oxidation iron catalysts we have been studying can in fact catalyze the *cis*-dihydroxylation of naphthalene, the substrate for naphthalene dioxygenase (NDO). NDO belongs to the family of Rieske dioxygenases, which are enzymes that initiate the bio-degradation of aromatic compounds in soil bacteria.The *cis*-1,2-dihydrodiol obtained in fact behaves like the authentic enzyme product by GC and GC-MS methods. This result was unexpected and is quite an exciting development. Several iron catalysts such as [Fe^{II}(TPA)$(MeCN)_2$]$(OTf)_2$, [Fe^{II}(BPMEN)$(MeCN)_2$]$(OTf)_2$, [α-Fe^{II} (BPMCN)$(OTf)_2$], and [β-Fe^{II}(BPMCN) $(OTf)_2$] were screened. Of these, the best catalyst for this reaction thus far is [Fe^{II}(TPA)$(MeCN)_2$]$(OTf)_2$. ^{18}O-labeling studies were carried out to determine the sources of the oxygen atoms incorporated into products. Figure 1 shows the % incorporation from labeled water as a function of [$H_2{}^{18}O$] concentration in the Fe(TPA)-catalyzed reaction, demonstrating that the *cis*-dihydroxylation of naphthalene operates by a water-assisted mechanism, analogous to that we have proposed for olefin *cis*-dihydroxylation. Indeed the water incorporation curve for naphthalene oxidation overlays that previously reported for Fe(TPA)-catalyzed cyclooctene *cis*-dihydroxylation, implicating a common oxidant. The proposed mechanism for the *cis*-dihydroxylation of naphthalene is shown in Scheme 1.

Scheme 1



(b) Future objectives

Continued detailed mechanistic studies of the reactions of peroxides with nonheme iron(II) complexes to understand the molecular basis for the observed branching between olefin epoxidation and *cis*-dihydroxylation.
Investigation of biomimetic arene *cis*-dihydroxylation.
Further development of work on asymmetric olefin oxidation by iron complexes.

(c) Special recognition for the PI

On April 8, 2008, the PI received the 2008 Alfred Bader Award for Bioorganic or Bioinorganic Chemistry from the American Chemical Society at its Spring meeting in New Orleans.

(d) Current support

NIH GM-33162 "Nonheme Iron Oxygen Activation in Enzymes and Models" $1,856,000 direct costs for the period 4/1/05-3/31/10
NIH GM-38767 "Synthetic Approaches for Modeling Metal-Oxo Proteins" $1,165,000 total costs for the period 4/1/07-3/31/11.
DOE DE-FG02-03ER15455 “Bio-inspired Iron Catalysts for Hydrocarbon Oxidations” $450,000 total costs for the period 9/1/06-8/31/09
NSF CHE-0446658 “Sterically Hindered Carboxylates for Modeling Nonheme Iron Proteins” $405,000 total costs for the period 9/1/2005-8/31/2008 (co-PI; WB Tolman, PI); renewal proposal submitted.

(e) 2007-2008 Publications

solely supported by this DOE grant

1. Mas-Ballesté, R.; Que, L., Jr., Iron-Catalyzed Olefin Epoxidation in the Presence of Acetic Acid: Insights into the Nature of the Metal-Based Oxidant. *J. Am. Chem. Soc.* **2007**, *129,* 15964-15972.
2. Suzuki, K.; Oldenburg, P. D.; Que, L., Jr., Iron-Catalyzed Asymmetric Olefin *cis*-Dihydroxylation with 97 % Enantiomeric Excess *Angew. Chem. Int. Ed.* **2008**, *47*, 1887-1889.
3. Mas-Ballesté, R.; Fujita, M.; Que, L., Jr., High-valent iron-mediated *cis*-hydroxyacetoxylation of olefins. *Dalton Trans.* **2008**, 1828-1830.

supported by US DOE and other agencies

4. Klotz, K. L.; Slominski, L. M.; Hull, A. V.; Gottsacker, V. M.; Mas-Ballesté, R.; Que, L., Jr.; Halfen, J. A., Non-heme iron(II) complexes are efficient olefin aziridination catalysts. *Chem. Commun.* **2007**, 2063-2065.
5. Company, A.; Gomez, L.; Guell, M.; Ribas, X.; Luis, J. M.; Que, L., Jr.; Costas, M., Alkane Hydroxylation by a Nonheme Iron Catalyst that Challenges the Heme Paradigm for Oxygenase Action. *J. Am. Chem. Soc.* **2007**, *129*, 15766-15767.

FWP ANL 57700 **Jerome W. Rathke**

Catalytic Synthesis of Aluminum Nanoparticles

Additional PIs: Robert J. Klingler
Collaborators:
Contacts: Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439; klingler@anl.gov

Goal

Our goal is to investigate the reaction mechanism by which the titanium catalyst functions in aluminum hydride based hydrogen storage systems using solution phase dispersions of nanoparticulate aluminum instead of bulk materials. This approach allows us to probe the reaction mechanism by powerful kinetic and spectroscopic techniques. In addition, we can use in situ SAXS or X-Ray diffraction to follow the aluminum nanoparticle growth in real time as we have been doing with gold and platinum nanoparticles that are grown within the aqueous cores of reverse micelles. A further goal is to use the mechanistic knowledge to identify second-generation catalysts that will be effective for the lighter cations $LiAlH_4$, $Mg(AlH_4)_2$, or $Be(AlH_4)_2$ that can meet the DOE hydrogen weight and volumetric storage targets.

DOE Interest

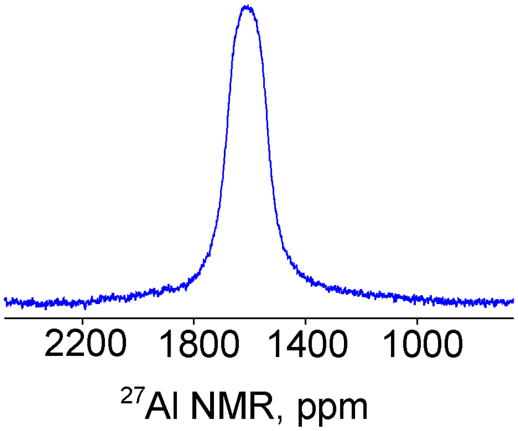
The development of a hydrogen-based automotive fuel cell drive train will require a lightweight mechanism for on-board hydrogen storage. Considerable world-wide interest has been devoted toward investigating sodium alanate which reversibly evolves hydrogen in the presence of titanium(IV) catalytic precursors under solid-state reaction conditions. Very little is known about the chemical details of the mechanism by which the titanium catalyst functions in these metal hydride systems. And, even less is known about the more general problem of how to activate a metallic substrate, such as aluminum or magnesium, for hydrogenation.

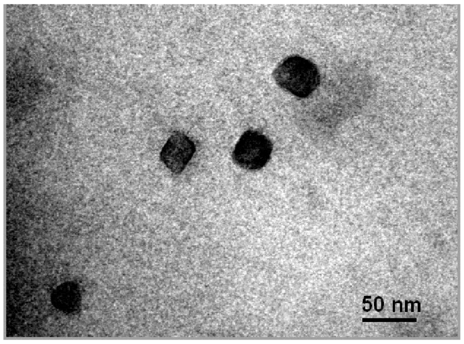
Recent Progress

The literature on aluminum particles is extensive. Yet, there are no known examples of soluble aluminum nanoparticles. We have found that polyethylene oxide (PEO) is quite effective at stabilizing and solubilizing aluminum nanoparticles. Large quantities of the hydride starting materials $NaAlH_3$, $LiAlH_3$, and AlH_3 can be loaded into a PEO matrix and the resulting ligated hydrides are very soluble in aromatic solvents. The aluminum hydride component of the AlH_3/PEO composite is readily characterized by NMR and IR spectroscopy: ^{27}Al NMR, -5.4 ppm; ^{1}H NMR, 4.0 ppm; Al-H IR, 1790 cm^{-1}. Addition of Ti(IV) catalyst precursors results in the smooth generation of aluminum metal. These dispersions of aluminum metal are stable for periods of over six months. The polymer stabilized aluminum nanoparticles can be isolated as a solid and redissolved in alternative solvents including tetrahydrofuran, acetonitrile, and methylene chloride.

The metallic nature of the product is confirmed by the ^{27}Al NMR Knight shift of 1600 ppm and, a plasmon resonance at 296 nm in the UV spectrum. The resultant aluminum nanoparticles are well separated as demonstrated by Transmission Electron Microscopy. The particles exhibit electron and X-ray diffraction patterns that are characteristic of aluminum metal.

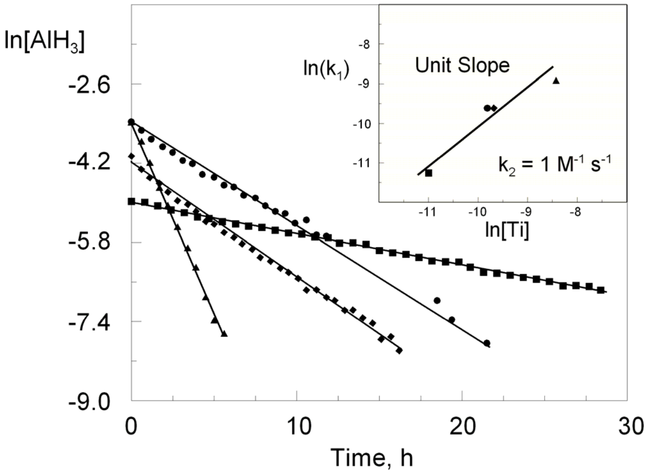
$$n\ AlH_3 \xrightarrow{Ti(OR)_4} Al_n + 3n/2\ H_2$$





TEM Image

The kinetics of the reaction are readily followed by in situ ^{27}Al NMR spectroscopy. The resonance for aluminum metal (at 1600 ppm) smoothly increases as the hydride signal decreases. The reaction is first order in the AlH_3 species and first order in titanium. One of the most remarkable aspects of this system is the simplicity of the kinetics for aluminum particle formation where the observed first-order rate plots are linear for over five half-lives despite the fact that the reaction product is a nanoparticulate solid. This behavior is different from that for many transition metal systems which tend to exhibit pronounced induction periods due to rate limiting nucleation reactions. Consistently, intermediate hydride clusters are not detected by ^{27}Al NMR spectroscopy during the reaction period.



In contrast to many transition metal systems, the rate limiting step in the main group alane/aluminum system involves activation of the first Al-H bond in the initial AlH_3 species by titanium and that all subsequent steps, including nanoparticle nucleation, leading to aluminum metal are fast.

Future Plans

One of the biggest unresolved issues in the alanate system is the nature of the titanium catalyst under steady-state reaction conditions. The lack of curvature in the kinetic plots suggests that the titanium remains in the solution phase throughout the reaction and is not alloying into the aluminum nanoparticles. Stiochiometric reactions between the $Ti(OR)_4$ catalyst precursor and the aluminum hydride species will be followed by ^{1}H, ^{27}Al, and ^{49}Ti NMR and IR methods at low temperatures if necessary to define the primary reactions pathways and gain insight into the nature of the active catalytic species. In addition, the oxidation state of the titanium species will be determined by in situ XANES at the Advanced Photon Source (APS). We have shown it is possible to obtain in situ SAXS data with solution phase samples loaded in capillary tubes and the same experimental approach is applicable to EXAFS and XANES. In addition, we have found that the APS has sufficient brilliance to obtain an X-Ray diffraction pattern with only 1s of exposure time again using a solution phase sample. This will allow us to investigate the nucleation process by probing the particle size in real time while the reaction is proceeding. We have found that the addition of silanes induces a pronounced induction period for the formation of aluminum metal. Trapping reactions of this type may provide further insight into the primary reaction pathways.

We have produced aluminum nanoparticles that are smaller by an order of magnitude, 0.7 nm, by eliminating the benzene solvent and conducting the reaction in a PEO polymer film. The latter particles were characterized within the PEO films by Grazing Incident Small Angle X-ray Scattering (GISAXS). We are currently collaborating with workers at the Center for Nanoscale Materials (CNM) to extend this approach to the generation of patterned arrays of aluminum nanoparticles. Arrays of this type are expected to exhibit unusual optical properties though the collective reinforcement of the Plasmon resonance. Thin films of AlH_3/PEO composite have been produced by spin coating techniques for the GISAXS experiments and films of this nature will be patterned into isolated islands at the CNM for subsequent conversion to nanoparticles.

Another area of work entails developing strategies for polymer production from non-petroleum based feedstocks. We have identified an iron based catalyst that converts biomass derivable CO/H_2 into a polymethylene product which has sufficiently high molecular weight that it precipitates out of polar reaction solvents. The activity of this catalyst is directly proportional to the soluble iron concentration as measured by IR spectroscopy. In addition, the fluid Catalysis group has recently begun work in the area of converting biomass derivable sugars into gasoline grade hydrocarbons. Existing heterogeneous catalysts that are designed to cleave the hydroxyl groups within the sugar molecules also concurrently cleave C-C bonds which degrades the product's value as a transportation fuel. We are working with homogeneous catalysts that promise to be more selective and robust.

Publications (2007-2008)

1)"Hydrolysis of Silicon-Hydride Bonds by Ferromagnetic Cobalt Nanoparticles" J.L. Rodgers, J.W. Rathke, R.J. Klingler and C.L. Marshall, *Catalysis Lett*. **114 (3-4)**, 145-150 (2007).

2)"Effect of Phosphines on the Thermodynamics of the Cobalt-Catalyzed Hydroformylation System" R.J. Klingler, M.J. Chen, J.W. Rathke, and K.W. Kramarz, *Organometallics* **26(2)**, 353-357 (2007).

3)"Toroid Cavity/Coil NMR Multi-Detector" R.E. Gerald II, A.D. Meadows, J.S. Gregar, and J.W. Rathke *U. S. Patent* No 7,271,592, issued September 18, 2007

4)"Capillary Toroid Cavity Detector for High Pressure NMR" R.E. Geraldd II, M.J. Chen, R.J. Klingler, J.W. Rathke, and M. ter Horst *U. S. Patent* No. 7,268,552, issued September 11, 2007.

5)"High Cation Transport Polymer Electrolyte" R.E. Gerald II, J.W. Rathke, and R.J. Klingler *U. S. Patent* No. 7,226,549 issued June 5, 2007.

6)"Stable Dispersions of Aluminum Nanoparticles" R.J. Klingler and J.W. Rathke *Organometallics*, (2008).

DE-FG02-90ER14146 **Thomas B. Rauchfuss**

Supramolecular Ensembles in Catalysis

Students: Julie Boyer, Zachariah Heiden, Swarnalatha Kokatam, Mark Ringenberg, Aaron Royer
Collaborators: S. P. Cramer (LBL - synchrotron spectroscopy), R. Thauer (MPI-Marburg, Germany - Biocatalysis), F. Gloaguen (CNRS-Brest - Echem), T. Martinez (UIUC - DFT), C. Mealli (CNR, Florence - DFT)
Contact: T. B. Rauchfuss, 505 S. Mathews, Urbana IL 61801;
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Goal

Bring ligand-based innovations to bear on organometallic catalytic chemistry, thereby providing new approaches to energy production and management.

Specific objectives for the previous year

(i) Demonstrate the utility of non-innocent ligands in catalysis of small molecules.
(ii) Investigate the role of supramolecular interactions in reactions of hydrogen, related to organometallic catalysis and, possibly, fuel cells.
(iii) Complete studies on organometallic cyanometallate receptors.

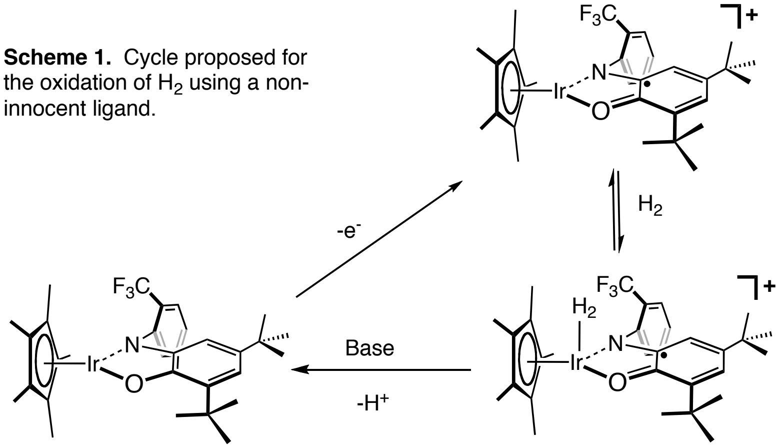
DOE Interest

(i) Our work on the role of acids for the activation of H_2 is relevant to the emergence of H_2 as an energy carrier.
(ii) The role of redox sites remote from the site of substrate activation is pervasive in biology but undeveloped in catalytic chemistry, preliminary results indicate significant opportunities for energy-related transformations.

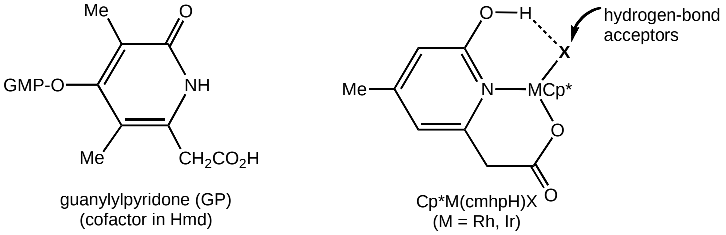
Recent Progress

Non-innocent Ligands in Catalysis. For this project we asked the question – what are the advantages to incorporating redox-active ligands in fundamental transformations involving energy-relevant substrates? We know that Nature employs many redox-active auxiliaries, and it was puzzling that synthetic homogeneous catalysts do rarely exploit this design feature. To address this question we designed test complexes which would be coordinatively unsaturated and contain a redox-active "non-innocent ligand" (NIL). For the NIL's, we chose *o*-amidophenolate ligands, complexes of which reversibly oxidize at mild potentials. These ligands are inexpensive and can be fitted with diverse substituents that allow control of the steric and electronic properties of the complexes. Initial experiments examined these ligands on a Cp*Ir(III) platform. We demonstrated that ligand-localized oxidation induce a reaction with H_2 (Scheme 1). The kinetics, stoichiometry, and crystallography provide a consistent pattern.

Scheme 1. Cycle proposed for the oxidation of H_2 using a non-innocent ligand.

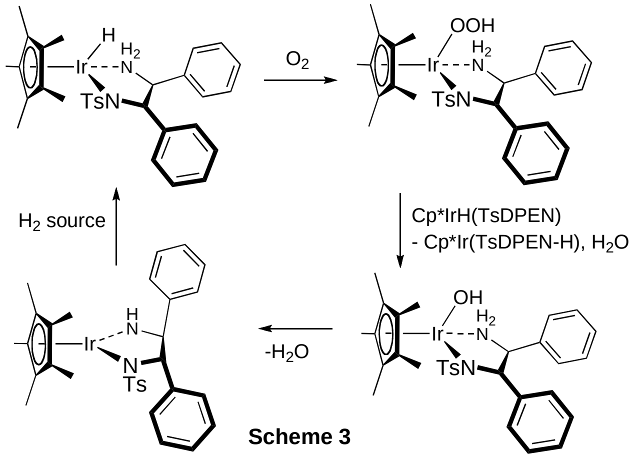


Bio-inspired ligands in homogeneous catalysis. Cp^*M^{2+} complexes (M = Rh, Ir) were described for 6-carboxymethyl-4-methyl-2-hydroxypyridine ($cmhpH_2$), an analogue of the recently discovered the GP cofactor in a hydrogenase enzyme (Scheme 2). Three findings indicate that $Cp^*M(Hcmhp)^+$ stabilizes the binding of hydrogen bond acceptors to the sixth coordination site: (i) water binds in preference to Cl^-, (ii) the adduct Cp*Rh(cmhp)(2-hydroxypyridine) exhibits a very short intramolecular hydrogen bond (r_{O---O} = 2.38 Å; ^1H NMR: δ_H = 17.2), and (iii) Cp*Ir(Hcmhp)Cl efficiently catalyzes the dehydrogenation of PhCH(OH)Me to PhC(O)Me.



Scheme 2. The GP cofactor in hydrogenases and a model complex that activates H_2.

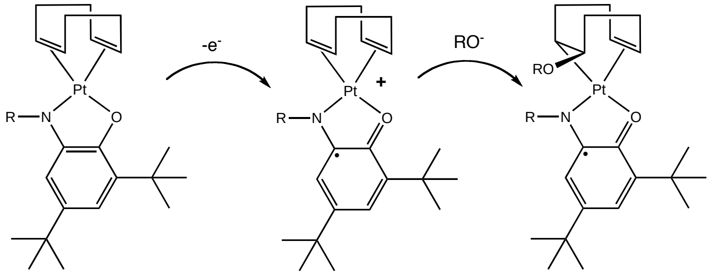
Hydrogen transfer to dioxygen. Transfer hydrogenation catalysts were shown to catalyze the reduction of dioxygen to water (Scheme 3). A hydroperoxide intermediate is implicated. The novelty of our approach is the use of catalysts that effect *heterolytic* activation of H_2.



Scheme 3

Future Plans

Activation of Organic Substrate via Non-innocent Ensembles: We have begun tests on the activation of other substrates of interest to the energy community. The promise of this direction is indicated by the following sequence, all members of which have been characterized by X-ray crystallography and either NMR or EPR spectroscopy.



Hydrogen Transfer to Coordinated Ligands: We will investigate the bimolecular transfer of hydrogen from a catalyst to a coordinated ligand on a second metal. Intermetallic transfers represent a new approach to utilizing H_2. In the current grant period, we have already performed feasibility studies on the reduction of dioxygen using transfer hydrogenation catalysts.

Publications (2006-2008)

"Supramolecular Architectures Based on Organometallic Half-sandwich Complexes" Rauchfuss, T. B.; Severin, K. in "Molecular Nanostructures" Atwood, J.; Steed, J. eds. Wiley-VCH, 2008.

"Expanded Cyanometallate Cages Derived from Dimetallic Dicyanide Building Blocks: $\{[Cp^*Rh]_4[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]_6\}^{4-}$" Boyer, J. L.; Rauchfuss, T. B. *Comptes Rendus* (special edition on hydrogenase models).

"Coordination Chemistry of a Model for the GP Cofactor in the Hmd Hydrogenase: Hydrogen-Bonding and Hydrogen-Transfer Catalysis" Royer, A. M.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.*, **2008**, *47*, 395-397.

"Redox-Switched Oxidation of Dihydrogen using a Non-innocent Ligand" Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.*, **2008**, *130*, 788-789.

"Highlight: Models for the Hydrogenases Put the Focus Where It Should Be - Hydrogen" Mealli, C.; Rauchfuss, T. B. *Angew. Chem. Int. Ed.*, **2007**, *46*, 8942-8944.

"Homogeneous Catalytic Hydrogenation of Dioxygen using Transfer Hydrogenation Catalysts" Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2007**, *129*, 14303-14310.

"Cyanometallate Cages with Exchangeable Terminal Ligands" Boyer, J. L.; Yao, H.; Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. *Eur. J. Inorg. Chem.* **2007,** 2721–2728.

"Evolution of Organo-Cyanometallate Cages: Supramolecular Architectures and New Cs+-Specific Receptors" Boyer, J. L.; Kuhlman, M. L.; Rauchfuss, T. B. *Accts Chem. Rsch.* **2007**, *40*, 233-242.

"Redox-Switched Complexation/Decomplexation of K^+ and Cs^+ by Molecular Cyanometalate Boxes" Boyer, J. L.; Ramesh, M.; Yao, H.; Rauchfuss, T. B.; Wilson, S. R.; *J. Am. Chem. Soc.* **2007**, *129*, 1931 -1936.

"Proton-Induced Lewis Acidity of Unsaturated Iridium Amides" Heiden, Z. H.; Rauchfuss, T. B. *J. Am. Chem. Soc.*, **2006**, *128*, 13048-9.

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DE-FG02-06ER15799 **Elena V. Rybak-Akimova**

Toward Mechanism-Based Design of Biomimetic Green Oxidation Catalysts

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Students: Olga Makhlynets, Wanhua Ye, Jeffrey Wikstrom, Olga Voronina, Sebastian Jara, Daniel Salas.
Collaborators: Lawrence Que, Jr. (University of Minnesota); Daniel Nocera (MIT); Miquel Costas (University of Girona, Spain); William M. Reiff (Northeastern U.); Richard S. Staples (Michigan State University); Bruce M. Foxman (Brandeis).
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Goal

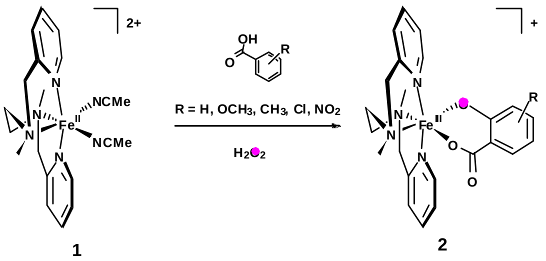
To determine the mechanisms of biomimetic catalytic hydrocarbon oxidations with hydrogen peroxide or dioxygen as terminal oxidants, and to identify iron-containing intermediates that are kinetically competent to carry out selective green oxidations. The long-term goal of the project is to apply mechanistic understanding of oxygen and peroxide activation for the development of new, efficient and selective catalytic systems for multi-electron oxidations.

DOE interest

Dioxygen and hydrogen peroxide are ideal oxidants because they are readily available and environmentally clean, producing water as the only byproduct. These reagents allow for the most efficient, atom-economy approach to oxidative functionalization of organic molecules, thus saving energy in chemical synthesis. In the absence of wastes, there is also no need to use energy for cleaning up the environment. Non-toxic, biocompatible iron complexes will be used as catalysts acting similarly to natural iron-containing oxidative enzymes. Fundamental understanding of multi-electron processes is important for addressing critical issues in converting renewable energy sources into liquid fuels (for example, oxidation nof methane into methanol, or catalytic photocleavage of water in to hydrogen and oxygen). Additionally, low-temperature kinetic methodology developed in this project will be widely applicable to mechanistic studies of a variety of transition-metal catalyzed homogeneous reactions.

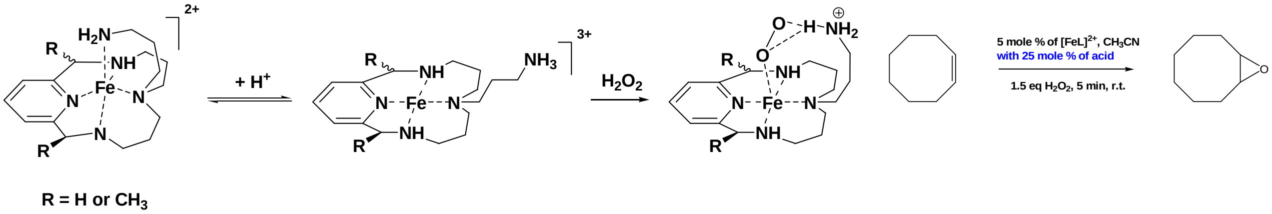
Recent Progress

Substituent-Directed Aromatic Hydroxylation at Non-Heme Iron: Aromatic hydroxylation of substituted benzoic acids with hydrogen peroxide in the presence of Fe(BPMEN)$^{2+}$ was recently discovered in our lab. The reaction likely involves coordination of both H_2O_2 and the substrate to the metal, and results in selective formation of salicylic acids from a range of substituted benzoic acids. The reaction is efficient (it is complete in 5-10 minutes at room temperature) and has a broad scope. Another reaction pathway also exists in the system: when ortho-hydroxylation is disfavored by the presence of 2,6-substituents in the aromatic ring, ipso-hydroxylation occurs instead. This new reaction was explored in detail for several electron-rich substrates. Phenolate products of this reaction were identified by mass spectrometry, NMR, and resonance Raman spectroscopy. These phenolates can undergo further radical-like reactions, eventually forming biphenols and/or adducts with the solvent molecules.



The reaction is controlled by the availability of protons: benzoic acid undergoes ortho-hydroxylation, while benzoate is entirely unreactive. Six-coordinate diiron(III) complexes are entirely unreactive, while oxo-bridged diiron(III) complexes with at least one labile site promote aromatic hydroxylation (albeit to a lesser extent than their monomeric counterpart). Iron(IV)-oxo intermediate is not a competent oxidant. The proposed mechanistic scheme includes initial oxidation of Fe(II) into Fe(III), followed by coordination of hydrogen peroxide and an aromatic substrate to the iron center. Acid-assisted heterolysis of the O-O in coordinated hydroperoxide would generate a yet-to-be-observed Fe(V)-oxo species, which can directly attack the aromatic ring in the ortho-position, or participate in a one-electron oxidation of coordinated carboxylate.

Olefin epoxidation with iron(II) aminopyridine macrocycles. Mononuclear iron(II) complexes with pyridine-containing macrocycles, which were designed as structural models of the active site in iron bleomycin, model oxygen transfer reactions of activated bleomycin. Efficient epoxidation of cyclic and terminal olefins with hydrogen peroxide occurs under mild conditions. Reactivity is controlled by the concentration of protons, suggesting iron(III)-hydroperoxo species as possible intermediates in oxygen transfer.



Progress in two aspects of this chemistry will be discussed: (1) identifying reactive intermediates responsible for oxygen atom transfer to olefins; (2) exploring the proximity effects by combining redox active macrocycle with a molecular recognition motif. In our mechanistic studies, we were able to generate iron(III)-alkylperoxo intermediates and Fe(IV)=O intermediates. As expected, Fe(III)-OOR intermediate did not react with olefins. Alkylperoxo species are usually nucleophilic, and do not function as efficient oxidants. In contrast, high-valent iron-oxo intermediates are often postulated as reactive species in oxygen atom transfer. Our system represents a rare example of the active catalyst that can generate a well-defined Fe(IV)=O intermediate. Detailed studies of the reactivity of Fe(IV)=O intermediates are currently in progress.

The presence of a primary amino group in our pentadentate macrocycles also allowed us to attach the catalyst to biotin, and to encapsulate biotin-macrocycle conjugate into streptavidin. This site-isolated iron macrocycle retained its ability to activate H_2O_2 in peroxidase-like reactions.

Future Plans

Now, when we identified useful, well-behaved reactions of substrate oxidation with hydrogen peroxide, and observed several potentially important iron-based intermediates in these systems, we plan to focus on detailed studies of the reactivities of these intermediates. Specifically, we will focus on epoxidation and hydroxylation reactions with iron-aminopyridine complexes (both mononuclear and dinuclear), and on catalytic oxidations with macrocyclic bleomycin models. In aromatic hydroxylation, iron chemistry will be compared and contrasted to copper chemistry. Additionally, inner-sphere pathways appear to dominate selective oxidation chemistry that we uncovered. We hypothesize that proximity effects may facilitate substrate oxidation, and to modulate the reactivity patterns of certain metal-peroxo and high-valent metal-oxo species. We will therefore design and study systems combining the redox-active iron center with the multi-point molecular recognition centers for supramolecular trapping and orientation of the substrate. In order to complement our current studies on protein-based molecular recognition systems, we will focus our attention on synthetic molecular recognition motifs. The objective is to design practical catalysts that will have relatively low molecular masses and will be stable under oxidative conditions.

Publications (2006 - 2008).

1. S. Taktak, S. V. Kryatov, T. E. Haas, E. V. Rybak-Akimova. Diiron(III) oxo-bridged complexes with BPMEN and additional monodentate or bidentate ligands: Synthesis and reactivity in olefin epoxidation with H_2O_2. *J. Mol. Cat. A* **2006**, *259(1-2)*, 24-34
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5. I.V. Korendovych, R.R. Roesner, E.V. Rybak-Akimova. Molecular recognition of neutral and charged guests using metallomacrocyclic hosts. *Advances in Inorganic Chemistry* (invited review), Academic Press: Amsterdam, **2007**. Edited by van Eldik, R., and Bowman-James, C. Volume 59: Template Effects and Molecular Organization; pp. 109 – 173.
6. I.V. Korendovych; S.V. Kryatov; E.V. Rybak-Akimova, Dioxygen activation at non-heme iron: Insights from rapid kinetic studies. *Acc. Chem. Res*. **2007**, *40*, 510-521.
7. J.D. Soper, S.V. Kryatov, E.V. Rybak-Akimova, D.G. Nocera. Proton-directed redox control of O-O bond activation by heme hydroperoxidase models. *J. Am. Chem. Soc.* **2007**, *129*, 5069-5075.
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Highly Selective Catalytic C–H Oxidative Cross-Coupling

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This poster will describe a new Pd-catalyzed reaction for the highly chemo- and regioselective oxidative cross-coupling of aromatic C–H bonds.[1] This transformation is proposed to proceed via two discrete C–H activation steps whose selectivities are predominantly controlled by proximity to a ligand (first C–H activation) or by the steric and electronic environment around the arene C–H bond (second C–H activation). We demonstrate that the selectivity of the second C–H activation reaction can be controlled by tuning the ligand environment around the Pd center. Both the synthetic scope of this transformation as well as mechanistic details will be discussed.

1. Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 11904-11905

Grant DE-FG02-86ER13564 **Richard R. Schrock**

The Living Polymerization of 1,6-Heptadiynes

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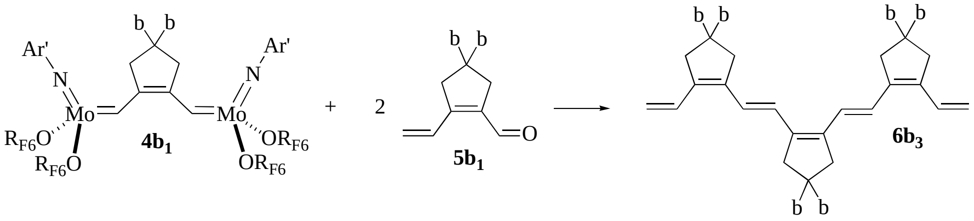
Goals. We have been exploring variations of well-defined alkylidene imido complexes of molybdenum for the living cyclopolymerization of 1,6-heptadiynes to give polyenes that contain six-membered rings (through head to tail cyclopolymerization) or five-membered rings (through tail to tail cyclopolymerization). In the past year the goals have been the (i) the development of *stoichiometric* methods for synthesizing long polyenes with a single structure analogous to the five-membered ring structure obtained through cyclopolymerization of dialkyldipropargylmalonates, and (ii) the development of *catalytic* methods that produce polymers made up of *exclusively* five-membered *or* six-membered rings.

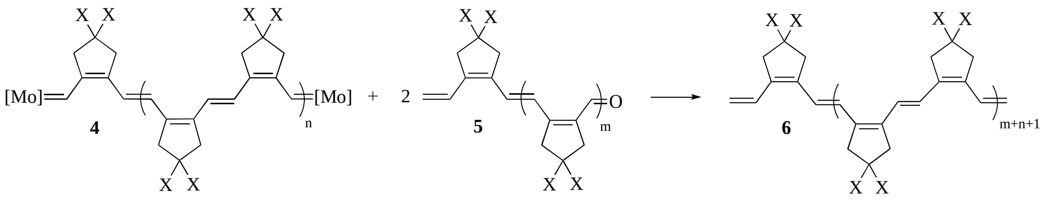
DOE Interest. Learning to control the structure of polymers through catalyst design is of fundamental interest for the synthesis of new polymers and applications that exploit their properties. The ability to control the structure and chain length of polyenes in living processes catalyzed by Mo alkylidenes, in particular, could have a significant impact on our understanding of the photophysics, photochemistry, and electronic and linear or nonlinear optical properties of one-dimensional, conjugated π-electron systems, and their potential in energy harvesting, photovoltaics, and other optical devices.

Recent Progress. We have developed *stoichiometric* methods of preparing long polyenes (up to 23 double bonds) that have a *fixed* chain length and that contain $=CH_2$ end groups instead of $=CMe_2$ end groups. This is the first time that a series of soluble and stable fixed-length polyenes in this length range have been prepared. The essential feature of this approach is the reaction between the *unsubstituted* aldehyde **5b₁** (equation 1) and (for example) the *bimetallic* "Wittig reagent" **4b₁** (Ar' = 2,6-dimethylphenyl, OR_{F6} = hexafluoro-t-butoxide) to yield the "trimeric" 7-ene **6b₃** and unstable oxoimido Mo complexes (not shown). Since **6b₃** contains $=CH_2$ end groups it can be employed to prepare another bimetallic reagent analogous to **4b₁** that contains a "trimeric unit" between the two Mo centers through reaction of **6b₃** with $Mo(NAr')(CHCMe_3)(OR_{F6})_2$, and that reagent can then be employed to prepare the pentamer (11-ene) upon treatment

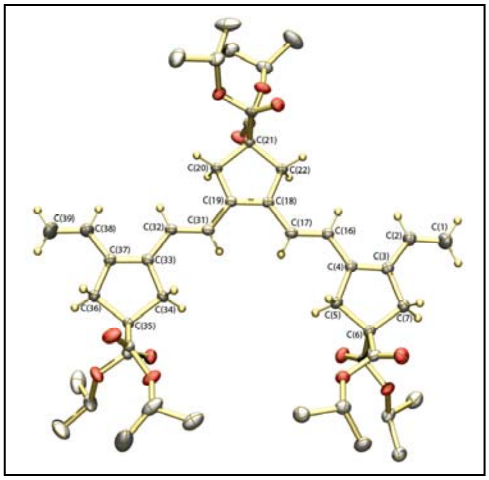


(1)

with two equivalents of **5b$_1$**. Related subsequent steps then yield the heptamer, nonamer, etc. Key features are that the product of a given Wittig-like reaction can be employed to prepare the next bimetallic "Wittig" reagent and that the chain can be grown in two directions. We also have shown that larger polyenes can be synthesized faster if aldehydes that contain m + 1 rings (**5** in equation 2; m = 0,1,...) are employed in reactions with bimetallic Mo reagents that contain n + 1 monomer units between two Mo centers (**4** in equation 2, where [Mo] signifies some generic molybdenum alkylidene complex and X some ester; n = 0,1,...). In this manner we have been able to prepare molecules with a *fixed* chain length, single five-membered structure, and up to 23 double bonds where X is an isopropylester.



(2)



X-ray studies on the metal-free "dimer" and "trimer" (see box) revealed that the five-membered rings are specifically *trans* with respect to one another and the olefinic carbons of the polyene chain lay in a plane. This is the first time that an X-ray structure has confirmed the assumptions made concerning the five-membered ring structures of such polyenes. X-ray structures of related bimetallic (Mo) species in which a $Mo(NAr')[OCMe(CF_3)_2]_2$ group is present in place of the terminal methylene group have also been obtained.

We have also explored the synthesis of carboxylate species, $Mo(NR)(CHCMe_2R')(O_2CR'')_2$ (R = various aryl groups or 1-adamantyl; R′ = Ph or Me; R" = CPh_3, CPh_2Me, $Si(SiMe_3)_3$, 2,6-$Me_2C_6H_3$, 2,6-Ph_2-4-MeC_6H_2, or 2,6-Ph_2-4-$(OMe)C_6H_2$) and their activity as initiators for 1,6-heptadiynes to give oligomers that contain largely *six-membered* rings. We find that polymers that contain all six-membered rings can be obtained when R" = CPh_3, and an X-ray structure of a PMe_3 adduct, which serves as a model for an initial alkyne adduct, reveals why formation of the required α,β-disubstituted molybdacyclobutene is favored. However, formation of the α,β-disubstituted molybdacyclobutene is very sensitive to the steric bulk of the carboxylate bound to the metal and to the 1,6-heptadiyne itself, with all six-membered ring structures being the exception rather than the rule. We now believe that formation of 1,6-heptadiyne polymers that contain only five-membered rings through formation of α,α' disubstituted metallacyclobutene intermediates will be more general.

Future Plans. Future plans include fundamental physical studies of polyenes that have a single chain length and a five-membered ring structure in collaboration with Ron

Christensen at Bowdoin. We also want to transform the esters in some fixed chain length species into other groups (e.g., hydroxymethyl) in clean, high yield reactions and compare the physical properties of these species with those of the malonate derivatives. Longer range plans include increasing the solubility of the polyenes, either by changing the nature of the ester, or in the long run, incorporating polyenes as blocks into long soluble polymers, e.g., polynorbornenes, prepared through ring-opening metathesis polymerization methods. Finally, we want to turn to an exploration of new initiators, especially those of the type Mo(NR)($CHCMe_2R'$)(pyrrolide)(OR") that are chiral at the metal, for controlling the structure (regiochemistry and stereochemistry) of not only 1,6-heptadiynes, but of a variety of monomers that include norbornenes, norbornadienes, and 3,3-disubstituted cyclopropenes.

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2. "Initiators of the type Mo(NAr)(CHR')($(OR")_2$) for the Controlled Polymerization of Diethyldipropargylmalonate" Adamchuk, J.; Schrock, R. R.; Tonzetich, Z. J.; Müller, P. *Organometallics* **2006**, *25*, 2364-2373.
3. "Synthesis of Oligoenes that Contain up to 15 Double Bonds from 1,6-Heptadiynes" Czekelius, C.; Hafer, J.; Tonzetich, Z. J.; Schrock, R. R.; Christensen, R. L.; Müller, P. *J. Am. Chem. Soc.* **2006**, *128*, 16664-16675.
4. "Thick, Optical Quality Films of Substituted Polyacetylenes with Large, Ultrafast $c^{(3)}$ Nonlinearities and Application to Image Correlation" Chi, S.-H.; Hales, J. M.; Fuentes-Hernandez, C.; Tseng, S.-Y.; Cho, J.-Y.; Odom, S.; Zhang, Q.; Barlow, S.; Schrock, R. R.; Marder, S. R.; Kippelen, B.; Perry, J. W. *Adv. Mat., in press.*
5. "Carboxylate-Based Molybdenum Alkylidene Catalysts. Synthesis, Characterization, and Use as 1,6-Heptadiyne Polymerization Initiators" Schrock, R. R.; Tonzetich, Z. J.; Lichtscheidl, A. G.; Müller, P. *Organometallics, submitted.*
6. "Synthesis of Oligoenes of 1,6-Heptadiynes that Contain up to Twenty-Three Double Bonds" Scriban, C.; Schrock, R. R.; Christensen, R. L.; Müller, P. *J. Am. Chem. Soc., submitted.*

DE-FG02-93ER14359 Lawrence T. Scott

High Temperature Chemistry of Aromatic Hydrocarbons

Additional PIs: none
Postdocs: none
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Collaborators: Armin de Meijere (University of Göttingen, Germany), Marina A. Petrukhina (University at Albany, SUNY), Mordecai Rabinovitz (Hebrew University of Jerusalem, Israel), David M. Grant (University of Utah), Ronald J. Pugmire (University of Utah)
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Goal

The primary goal of this research is to uncover all the principal reaction channels available to polycyclic aromatic hydrocarbons (PAHs) at high temperatures in the gas phase and to establish the factors that determine which channels will be followed in varying circumstances. New structure-property relationships for PAHs are also studied.

DOE Interest

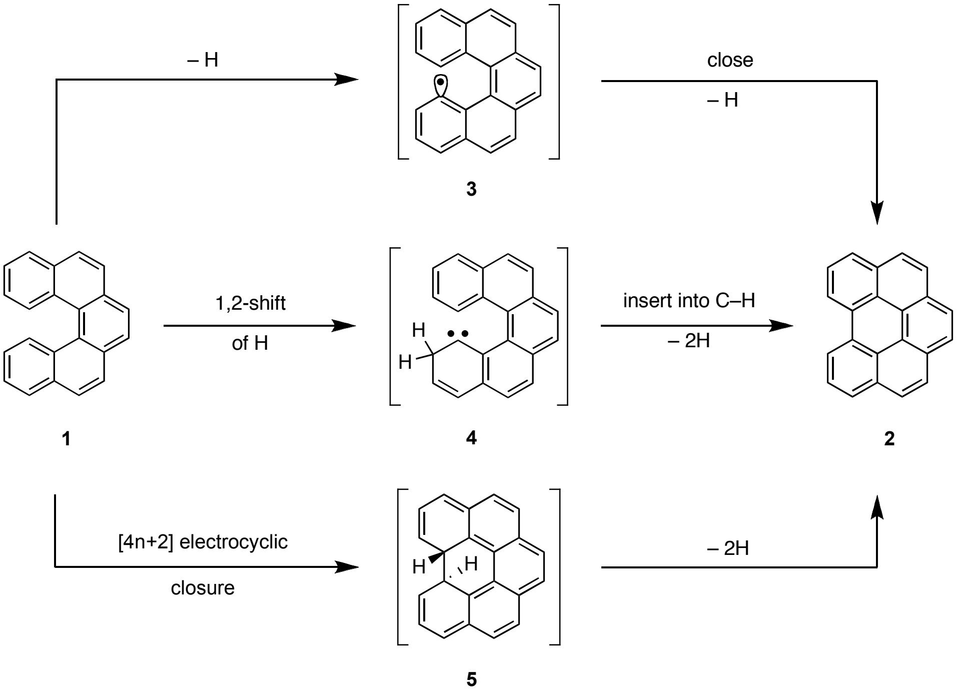
An understanding of the fundamental molecular transformations, rearrangements, and interconversions of PAHs at high temperatures in the gas phase, as revealed by careful studies on small, well-designed, molecular systems, provides insights into the underlying chemistry of many important processes that are more complex, such as the generation of energy by the combustion of fossil fuels, the uncatalyzed gasification and liquefaction of coal, the production of fullerenes in fuel-rich flames, and the formation of soot and carcinogenic pollutants in smoke. The rational control of any of these processes, whether it be the optimization of a desirable process or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved.

Recent Progress

Experiments designed to increase our understanding of thermal cyclodehydrogenation reactions currently occupy much of our attention. In fuel-rich flames, the fusion of simple hydrocarbons into highly condensed, carbon-rich products such as fullerenes, soot particles, and discrete PAHs (*e.g.*, benzo[*a*]pyrene, a potent carcinogen) is accompanied by the loss of many hydrogen atoms. Though the exact sequence of events leading to these products is not known in detail, much of the hydrogen is almost certainly lost in conjunction with the generation of new rings by *intra*molecular C–C bond formation ("cyclodehydrogenation").

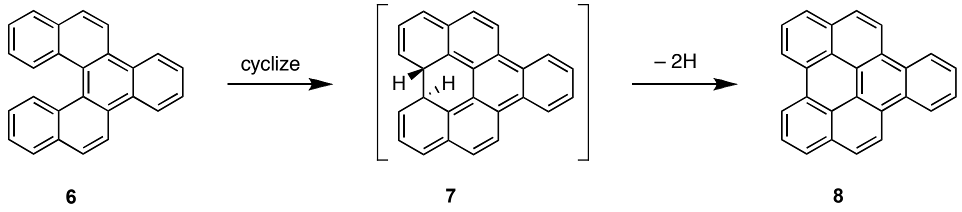
Surprisingly little is known about the mechanism(s) of these ubiquitous high temperature transformations. Experimental studies are virtually nonexistent, and very little computational work has been published on such reactions. As illustrated in Scheme 1, at least three distinct mechanisms can be envisioned for cyclodehydrogenations that form a new 6-membered ring (*e.g.,* **1** → **2**); the reaction might proceed through a radical intermediate (**3**) or through a carbene intermediate (**4**) or through a concerted electrocyclic reaction (**5**). We have carried out experiments to determine which of these three pathways is favored, using the cyclodehydrogenation of [5]helicene (**1**) as a prototypical case.

Scheme 1



Our strategy involved a careful comparison between the ease of thermal cyclodehydrogenation of [5]helicene (**1**) and that of the benzannulated analog **6**. All three pathways in Scheme 1 are calculated to require substantial inputs of energy (UB3LYP/6-31G*), but the predicted effects of benzannulation on these three pathways differ significantly. Whereas the energetic requirements for the radical pathway and the carbene pathway remain relatively unperturbed by the benzannulation in **6**, the electrocyclization pathway is predicted to show a marked response. Specifically, benzannulation as in **6** is predicted to *slow down* the thermal cyclodehydrogenation, compared to that in **1**.

Scheme 2



The origin of this predicted rate retardation can be appreciated most easily by examining the electrocyclization intermediate **7**, in which the aromaticity of every ring, including that of the appended benzene ring, has been temporarily destroyed. The loss of aromatic stabilization energy in going from **6** to **7** is calculated to exceed that in going from **1** to **5** by approximately 5 kcal/mol. Experimentally, we observe that the benzannulated helicene **6** does indeed suffer thermal cyclodehydrogenation significantly less readily than **1** and conclude that the mechanism in this prototypical case proceeds by the electrocyclization mechanism. Full details concerning this representative project can be found in publication no. 8 below. Results from other projects can be found in the other publications listed.

Future Plans

Further experiments to elucidate the mechanism(s) of thermal cyclodehydrogenations in other well defined systems are underway. The formation of both 6-membered rings and 5-membered rings are being studied; the electrocyclization mechanism is *not likely* to be favored in the latter cases. The high temperature chemistry of PAHs containing a sulfur atom embedded in the polycyclic ring system (as commonly found in coal) are also being investigated, and new insights are beginning to emerge on the effects of external radical sources on several high temperature processes involving aromatic hydrocarbons.

Publications (2006-08)

1. "Corannulene: A Preference for exo-Metal Binding. X-Ray Structural Characterization of $[Ru_2(O_2CCF_3)_2(CO)_4 \cdot (\eta^2\text{-}C_{20}H_{10})_2]$," Petrukhina, M. A.; Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T., *Organometallics* **2006**, *25*, 5492-5495.
2. "X-Ray and DFT Structural Study of 1,3,5,7,9-Penta-*tert*-butylcorannulene, $C_{40}H_{50}$," Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T.; Petrukhina, M. A. *J. Org. Chem.* **2006**, *71*, 6615-6618.
3. "Synthesis and Aldol Cyclotrimerization of 4,7-Di-*tert*-butylacenaphthenone," Amick, A. W.; Griswold, K. S.; Scott, L. T. *Can. J. Chem*. **2006**, *84*, 12
4. "Corannulene "Hub" Carbon Coordination by $Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5$" Petrukhina, M. A.; Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T. *Angew. Chem. Int. Ed.* **2006**, *45*, 7208-7210.
5. "Anions and Polyanions of Oligoindenopyrenes: Modes of Electron Delocalization and Dimerization," Aprahamian, I.; Wegner, H. A.; Sternfeld, T.; Rauch, K; de Meijere, A.; Sheradsky, T.; Scott, L. T. ; Rabinovitz, M. *Chem. – Asian J.* **2006**, *1*, 678-685
6. "Synthesis of Geodesic Polyarenes by Flash Vacuum Pyrolysis," Tsefrikas, V. M.; Scott, L. T. *Chem. Reviews* **2006**, *106*, 4868 - 4884.
7. "Ring Current Effects between Molecules in a Crystal. Evidence from ^{13}C Chemical Shielding Tensors for Intermolecular Shielding and Molecular Magnetic Susceptibility in 4,7-di-*t*-butylacenaphthene versus 4,7-di-*t*-butylacenaphthylene," Ma, Z.; Halling, M. D.; Solum, M. S.; Harper, J. K.; Orendt, A. M.; Facelli, J. C.; Pugmire, R. J.; Grant, D. M.; Amick, A. W.; Scott, L. T. *J. Phys. Chem. A* **2007**, *111*, 2020-2027.
8. "Thermal Cyclodehydrogenations to Form 6-Membered Rings: Cyclizations of [5]Helicenes," Xue, X.; Scott, L. T. *Org. Letters* **2007**, *9*, 3937-3940.
9. "Gas Phase Assembly and X-Ray Crystal Structure of Copper(I) 3,5-Bis(Trifluoromethyl) Benzoate Network with Corannulene," Y. Sevryugina, E. A. Jackson, L. T. Scott, and M. A. Petrukhina *Inorg, Chim. Acta* **2008**, published on the web Feb. 5.

DE-FG02-05ER15729 **Jorge M. Seminario**

Theory-guided design of nanoscale multimetallic nanocatalysts for fuel cells

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Postdoc: Juan C. Sotelo
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Local chemistry and nonlocal physics in multi-atomic substrates for studies of reactivity of molecules have been performed with applications to the catalysis of oxygen. We develop a novel ab initio technique that considers the effects of the discrete and continuum nature in the reactivity of molecules on multimetallic substrates and put both types of effects together through a Green's function approach [1,2]. We have analyzed several biatomic substrates for bulk-molecule interfaces, the local reactivity of oxygen on bimetallic substrates, the proton transfer to molecular oxygen adsorbed on Pt based nanotips, including nanotips of CoPt, Co, and Ni. Our ab initio procedure is developed to include multi-atomic backgrounds as materials participating in electron transfer reactions. The reactivity of molecular oxygen on bimetallic clusters of Pt and Co is initially studied with this procedure in order to understand and develop the basic chemistry and physics to get reliable results. We focused on the reaction of molecular oxygen on the surface of the $L1_2$ phase of Co_3Pt, which yield three distinct chemisorbed precursors, two of which are energetically almost degenerate. We also study the local reactivity of O_2 with bimetallic substrates of a Pt_3 island supported on nanotips of CoPt, Pt, Co, Ni, and Fe. Because of reduced interatomic distances and varying interaction strengths with the substrates, the supported island interaction with O_2 can be tuned from stronger to weaker relative to the interaction of a freestanding island with O_2. The reactivity can be approximately correlated with the binding energy of the island to the substrates. Finally, we study the interaction of solvated hydronium ions with a local nanotip of Pt, and bimetallic nanotips of CoPt, Co, and Ni. The nanotip is modeled as a trimer Pt-island supported on Pt, Co, Ni, and Co_3Pt substrates. Locally, the interaction is modeled as the protonation of adducts $Co_3Pt_3O_2$, $Ni_3Pt_3O_2$, $Pt_6Pt_3O_2$, and $Co_3Pt_3Pt_3O_2$.

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DE-FG02-88ER13880 **Paul R. Sharp**

Alkene Reactions of Platinaoxetanes and Platinum Oxo Complexes

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Goals

Understand the relationship of late transition metal oxo complexes to molecular oxygen activation and hydrocarbon oxidation.

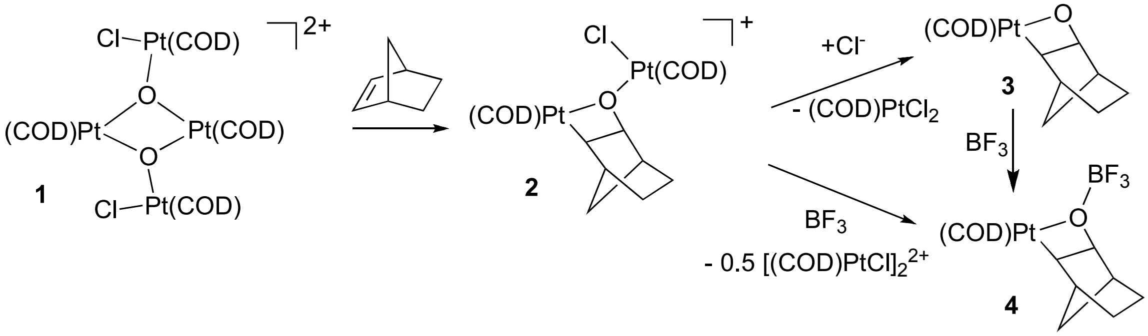
DOE Interest

Understanding of the chemistry of metal oxo complexes is fundamental to understanding many important catalytic processes of direct and indirect impact on energy conversion. Potential benefits include increased efficiency, new processes, and reduced pollution.

Recent Progress

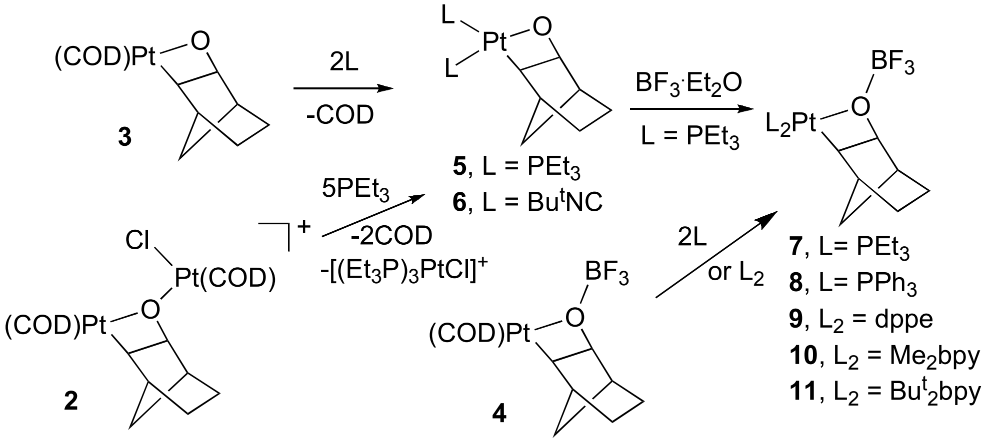
Platinaoxetanes chemistry. Previously, we reported the novel reaction in Scheme 1, formation of platinaoxetane **2** from oxo complex **1** and norbornene. Though rare, metallaoxetanes such as **2** are key postulated intermediates in a number of reactions. We therefore sought to expand this family of platinaoxetanes and explore their reactivity.

Scheme 1



Complex **2** is readily converted into **3** and **4** by displacement of the Lewis acid fragment $[(COD)PtCl]^+$ from **2** (Scheme 1). Complexes **2**, **3**, and **4** undergo COD ligand displacement with phosphines and diimines (Scheme 2) allowing ligand and Lewis acid effects on platinaoxetanes reactivity to be studied. The reaction chemistry of these platinaoxetanes is diverse and depends on the ligand L or L_2 and the solvent. While the BF_3 adducts **4** and **7**-**11** are stable, the analogous H^+ adducts are apparently not and extrude alkene. Similarly, the Me^+ and Ph_3PAu^+ appear unstable and give alkene extrusion.

Scheme 2



Lewis acid free complexes **3**, **5**, and **6** are active in insertion reactions. CO, Bu^tNC, and activated alkenes and alkynes insert into the Pt-O bond to give insertion products.

Oxo complex alkene reactivity. The reaction of **1** appears to be catalyzed (Fig 1).

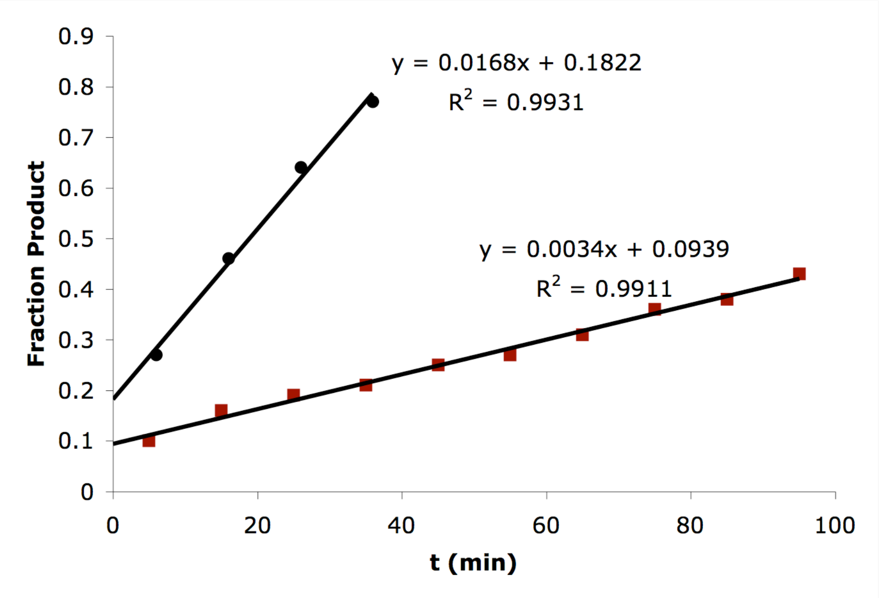


Figure 1. Plot of fraction product **1** against time for the reaction of **1** and 20 equiv NB in $MeNO_2$ at 15 °C. Red squares without additives. Black circles with 10% HBF_4.

Future Plans

We will continue our work on the platinum oxo and metallaoxetane chemistry with the goal of understanding reactivity. Kinetic studies on the reaction of **1** and alkenes in the presence of H^+ will be expanded and complimented with stoichiometric reaction studies. Reductive elimination of epoxide from the platinaoxetanes will be studied by DFT and by experiments with **2-11**.

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KC-03-04-01 **Peter C. Stair (Argonne National Lab)**
DEFG02-03ER15457 **Peter C. Stair (Northwestern University)**

Nanostructured Membrane Catalysis

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Goal

The goal of this project is to significantly advance the molecular-level control and understanding of reactions for selective catalytic oxidation of hydrocarbon molecules by the synthesis and characterization of ultra-uniform supported catalysts. The ultra-uniform support is fabricated by a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD) to produce a platform with a highly uniform pore structure and wall structure and composition. Highly uniform metal, metal-oxo, and organometallic catalytic species are introduced into the membrane pores. This approach can produce catalytic systems with exquisite control over reagent delivery, product removal, catalyst aging, reactive site sequencing, etc. The materials and catalytic chemistry are characterized by a variety of techniques including ICP, XRF, SEM, UV-Vis, FTIR, Raman, EXAFS, and XANES. Relationships between the physical and electronic properties of the catalyst material and its performance in catalytic oxidation (activity and selectivity) are studied both experimentally and computationally. This approach provides fundamental insight at the atomistic level into the catalytic properties of catalyst system.

DOE Interest

The understanding and control of reactions catalyzed on solid surfaces *at the molecular-level* is a “grand challenge” for 21st Century catalysis science. The development of fundamental understanding of structure-function relationships between catalytically active sites and the chemical reactions they catalyze that are at the heart of this challenge. This project brings together a team of university and national laboratory researchers who develop methods for the controlled design and synthesis of active catalytic sites at the atomic scale and tailored support structures at the nanometer scale, diverse spectroscopy, microscopy, and x-ray scattering techniques for detailed characterization (both ex-situ and in-situ) of catalyst structure and dynamics, elucidation of catalytic reaction mechanisms, and theory applied to catalytic processes.

Recent Progress

- ***Development of Nano-Structured Membrane Catalyst Systems***

Nanostructured membrane catalyst systems have been successfully fabricated using a combination of AAO and ALD. Electrochemical AAO reactions are controlled to produce uniform pore diameters in the range 20 to 400 nm and membrane thicknesses (pore lengths) from 0.5 to >250 µm. ALD deposits films in a layer-by-layer fashion that uses alternating, saturating reactions between gaseous precursor molecules and a substrate to produce uniform supports and catalytic species. By repeating the binary reaction sequence in an ABAB… fashion, films of micrometer thickness can be deposited with atomic layer precision to control pore diameter and wall composition. Al_2O_3, TiO_2, and Nb_2O_5 supports and V_2O_5 catalytic layers have been synthesized by ALD and studied via physical measurements and catalytic performance. A complete catalytic system, produced by embedding the AAO structure in an aluminium ring that can be mounted in a standard gas-tight fitting for catalytic reaction experiments, is shown in Fig. 1. Product analysis following a single pass of the reagents through the membrane is performed using a gas chromatograph. The product distribution from cyclohexane oxidative dehydrogenation at 480°C are shown for several preparations of vanadium oxide prepared by wet impregnation and ALD and supported on alumina, titania, and niobia.

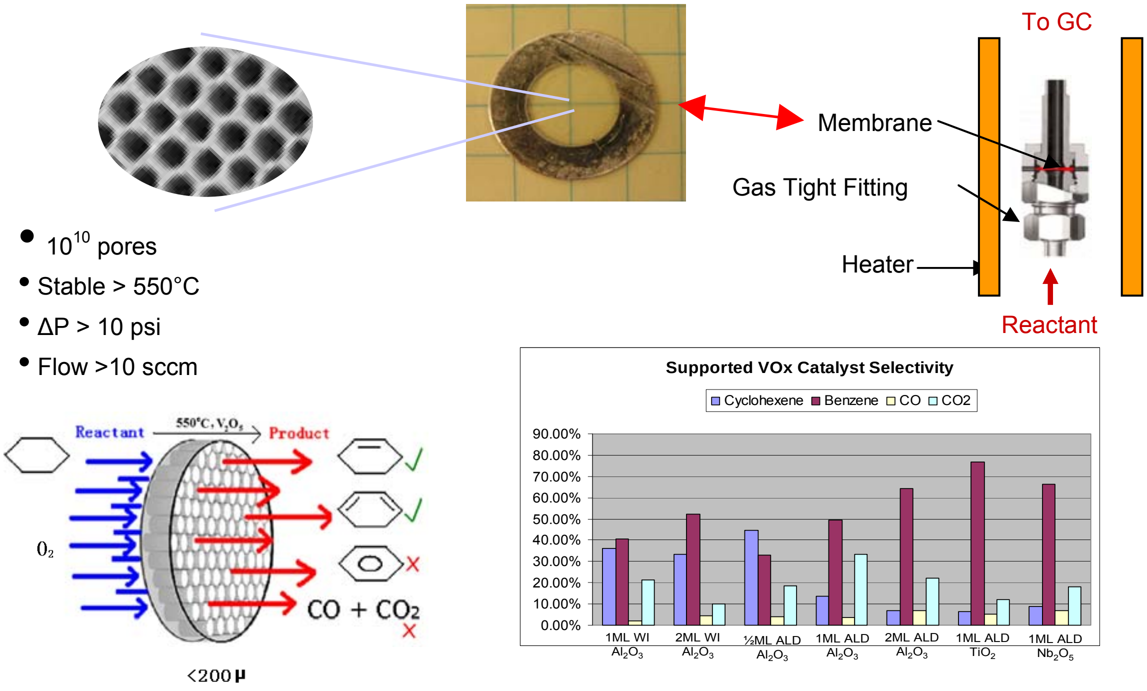

Figure 1: Nanostructured Membrane Catalytic System

- ***Enhanced Performance of Nanostructured Membrane Catalytic System***

The catalytic performance of the nanostructured membrane vanadia/alumina system was compared to the same material in powdered form for the oxidative dehydrogenation of cyclohexane. The selectivity of this reaction to cyclohexene, benzene and carbon oxides is diagnostic of the degree to which the catalyst performs C-H bond breaking and C-C bond activation, whether the formation of products beyond cyclohexene takes place in one or more than one contact with the catalyst, and whether homogeneous radical reactions are operative. From the comparison between the membrane and powder forms of the catalyst shown in Figure 2 it is evident that the membrane is superior in terms of both activity and selectivity toward the desired olefin product. Of particular interest is the low selectivity toward CO_x formation in the membrane structure at all reaction temperatures and conversions. We attribute this to the suppression of homogeneous radical reactions.

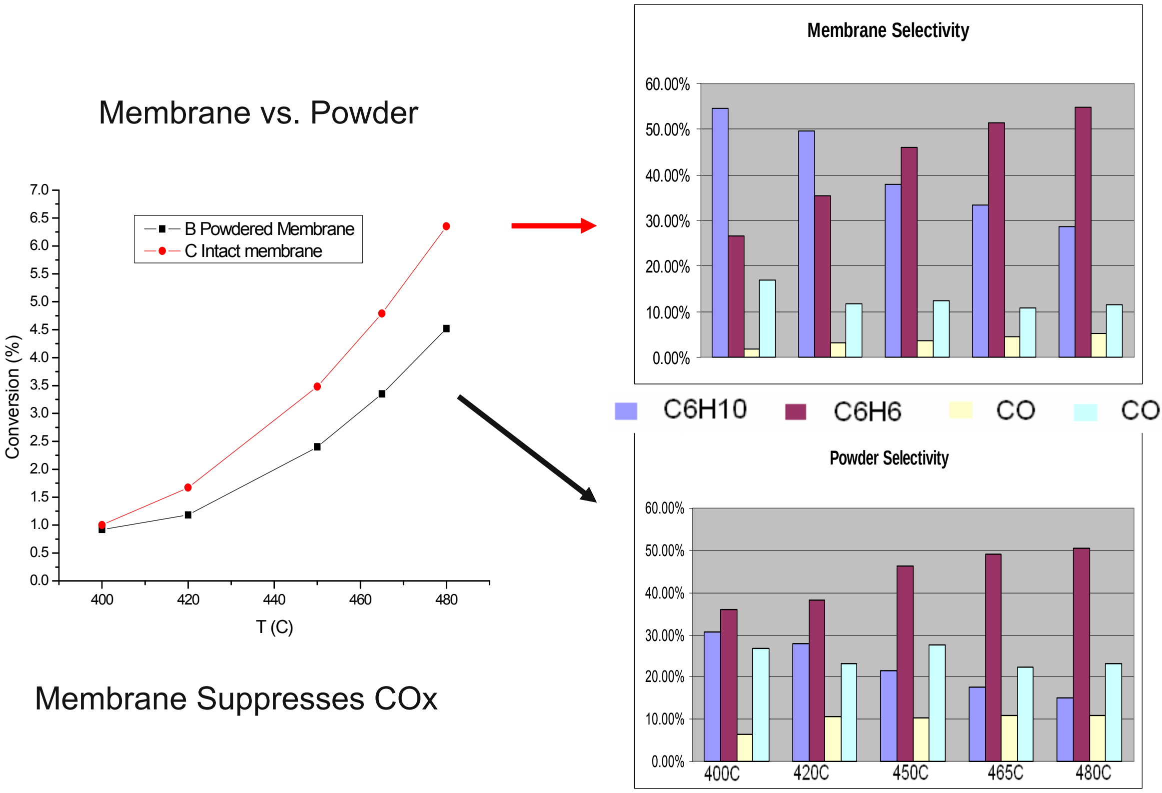

Figure 2: Comparison of membrane and powder forms of alumina-supported vanadia for the ODH of cyclohexane.

- ***Structure-Function Relationship in Cyclohexane ODH***

The dependence of catalytic cyclohexane ODH activity and selectivity on the vanadia coverage and method of deposition was studied using the nanostructured membrane catalysis system. The results are shown in Fig. 3. The activity, on a per vanadium basis (TOF), increases with vanadium loading up to approximately 1 ML coverage when ALD is used. By contrast the TOF for vanadium introduced by wet impregnation is essentially independent of loading and much lower than for the ALD method. This is due to the poor dispersion of vanadium on the support using wet impregnation compared to ALD.

The selectivity toward olefin product decreases dramatically with vanadium coverage. Careful measurements of the changes in reaction rates for cyclohexane, cyclohexene, and benzene show that this shift in selectivity for benzene vs. olefin with vanadia coverage is largely

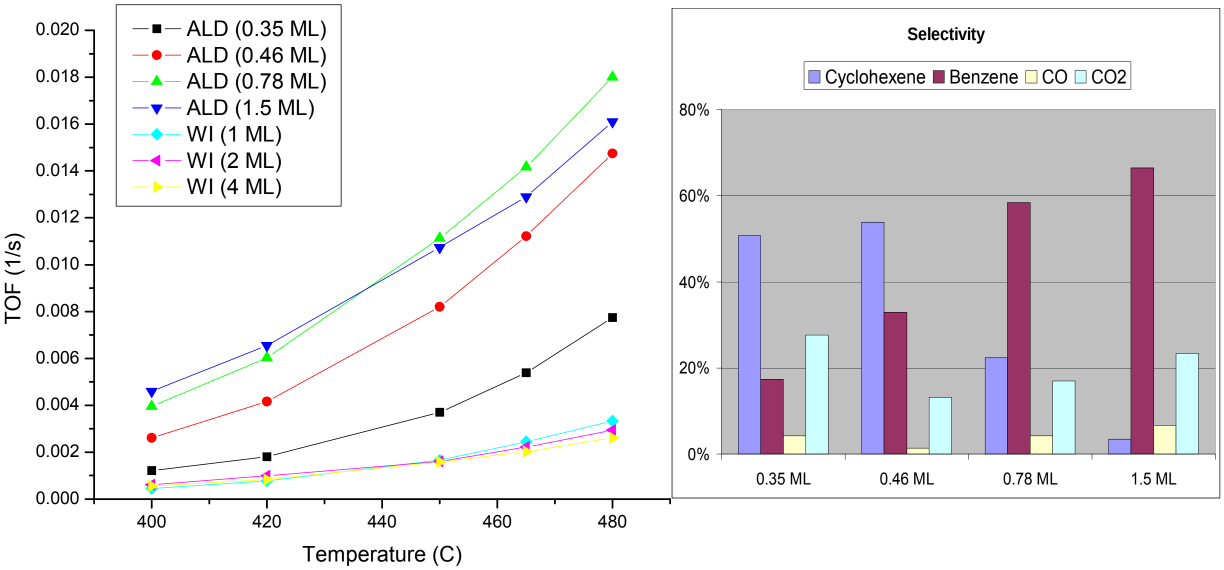

Figure 3: Catalytic performance of vanadia supported on alumina as a function of vanadia loading.

due to an increased rate of C-H bond dissociation vs. olefin desorption. We attribute these changes to the formation of vanadia clusters on the support with increasing coverage. The formation of these species is confirmed by red shifts in the measured UV-Vis absorption edge with vanadia coverage.

- ***Computational Studies of Supported Catalysts for ODH***

Computational methods of quantum chemistry were used to obtain quantitative geometrical and energetic information about vanadia sites on titania and alumina supports, which are especially difficult to probe experimentally in the sub-monolayer coverage regime. We have investigated the structure of monomeric and dimeric sites on both supports. In the case of the monomeric species, di-oxo species as well as mono-oxo species bound to the support by one, two or three V-O-M (M=Ti, Al) bridges were considered. We also considered a “molecular” monomer structure, which consist of VO_4H_3 molecules that graft onto the surface while maintaining 2 V-O-H bridges. Based on the energetics it seems likely that both the “molecular” and tridentate species are present in significant concentrations under conditions of low VO_x coverage with the concentrations dependent on the temperature. The dependence of relative free energies of monomeric species on different water partial pressures shows that species with smaller number of OH groups become more stable under dry conditions. The vibrational frequencies of the monomeric $V_xO_yH_z/Al_2O_3$ species were calculated. Calculated shifts in vanadyl stretching frequencies of the “molecular” and tridendate structures compare favorably with experimental Raman results. We have also investigated various structures for the vanadia dimer on both the Al_2O_3 and TiO_2 surfaces and found that $V_2O_7H_4$ molecules graft onto the surface while maintaining 4 V-O-H bridges to form a “molecular” structure similar to that for the monomer. Preliminary results indicate that the “molecular” species of both the dimer and monomer are catalytically active for ODH. These models for the catalytically active sites of vanadia form the basis for our computational studies of the propane ODH reaction.

Computational studies were also used to identify the structure of the amorphous alumina surface focusing on the concentration and type of hydroxyl groups, which play an important role in reactivity of the surface. Surface hydroxyl groups are primary reaction sites during ALD growth of alumina, and this is utilized in coating the pores of AAO membranes. The knowledge of the structure of hydroxylated amorphous alumina is thus crucial to better understand and control its surface properties relevant to its function as a catalytic support. The effect of hydroxylation on the surface structure of amorphous alumina was investigated using classical molecular dynamics simulations. The hydroxylated amorphous alumina surfaces have two key differences as compared to dry surfaces. First, the surfaces are found to be hydroxyl decorated with a preference for hydrogen termination. It was found that hydroxylated amorphous alumina surface is terminated by hydroxyl groups singly and doubly coordinated to aluminum atoms. Second, the subsurface Al enrichment in O-terminated, nonhydroxylated amorphous alumina surface disappears with increased loading by hydroxyl groups. Root mean square roughness calculations and density profiles across the film indicate that hydroxylated surfaces are rougher than nonhydroxylated surfaces. The power spectrum identifies different vibrational stretching frequencies for the single and double coordinated surface OH groups. Periodic DFT calculations of surface models derived from molecular dynamics results confirm these findings. The role of the surface OH groups in surface reactivity is important for both understanding of ALD growth and of anchoring catalytically active species to the support.

Future Plans

Synthesis, characterization, and evaluation of membrane nanostructures with shorter and smaller diameter pores will be conducted to investigate the influence of these properties on catalytic activity and selectivity. At a sufficiently small pore diameter, the chemical nature of catalytic layers will be influenced by curvature of the pore wall. Structures with controlled and sequenced wall compositions will be investigated, particularly to determine the influence of wall composition at the end of the pores on possible gas phase chemical reactions. Reactors designed to probe changes in flow geometry, through flow, cross flow, reflected flow, have been constructed and will be evaluated. Organometallic cluster species will be synthesized to enable the fabrication and catalytic study of supported cluster materials. The computational effort will expand the modeling to include catalytic reactions of both propane and cyclohexane.

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DE-FG02-04ER15514 **Andrzej Sygula**

Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

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Goal

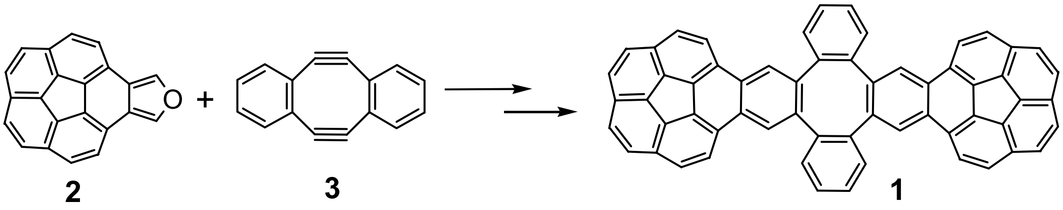
This program deals with the synthesis, structural study, and chemistry of polynuclear aromatic hydrocarbons (PAHs) with bowl-shaped carbon frameworks that can be identified on the buckminsterfullerene (C_{60}) surface. We have referred to this novel class of hydrocarbon as buckybowls.

DOE Interest

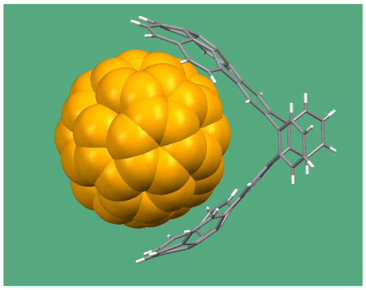
Besides the pure scientific interest in the studies of this novel class of PAHs there is also an opportunity for new applications. The potential impact from this work comes, in part, from the fact that these bowl-shaped structures may be involved in host-guest relationships that have potential for catalysis and nanodevices; they represent the end-caps of nanotubes and, as such, could serve as precursors for controlled nanotube synthesis; and they could become an environmental concern if the wide-scale use of fullerenes is ever realized due to potential fragmentation processes of the latter.

Recent Progress

Molecular Clips and Tweezers: Buckycatcher. Progress in synthetic methodologies leading to buckybowls achieved by our research group under previous DOE support allows for a construction of large, nanometric molecular assemblies with bowl-shaped subunits. We have long envisioned a potential of such systems for molecular recognition of curved surfaces of fullerenes by $\pi-\pi$ stacking of their convex faces with the concave surfaces of buckybowls. In 2003 we synthesized a potential "buckycatcher" with two corannulene moieties but we failed to find any experimental evidence for it to form an inclusion complex with buckminsterfullerene C_{60}. Recently we synthesized a hydrocarbon $C_{60}H_{28}$ (**1**) in two steps from corannulenoisofuran **2** introduced recently by our group and the known dibenzocyclooctadienediyne **3**. The central cyclooctatetraene ring orients the corannulene "pincers" in such a way that a significant cleft is formed.

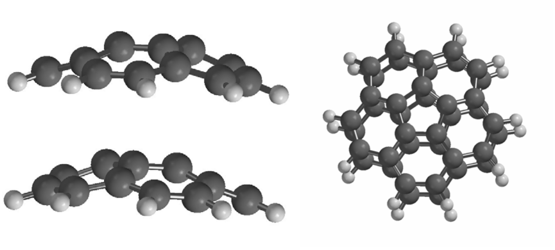


We were delighted to find that co-crystallization of **1** with buckminsterfullerene C_{60} produced an inclusion 1:1 complex which was characterized by single-crystal x-ray crystallography showing that the fullerene molecule is placed nicely in the center of a doubly concave cleft of **1** with most of the corannulene pincers carbon atoms being in van der Waals contact with the fullerene cage. A strong association of the two components was also detected in toluene solutions by NMR titration experiments. The association constant K_{as} was estimated at 8600 M^{-1} at room temperature. The formation of the complex demonstrates the importance of convex-concave interactions between buckybowls and fullerenes. The discovery, published in *J. Am. Chem. Soc.*, was announced in the "Research Highlights" sections of *Nature* (**2007**, *446*, 360), *Chem. Eng. News* (**2007**, *85*, 37) and *Nature Nanotech*. (**2007**, March 23).



More recently we determined an association constant for fullerene C_{70} and **1** in toluene-*d8* at 6500 M^{-1}. Preliminary results of x-ray crystal structure determination study indicate that C_{70} forms an inclusion complex with **1** quite similar to the C_{60} complex with the carbon cage placed between the corannulene pincers.

Theoretical Studies of π–π Stacking of Curved Carbon Networks. In collaboration with Prof. Svein Saebo (MSU) we have studied the energetics of van der Waals interactions of curved conjugated carbon surfaces in comparison with the "classic" planar aromatics. We considered the binding energies of a concave-convex corannulene dimer (**4**) with the analogous dimer in which both corannulene units are forced to be planar (**5**). Our calculations demonstrate that the interactions between curved π-systems are of comparable magnitude as for planar systems of the same size so stacking is important in supramolecular assemblies of curved aromatic systems. However, a significant part of binding energies of the bowl-shaped systems can attributed to the electrostatic dipole-dipole attraction which is absent in "planar" dimers. The interaction energy for the corannulene dimer is ca. 18 kcal/mole with an equilibrium distance of 3.6 Å at the best level of theory applied (SCS-MP2/cc-pVTZ). For the curved corannulene dimer the eclipsed conformation is preferred while a staggered conformation is preferred for the planar dimer.



side view top view

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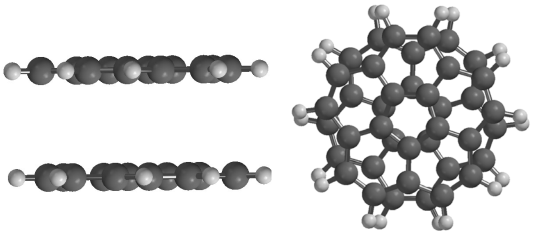

side view top view

5

Transition metal Complexes of Buckybowls. Other work, in collaboration with Prof. Robert J. Angelici at Iowa State University, produced several complexes of corannulene with Ruthenium and Osmium which were fully characterized, including x-ray crystal structure determination. These η^6 coordinated complexes are unusually stable surviving for several months in dry air. In addition we have shown that one of the complexes, $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}C_{20}H_{10})][SbF_6]_2$ is susceptible to nucleophilic attack by phosphines (PR_3). Although it was not possible to isolate products of these reactions it is evident that the $(\eta^6\text{-}C_6Me_6)Ru^{2+}$ unit does activate the corannulene to react with these nucleophiles.

Future Plans.

Molecular Clips and Tweezers: We will continue our efforts toward the synthesis of molecules with two (or more) corannulene subunits capable of molecular recognition of carbon cages. Variation of the size and shape of the molecular tether will potentially increase the specificity of molecular recognition of fullerenes with different sizes. Also, we will pursue the synthesis of "buckycatchers" with chemical anchors at the tethers to allow their binding to solid surfaces.

Synthetic Methodologies. The development of practical methods for the synthesis of buckybowls remains the main focus of our research. In particular we have been working on the synthesis of "mild" precursors for corannulyne (1,2-didehydrocorannulene) since its availability would allow for the efficient construction of large conjugated systems with corannulene subunits. Unfortunately, literature procedures which work well for simpler benzene analogs of such precursors like *o*-trimethylsilyltriflates fail with corannulene-based systems due to the chemical instability of the intermediates. Considering the importance of efficient corannulyne precursors we are determined to pursue further their synthesis.

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DE-AC02-05CH11231 **T. Don Tilley**

Molecular Precursor Methods for the Controlled Generation of Active and Selective Catalytic Sites on an Oxide Surface

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Goal

The primary goal of this project is to develop molecular chemistry that allows atomic-level and nanoscopic control over the structures of heterogeneous catalysts. Most recently, these efforts have been devoted to use of this chemistry for producing well-defined, single-site catalysts via chemical reactions on an oxide surface. Catalysts prepared in this way have been studied in selective hydrocarbon oxidations such as olefin epoxidation.

DOE Interest

This program is focused on the strategic design of novel catalysts of potential interest for the production of fuels and chemicals in an energy-efficient and environmentally acceptable fashion. Of particular interest is the development of structure-reactivity relationships via the controlled synthesis of catalytic centers, extensive characterization of catalyst structure, and evaluation of catalytic properties.

Recent Progress

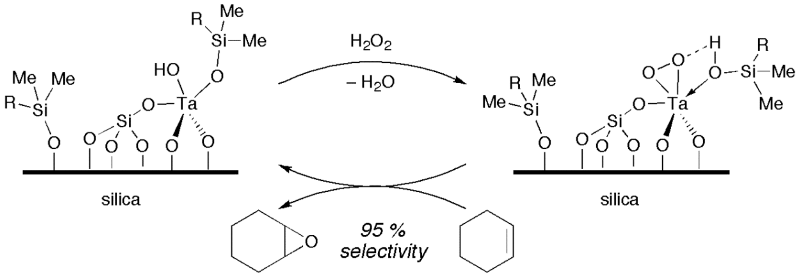
For surface-bound catalytic centers, the chemical properties of the surface play an important role in determining catalyst activity and selectivity. For example, structural and electronic properties of the surface may facilitate binding of the reactants, thereby promoting their interaction with the active sites. In addition, surface properties should influence the rate of product desorption, and such principles are well established in the mechanisms of enzyme catalysis. Thus, a general interest of our group is to investigate the role of surface functionalizations in promoting catalysis. These studies began with attempts to determine the influence of surface hydrophilicity/hydrophobicity on catalyst performance. The TMP method was used to introduce site-isolated Ti(IV) centers onto the surface of SBA15, and the resulting surface Si-OH/Ti-OH sites were modified with $Me_2N\text{-}SiMe_2R$ (R = Me, ${}^{n}Bu$, or ${}^{n}Oc$) reagents to give hydrophobic surfaces via introduction of $Si_{surf}\text{-}OSiMe_2R$ and $Ti\text{-}OSiMe_2R$ groups. This treatment produces catalysts that give significantly better performance for epoxidations with aqueous H_2O_2 (up to 58% selectivity for epoxidation of cyclohexene, vs. 12% selectivity with no treatment). In-situ FTIR and DRUV-vis spectroscopies were used to probe this phenomenon, and it was determined that active sites with capped titanol centers, $(SiO_{surface})_3Ti(OSiMe_2R)$, react with H_2O_2 to produce a hydroperoxy Ti-OOH intermediate. Overall, the results of this investigation indicate that the greater selectivity for the surface-modified catalysts are associated with the $Ti\text{-}OSiMe_2R$ siloxy group. This group may facilitate oxygen transfer from the hydroperoxy ligand to the olefin, by giving a more electrophilic metal center or by providing a strong hydrogen-bonding interaction in the intermediate.

The results described above indicated that tantalum centers on the surface of an organically modified silica might exhibit high selectivities in the epoxidation of olefins with aqueous H_2O_2. Supported Ta centers have been much less studied as oxidation catalysts than their Ti analogues, and therefore, it seemed that examination of such catalysts might probe the role of more electrophilic metal centers in efficient oxygen transfers. Modified Ta-SBA15 catalysts were prepared as described above for Ti, to give a hydrophobic surface and Ta-OSiMe$_2$R functionalities. The hydrophobicity was measured by TGA, and the modified catalysts exhibited a 10-fold decrease in water adsorption. The presence of a direct Ta-OSiMe$_2$R linkage was confirmed by ^{29}Si solid-state MAS NMR spectroscopy. DRUV-vis spectroscopy was used to compare the supported Ta centers to the molecular precursor. The absorption profiles display similar features, suggesting a similar five-coordinate Ta(V) environment for the supported sites.

These catalysts are highly selective in the epoxidation of cyclohexene with aqueous H_2O_2, and exhibit dramatically increased lifetimes. A product selectivity of >95% epoxide is observed for at least 6 h of reaction time versus 11% for the unmodified catalyst [8]. Reactivity studies indicate that the Ta-OSiMe$_2$R group plays an important role in determining this selectivity. It was further demonstrated that the modified catalysts exhibit high efficiency with respect to the utilization of H_2O_2 (>95%). The modified catalysts do not decompose H_2O_2 under reaction conditions, but the unmodified TaSBA15 catalyst decomposes 30% of the added H_2O_2 after 6 h. Due to the high selectivity for epoxide, these modified TaSBA15 catalysts are among the most productive epoxidation catalysts using aqueous H_2O_2 as the oxidant.

Radical trapping experiments indicate that oxidation by the TaSBA15 catalysts is similar to Ti catalysts in that an oxygen transfer pathway results in epoxidation, whereas radical generation results in allylic oxidation. However, oxygen transfer is greatly favored for the surface modified catalysts. DRUV-vis spectroscopy of the modified TaSBA15 materials after reaction with H_2O_2 suggests that the key intermediate involved in oxygen transfer may be a Ta(η^2-O_2) species (Scheme 1). Preliminary kinetic data for the Ta(V)-based epoxidation in a hydrophobic environment suggest a saturation profile similar to those displayed by enzymes. For example, double reciprocal plots of initial rate versus substrate concentration are linear. In addition, the reaction is first-order in Ta and the active catalytic centers appear to be single-site in nature. The kinetic data are similar to epoxidations with H_2O_2 catalyzed by the highly selective zeolite catalyst TS-1, and the mechanism proposed in Scheme 1 is supported by the observed kinetics.

Scheme 1



Future Plans

We intend to explore this system in detail and derive as much mechanistic information as possible from the kinetic data, using the most applicable kinetic models available. It is of interest to (1) characterize possible substrate binding steps in this system and (2) elucidate details of the mechanism of this epoxidation including identification of intermediates and the sequence of events at the active site. We have preliminary evidence for a Ta(V)(η^2-O_2) intermediate, and future experiments will include attempts to characterize this species by EXAFS. Additional work involving *in situ* spectroscopic methods will address the formation, stability, and reactivity of this intermediate.

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DE-FG02-07ER15895 **YuYe Tong**

An *in situ* Electrode-Potential-Controlled Nuclear Magnetic Resonance Investigation of Sulfur-Poisoning Effect on Pt-Based Mono- and Bi-metallic Nanoscale Electrocatalysts

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Goal

1. Advance significantly our fundamental understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale electrocatalyts through careful interrogation of long and short range electronic effects caused by the poisonous sulfur-metal bonding.
2. Investigate and establish correlations among the surface *d* band center, the frontier orbitals of the metal surface as represented by the surface local density of states at the Fermi level (E_f – LDOS), and the associated electrochemical reactivity.

DOE Interest

The prevailing sulfur poisoning of cathode and anode materials is a central issue that underlies the practical durability and performance of fuel cells and also determines the fuel specifications. Thus, achieving a mechanistic understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale materials that are widely used as cathode and anode in fuel cell applications is of both fundamental and practical importance. The project is using and developing further the surface ^{195}Pt and ^{13}C of chemisorbed ^{13}CO as the key complementary pair of local probes of electrode-potential-controlled nuclear magnetic resonance (NMR) spectroscopy to investigate the local (surface) electronic alternations of the Pt-based electrocatalysts, in an unprecedented detailed fashion, as functions of sulfur coverage, electrode potential, alloying element (such as Ru/Rh, Sn/Pb, Au/Ag, or other elements), and surface coordination number (particle shape). The anticipated great stride brought to bear by this project on our fundamental understanding of the sulfur poisoning will facilitate the design and development of new impurity-resistant Pt-based electrocatalysts which will in turn contribute in a significant way to the development of more sustainable and reliable fuel cells.

Recent Progress

In situ Spatially-Resolved ^{195}Pt NMR spectroscopy of PtRu Alloy Electrocatalysts: A unique spatially-resolved ^{195}Pt NMR approach has been developed [1-3]. It utilizes two unique and well-known features of the ^{195}Pt NMR of Pt nanoparticles (NPs): the spectral frequency (*f*)-geometric position (*r*) correlation and the Ruderman-Kittel-Kasuya-Yosid (RKKY) J-coupling caused oscillatory modulation (slow beat) of spin-spin relaxation. The former encodes the spatial information (*r*) in the resonance frequency (*f*) of different Pt nuclear spins located at different places in a NP. The latter exploits the sensitive distance dependence of the J coupling among the neighboring Pt spins. The technique enabled us to determine quantitatively the local Pt concentration in PtRu NPs supported on diverse carbon supports and correlate their respective electrocatalytic activity with local electronic properties.

Electocatalytic Activity of Shape-Controlled Pt NPs and Surface Enhanced Infrared Spectroscopy: The Pt NPs with different (octahedral/tetrahedral and cubic) shape and size have been synthesized [4] and their electrocatalytic activity in methanol electro-oxidation has been investigated [5]. It was found that the octahedral/tetrahedral NPs showed impressive more than 3 times higher reactivity than commercial Pt black. Initial steps towards developing in situ surface enhanced infrared spectroscopy have been initiated with the collaboration with Professor Masatoshi Osawa from Hokkaido University, Kita-ku, Sapporo, Japan.

Polyoxometalate (POM)-Stabilized Pt NPs for Oxygen Reduction Reaction (ORR): Long-term stable POM (Keggin-type silicotungstate and metatungstate) stabilized Pt NPs have been synthesized and studied for oxygen reduction reaction[6]. It has been found that the surface-bound POMs became highly active for the ORR [6].

Future Plans

Follow the timelines outlined in the proposal:

Year 1: comparative electrode-potential-dependent ^{195}Pt and ^{13}CO NMR investigations of Pt black, PtRu (1:1) black, carbon supported Pt and PtRu(1:1) with and without sulfur adsorption and deduction of the corresponding E_f–LDOS; correlations with catalytic activity analyzed and established; in situ capability of SEIR and Raman on Reinashaw spectrometer developed and deployed for the investigation of the above systems.

Year 2: comparative electrode-potential-dependent ^{195}Pt/^{13}CO NMR, SEIR, and Raman investigations of Pt-based bimetallic systems Au/Pt vs Ag/Pt and Sn/Pt vs Pb/Pt with and without sulfur adsorption and deduction of the corresponding E_f–LDOS; ^{109}Ag, ^{119}Sn, and ^{207}Pb NMR developed and deployed; correlations with catalytic activity analyzed/established and possible remedies to the sulfur poisoning proposed; expand the work of Year 1 to particle size dependent regime.

Publications (2007 – 2008)

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DE-FG02-07ER15885 **David A. Vicic**

Mild Catalytic Methods for Alkyl-Alkyl Bond Formation

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Goal

To develop new methods for alkyl and fluoroalkyl bond forming reactions based n a mechanistic understanding of the organometallic chemistry involved therein.

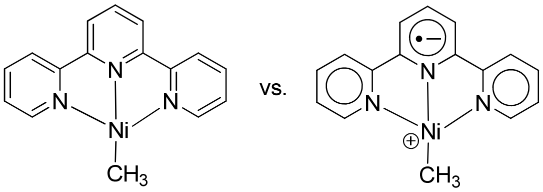
DOE Interest

Improving modern catalysts for commonly employed catalytic processes is a critical step in reducing energy expenditures. An energy efficient catalyst will enable a reaction to be carried out at room temperature conditions in a relatively short amount of time using environmentally friendly reagents. We have developed a new catalyst for a synthetically important reaction that has the potential to meet all of these criteria, and we plan to fully understand the mechanism of the reaction to enable its process feasibility. The reaction of interest involves the coupling of alkyl and fluoroalkyl groups. As many of today's materials contain fully saturated carbon-carbon linkages, it is important to develop new ways to manipulate alkyl electrophiles and alkyl nucleophiles so that new C(sp^3)-based architectures can be efficiently synthesized. The fluoroalkyl version is gaining more attention because of the ability of fluorinated oils to change interfacial and emulsion properties in liquid-liquid systems. The use of fluorinated oils has also been explored in improved hydraulic fluids, fluorinated surfactants, and even blood substitutes. Moreover, replacing functional groups in small organic molecules with the most basic fluoroalkyl moiety such as a trifluoromethyl group is becoming increasingly important in the medicinal, materials, and agricultural fields, so a mechanistic understanding of the fluoroalkyl cross-couplings can impact a number of catalytic processes.

Recent Progress

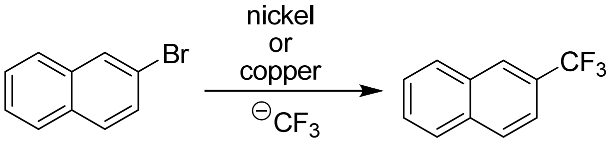
Two of our specific objectives were to 1) obtain a proper electronic description of an active catalyst for alkyl-alkyl cross-coupling reactions and 2) to determine the effect of ligand structure on the rate, scope, selectivity, and functional group compatibility of C(sp^3)-C(sp^3) cross-coupling catalysis. We have completed both of these initial objectives and established a firm base for further studies.

Some highlights include: 1) We have performed magnetic and computational studies on (terpyridine)NiMe, an active catalyst for alkyl-alkyl cross couplings, and have discovered that the unpaired electron resides heavily on the terpyridine ligand and that the proper electronic description of this nickel complex is a Ni(II)-methyl cation bound to a reduced terpyridine ligand:



2) We have also shown that alkyl halide reduction by terpyridyl nickel catalysts is substantially ligand based. 3) Isotopic labeling studies that the active catalyst (terpyridine)NiMe is not produced via a mechanism that involves the formation of methyl radicals when (TMEDA)$NiMe_2$ is used as the catalyst precursor; 4) We have performed an extensive ligand survey for the alkyl-alkyl cross-coupling reactions and have found that electronic factors only moderately influence reactivity in the terpyridine-based catalysis and that the most dramatic effects arise from steric and solubility factors; 5) We have found that the use of bis(dialkylphosphino)methanes as ligands for nickel does not produce active catalysts for cross-coupling but rather leads to bridging hydride complexes of varying geometries; 6) We have determined that the geometry of aforementioned bridging hydride complexes is largely determined by external forces such as hydrogen bonding interactions and crystal packing forces; 7) We have found that the rate of reductive elimination of alkane from a (pyridyl-2-pyrrolide)$AuMe_2$ complex is severely inhibited due to the rigid geometry of the pyridyl-2-pyrrolide ligand; 8) we have prepared, structurally characterized, and explored the reactivity of 1-adamantylzinc reagents as model nucleophiles for sterically challenging alkyl-alkyl cross-coupling reactions.

We have also been able to prepare the first example of an isolable Cu^I-CF_3 complex. Importantly, the thermal instability of previously reported *in situ*-generated "Cu^I-CF_3" and the nature of reported decomposition products demonstrated that solvated Cu^I-CF_3 is more complex (in terms of aggregation) than previously appreciated, and that control of nuclearity can have significant consequences in the ability to control fluoroalkylations. The steric bulk of the ligand in our isolable complex rigorously controls the nuclearity, even in solution, as no evidence of dimers or higher aggregates are observed by NMR spectroscopy. A structural, electrochemical, and reactivity study were part of our initial efforts to understand the many factors controlling trifluoromethylations with copper and nickel.



Future Plans

Alkyl-Alkyl Cross-Couplings: Now that mechanistic details of the nickel-catalyzed alkyl-alkyl cross-coupling reactions are emerging, more sophisticated ligands are being targeted to perform enantioselective cross-coupling reactions. These ligands not only provide a chiral environment around a metal, but also can support ligand-centered redox reactions inherent to the nickel chemistry.   The ligands developed can also support a new alpha-alkynylation procedure that could serve as an important synthetic protocol.

Fluoroalkyl Cross-Couplings: A key discovery in the copper catalyzed trifluoromethylation reactions employing the use of F_3C-$SiMe_3$ as the trifluoromethyl source suggests that a specific modification to our ligands is essential for clean reactivity. We plan to incorporate this modification into our ligands as well as understand the steric effects on the reaction to develop a catalytic process. We plan on extending the scope of our reactions to include longer fluoroalkyl chains to prepare fluorinated oils of interest. A new transmetalating agent has also been prepared that will allow us to explore a variety of metals and ligands to help identify reaction conditions that can support new perfluoroalkylations.

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Gold Metal-Catalyzed Reactions of Isocyanides and CO with Amines and Oxygen

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Abstract

Despite its generally poor catalytic properties, bulk gold metal is proficient at catalyzing reactions of isocyanides (C≡N–R) with primary amines (H_2N–R′) and O_2 to give carbodiimides (R–N=C=N–R′) at room temperature and above.[1] When secondary amines are employed, the resulting products are substituted ureas.[2] IR and kinetic studies show that both reactions occur by an initial η^1-adsorption of the isocyanide on the Au surface, which activates the isocyanide to attack by the amine. CO was also studied as an isoelectronic analogue of isocyanides. Although CO is not detectably adsorbed on bulk gold at room temperature, it undergoes reaction with primary amines and O_2 in the presence of bulk gold at 45 °C to afford isocyanates.[3] In many cases, the isocyanates subsequently convert to ureas in the presence of excess primary amine.

$$\mathrm{C{\equiv}N{-}R + H_2N{-}R' + 1/2\,O_2 \xrightarrow{Au} R{-}N{=}C{=}N{-}R' + \text{“}H_2O\text{”}}$$

$$\mathrm{C{\equiv}N{-}R + HNR_2' + O_2 \xrightarrow{Au} O{=}C(NHR)(NR_2') + \text{“}H_2O\text{”}}$$

$$\mathrm{C{\equiv}O + 2\,H_2N{-}R' + 1/2\,O_2 \xrightarrow{Au} O{=}C(NH{-}R')_2 + \text{“}H_2O\text{”}}$$

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Computational Studies of Supported Vanadia Catalysts for ODH

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Computational studies were used to investigate the structure of amorphous alumina surface focusing on the concentration and type of hydroxyl groups, which play an important role in reactivity of the surface. The effect of hydroxylation on the surface structure of amorphous alumina was studied using classical molecular dynamics simulations[1]. It was found that hydroxylated amorphous alumina surface is terminated by hydroxyl groups singly and doubly coordinated to aluminum atoms. The power spectrum identifies different vibrational stretching frequencies for the single and double coordinated surface OH groups. Periodic DFT calculations of surface models derived from molecular dynamics results confirm these findings. The knowledge of the structure of hydroxylated amorphous alumina is crucial to understand its role as a catalytic support.

Computational methods of quantum chemistry were used to obtain quantitative geometrical and energetic information about vanadia sites on titania and alumina supports, which are especially difficult to probe experimentally in the sub-monolayer coverage regime. We have investigated the structure of monomeric and dimeric sites on both supports. In the case of the monomeric species, di-oxo species as well as mono-oxo species bound to the support by either one, two or three V-O-M (M=Ti, Al) bridges were considered. We also considered a "molecular" monomer structure, which consists of a VO_4H_3 molecule that grafts onto the surface while maintaining 2 V-O-H bridges. Based on the energetics, it seems likely that the "molecular", monodentate and tridentate species are present in significant concentrations under conditions of low VO_x coverage with the concentrations dependent on the temperature. Calculated shifts in vanadyl stretching frequencies of the "molecular" and tridendate structures compare favorably with experimental Raman results for alumina [2]. These models for the catalytically active sites of vanadia form the basis for our computational studies of the propane ODH reaction. Preliminary results indicate that the "molecular" species of both the dimer and monomer are much more active for ODH than a V_2O_5 surface [3].

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