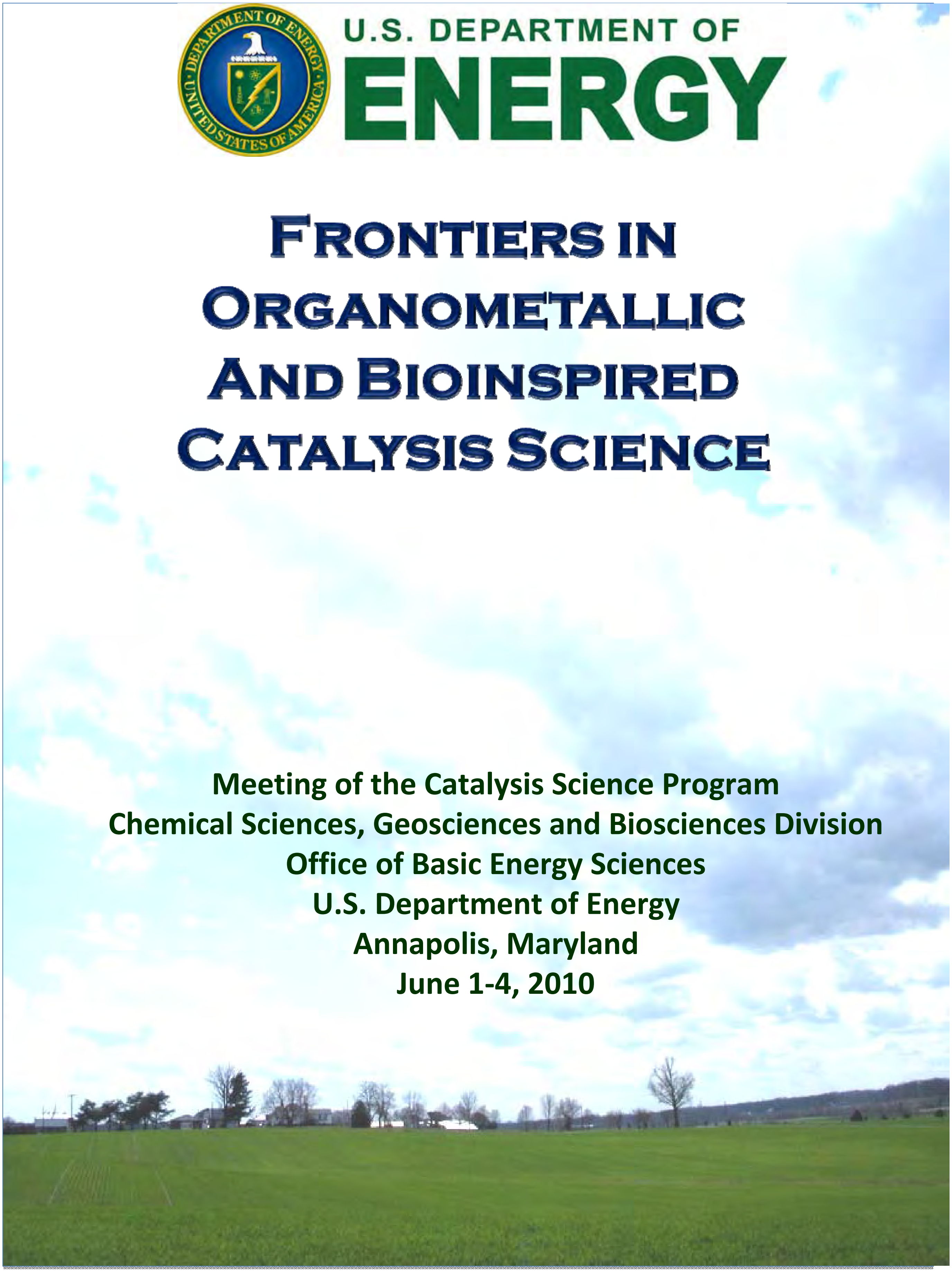
U.S. DEPARTMENT OF ENERGY



Frontiers in Organometallic And Bioinspired 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
June 1-4, 2010

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FOREWORD

The 2010 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 June 1 through June 4, 2010, at the Westin Annapolis Hotel, Annapolis, Maryland. The purposes of this meeting are to discuss the recent advances in the chemical, physical and biological bases of catalysis science, to foster exchange of ideas and cooperation among participants, and to discuss the new challenges and opportunities recently emerging in energy technologies.

Catalysis activities within OBES emphasize fundamental research aimed at initially understanding and finally controlling the chemical reactivity of matter in all its states. The long-term goal of this research is to discover fundamental principles and produce ever more insightful approaches to predict structure-reactivity relations. Such knowledge, integrated with advances in chemical and materials synthesis, *in situ* analytical instrumentation, and chemical kinetics and dynamics methods, will allow the control of chemical reactions along desired pathways. Ultimately, this new knowledge should impact the efficiency of conversion of natural resources (mass and energy) into fuels, chemicals, materials, or other forms of energy, while minimizing the impact to the environment.

Special thanks go to our invited speakers and guest junior scientists, 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 for Science and Education staff for the logistical and web support and the compilation of this volume.

Richard Kemp[1], Elena Rybak-Akimova[2] and Raul Miranda[3]
[1] University of New Mexico and Sandia National Laboratory
[2] Tufts University
[3] Office of Basic Energy Sciences - U.S. Department of Energy

MEETING OVERVIEW
2010 DOE/BES Catalysis Sciences Meeting
June 1–4, 2010 Annapolis, MD

Time	Tuesday, June 1	Wednesday, June 2	Thursday, June 3	Friday, June 4
7:00 AM		**Breakfast** Outside Senate A&B	**Breakfast** Outside Senate A&B	**Breakfast** Outside Senate A&B
8:30		**Wednesday morning session** Capitol D	**Thursday morning session** Capitol D	**Friday morning session** Capitol D
11:15				**Working lunch**
noon			**Lunch** Outside Senate A&**B**	
12:20 PM		**Lunch** Outside Senate A&**B**		
1:00		**Networking**	**Networking**	**Poster take-down** **Meeting adjourns**
3:00	**Registration/Poster setup** Outside Senate A&B (until 6:00)			
5:00	**Reception** Capitol C&D	**Dinner** Capitol B&C	**Dinner** Capitol B&C	
6:00	**Dinner** Capitol C&D			
6:15		**Wednesday evening session** Capitol D	**Thursday evening session** Capitol D	
7:00	**Tuesday evening session** Capitol C&D			
8:20		**Social hour /** **Poster session II:** **even-numbered posters** Senate A&B	**Social hour /** **Poster session III:** **all posters** Senate A&B	
8:40	**Social hour/Poster session I:** **odd-numbered posters** Senate A&B			

AGENDA

Tuesday Evening, 1 June 2010

Registration: 3:00 – 6:00 (Outside Senate A&B)
Reception: 5:00 – 6:00 (Capitol C&D)
Dinner: 6:00 – 7:00 (Capitol C&D)

Session Chair: Thomas Rauchfuss

7:00 – 7:10 Welcoming Remarks

7:10 – 7:55 **Invited Speaker:** William Tolman (U Minnesota)
Mechanistic Insights Into O_2 *and* N_2O *Activation By Copper Complexes*

7:55 – 8:40 **Invited Speaker:** Licheng Sun (Royal Inst Techn (KTH) Sweden)
Bioinspired Molecular Catalysts for Efficient Water Oxidation Driven by Visible Light and Mechanism for O-O Bond Formation

8:40 – 10:00 Social Hour / Poster Session I (Senate A&B)

Wednesday Morning, 2 June 2010

7:00 – 8:15 Breakfast (Outside Senate A&B)

Session Chair: Ayusman Sen (Capitol D)

8:30 – 9:15 **Invited Speaker:** Philip Power (UC-Davis)
Activation of Hydrogen under Ambient Conditions by Main Group Molecules

9:15 – 9:50 Dan DuBois (PNNL)
A Modular Energy-Based Approach to Molecular Catalyst Design

9:50 – 10:15 Coffee Break (Outside Senate A&B)

10:15 – 10:50 Keith Woo (Iowa State U)
Organometallic Chemistry and Catalysis on Metal Surfaces

10:50 – 11:25 John Hartwig (U Illinois)
Chemistry of Complexes with Transition Metal-Heteroatom Bonds: Novel Insertion Chemistry and X-H Bond Activation

11:25 – 12:05 Morris Bullock (PNNL) Center for Molecular Electrocatalysis; and Brent Gunnoe (Virginia) Center for Catalytic Hydrocarbon Functionalization
Overview of New Energy Frontier Research Centers

12:20 Lunch (Outside Senate A&B)

Wednesday Evening, 2 June 2010

5:00 – 6:00 Dinner (Capitol B&C)

Session Chair: Shannon Stahl (Capitol D)

6:15 – 7:00 **Invited Speaker:** Andrew Bocarsly (Princeton U)
The Electrocatalyzed Conversion of Carbon Dioxide and Water to Alcohols

7:00 – 7:35 Roy Periana (Scripps Res Inst)
Low Oxidation State Catalysts for Oxidation Reactions: Overcoming the Seeming Dilemma and Realizing the Advantages

7:35 – 7:45 Break (Outside Senate A&B)

7:45 – 8:20 **Invited Speaker:** Nancy Jackson (SNL, ACS President-Elect)
Changing Paradigms in the Chemical Sciences

8:20 – 10:00 Social Hour / Poster Session II (Senate A&B)

Thursday Morning, 3 June 2010

7:00 – 8:15 Breakfast (Outside Senate A&B)

Session Chair: Lawrence Sita (Capitol D)

8:30 – 9:15 **Invited Speaker:** Gerard van Koten (Utrecht U)
Cascade Catalysis and Homogeneous Metal Catalysts

9:15 – 9:40 Christine Thomas (Brandeis U)
Early/Late Heterobimetallic Complexes Linked by Phosphinoamide Ligands: Rational Tuning of Redox Potentials and Capacity for Small Molecule Activation

9:40 – 10:05 Wendy Shaw (PNNL)
Enhancing Hydrogen Production and Oxidation Catalysts with Proton Channels

10:05 – 10:40 Coffee Break (Outside Senate A&B)

10:40 – 11:15 Daniel Mindiola (Indiana U)
Low-Coordinate and Terminal Nitrido Complexes of Vanadium and Titanium for N-atom Transfer Chemistry

11:15 – 11:40 John Berry (U Wisconsin)
Catalytic C–H Functionalization: Synthesis of Intermediate Analogs and Tuning the Redox Properties of New Catalysts

12:00 Lunch (Outside Senate A&B)

Thursday Evening, 3 June 2010

5:00 – 6:00 Dinner (Capitol B&C)

Session Chair: Richard Finke (Capitol D)

6:15 – 7:00 **Invited Speaker:** Vincent Artero (Commissariat à l'Energie Atomique et aux Energies Renouvelables (CEA), France)
From Hydrogenase Mimics to Noble-Metal Free Hydrogen-Evolving Electrocatalytic Nanomaterials

7:00 – 7:35 Guy Bertrand (UC-Riverside)
Transition-Metal-Catalyzed Hydroamination of Non-activated Carbon-Carbon Multiple Bonds with Ammonia

7:35 – 7:45 Break (Outside Senate A&B)

7:45 – 8:20 Gerard Parkin (Columbia U)
Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

8:20 – 10:00 Social Hour / Poster Session III (Senate A&B)

Friday Morning, 4 June 2010

7:00 – 8:15 Breakfast (Outside Senate A&B)

Session Chairs: Elena Rybak-Akimova and Richard Kemp (Capitol D)

8:30 – 9:15 **Invited Speaker:** Philip Jessop (Queens U)
Persuading CO_2 *to be Useful*

9:15 – 9:50 John Bercaw (Caltech)
Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

9:50 – 10:00 Coffee Break (Outside Senate A&B)

10:00 – 10:35 Richard Kemp (U New Mexico/SNL)
Direct Partial Oxidations Using Molecular Oxygen

10:35 – 11:00 Theodore Betley (Harvard U)
New Methods for Small Molecule Activation

11:15 – 1:00 Working lunch: Future directions for the program. Discussion and conclusions.

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Poster Presentations

Abstracts from Other Investigators Funded in the Area of This Meeting

Tuesday Evening Session

Mechanistic Insights into O_2 and N_2O Activation by Copper Complexes

William B. Tolman
Department of Chemistry and Center for Metals in Biocatalysis,
University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455
email: wtolman@umn.edu

Inspired by the unusual active site structures and reactivities exhibited by copper enzymes, we seek to prepare and characterize synthetic complexes in order to test hypotheses developed to explain the novel functions of the biological sites. For example, monocopper-oxygen species[1] and multicopper-sulfur clusters[2] have been implicated as intermediates in enzymatic hydroxylation[3] and nitrous oxide reduction[4] reactions, respectively, making them attractive targets for biomimetic synthetic studies. Further impetus for study comes from the key role copper complexes play in other catalytic processes that involve activation of the 'green' oxidants O_2 and N_2O. Progress will be described toward the characterization and study of the reactivity of (a) novel copper-oxygen molecules relevant to intermediates proposed in oxidation/oxygenation catalysis, and (b) unusual copper-sulfur complexes relevant to the nitrous oxide reductase active site cluster.

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Bioinspired Molecular Catalysts for Efficient Water Oxidation Driven by Visible Light and Mechanism for O-O Bond Formation

Licheng Sun,* Lele Duan, Andreas Fischer, Yunhua Xu, Lianpeng Tong
Department of Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden
Email: lichengs@kth.se

One of the most attractive ways to solve our climate problems and to meet the increasing demanding of global sustainable energy systems is light-driven water splitting into H_2 and O_2. Inspired by the structure and function of OEC in Photosystem II (PSII), we have recently designed and synthesized a series of mononuclear as well as dinuclear Ru complexes using negatively charged ligands. These molecular Ru complexes have been demonstrated to be highly efficient catalysts towards water oxidation in homogeneous systems driven either by chemical oxidant or by visible light. The turnover number of water oxidation by some of the Ru catalysts has reached 3000. During the process of oxygen evolution, a rare seven-coordinate Ru(IV) dimer complex containing a $[HOHOH]^-$ bridging ligand has been successfully isolated as an important intermediate, indicating that water can attack directly to high valent six-coordinate Ru(IV) complex without ligand exchange. Details on the reaction mechanism for catalytic water oxidation and the O-O bond formation will be dicussed.

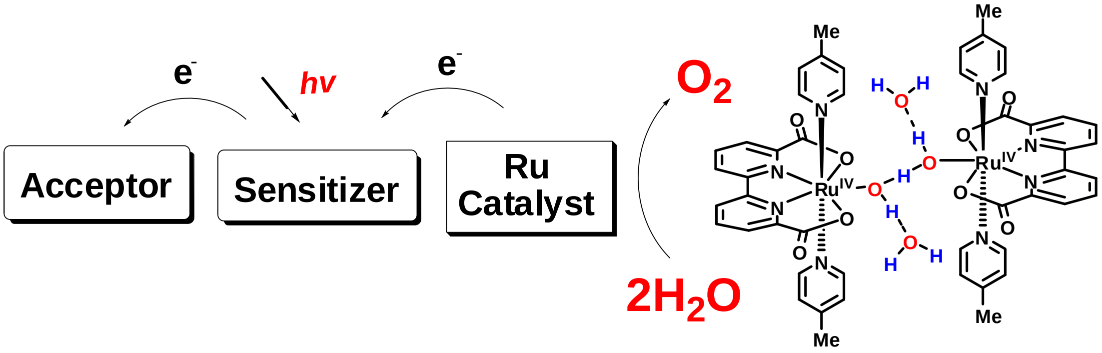

Fig. 1 Visible light driven water oxidation with a three component system in aqueous solution and the isolated intermediate with seven coordinate water molecules and hydrogen bonding network.

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2. L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **131**, 10397 (2009).
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4. L. Duan, Y. Xu, L. Sun, *Inorg. Chem.* **49**, 209 (2010).
5. J. Nyhlén, L. Duan, B. Åkermark, L. Sun, Timofei Privalov, *Angew. Chem. Int. Ed.* **49**, 1773 (2010).

Wednesday Morning Session

DE-FG02-07ER46475 **Philip P. Power**

Activation of Hydrogen Under Ambient Conditions by Main Group Molecules

Postdoc: Elke Hoppe, Xinping Wang, Owen Summerscales
Students: Yang Peng, Christopher Melton, Hao Lei
Contacts: Chemistry Department, One Shields Avenue, University of California, Davis, CA 95616: pppower@ucdavis.edu

Goal

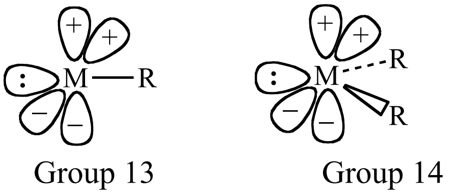
Obtain basic information on the factors that control the reaction of main group molecules with hydrogen under ambient conditions. More recently this goal has been expanded to include other small molecules such as NH_3, C_2H_4, CO or O_2.

DOE Interest

The research addresses a long-term BES-HFI objective that involves the storage and release of hydrogen under mild conditions. The proposed work seeks basic information underlying such processes in main group compounds. The main group hydrides produced by hydrogen addition can also display heightened reactivity toward unsaturated molecules such as olefins or carbon monoxide that may lead to the development of catalytic cycles based on main group metals.

Recent Progress

We have demonstrated that hydrogen reacts with several classes of main group molecules under ambient conditions to afford the corresponding hydrides [1-6,8]. These molecules are derivatives of heavier main group 13 and 14 elements that are unsaturated in some way. For example, low-valent group 13 element monomers such as :GaAr (Ar = terphenyl ligand) [4] or group 14 element carbene analogues such as :MAr_2 (M = Ge or Sn) [6] feature unoccupied p-orbitals in their valent shells plus an occupied lone pair orbital (Figure 1). These orbitals are separated by modest energies ($\leq$ ca. 4 eV, they are also highly colored) so that they can activate H_2 (and other small molecules, e.g., NH_3) in a synergic manner as shown in Figure 2. Several other main group molecules also have this property. Examples include heavier group 14 element analogues of olefins and alkynes of formula R_2MMR_2 or RMMR as well as various diradicaloids which possess "strained" geometries and resemble metal surfaces in their reactivity.



Group 13 Group 14

Figure 1. Low-valent monomeric group 13 or 14 species with donor and acceptor sites.

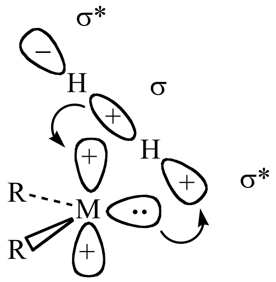
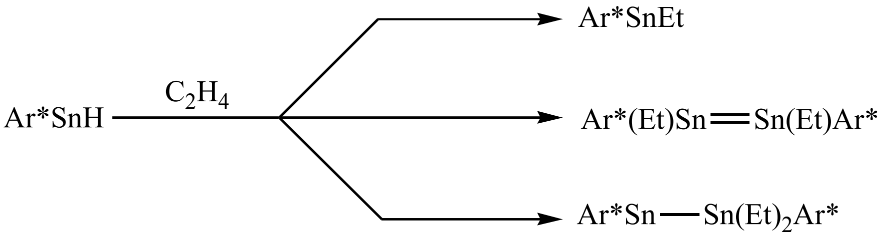


Figure 2. Illustrating the activation of H_2 by a divalent group 14 species.

The reactivity of the hydride products obtained from these reactions also exceeds that of typical hydride derivatives of these elements. For example, the addition of H_2 to ArSnSnAr (Ar = terphenyl group) molecules produces hydrides of the type ArSn(μ-H)SnAr in essentially quantitative yield [3]. The direct reaction with H_2 is the most efficient synthetic route to these hydrides. They react with a wide variety of olefins without initiators, irradiation or catalysis to afford alkyl products in quantitative yield. For example, the reaction of Ar*SnH with ethylene gives three isomeric products as shown by Scheme 1



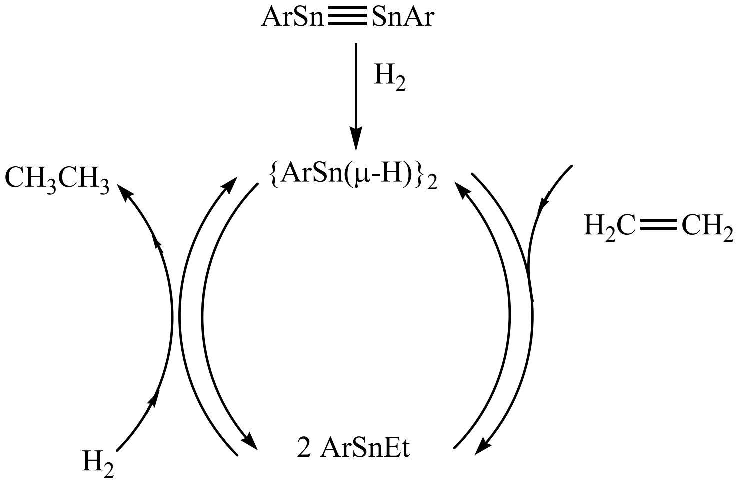
Scheme 1. Different isomeric forms of Ar*SnEt

These exist as an equilibrium mixture in solution at room temperature. Variable temperature spectroscopy and computational work show that the monomer is more stable than either of the dimeric structures by 8-9 kcal mol^{-1} [7].

We are also investigating the reactions of numerous other olefins with either tin(II) hydrides or with distannynes. These give a variety of unusual products [9] which will be discussed in the lecture.

Future Plans

The addition of hydrogen to main group molecules and the subsequent insertion of olefins into the main group element hydrogen bond represent main group versions of two key reactions in transition metal catalytic systems. A similar main group catalytic cycle can be envisioned as shown in Scheme 2.



Scheme 2. Possible hydrogenation cycle for olefins catalysed by tin(II) hydrides.

We intend to focus on demonstrating the viability of the alkane elimination step which has not yet been demonstrated. In addition, it is planned to explore a similar catalytic cycle with use of an aluminium rather than a tin system. In addition, we plan to continue to work to obtain compounds that reversibly bind hydrogen under ambient conditions.

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DE-AC05-76RLO1830 **Dan DuBois**

A Modular Energy-Based Approach to Molecular Catalyst Design

Additional PIs: Aaron M. Appel, R. Morris Bullock, James A. Franz, John C. Linehan, Wendy J. Shaw

Post-docs: Avijita Jain, John Roberts, Brian Boro, Brandon Galan

Contact: Dan DuBois, Chemical and Materials Sciences Division, Pacific Northwest NationalLaboratory, Richland, Washington 99352; daniel.dubois@pnl.gov

Goal

The goal of this project is to develop a modular energy-based approach for designing and developing molecular catalysts for the interconversion of electrical energy and chemical energy in carbon-based fuels. This modular approach involves detailed studies of first, second, and outer coordination spheres of potential catalysts. Studies of the first coordination sphere are designed to improve our understanding of such fundamental processes as M-H and MS-H bond formation and cleavage, CO_2 binding, C-O bond cleavage, and C-H bond formation and cleavage. Design of the second coordination sphere involves the incorporation of properly positioned acids/bases to enhance substrate binding, promote bond formation and cleavage, and facilitate intra- and intermolecular proton transfer reactions. Stimulus controlled catalysts are being used to delineate the role of the outer coordination sphere in catalysis and to exert control over catalyst properties such as solubility, rates, and specificity.

DOE Interest

The reactions being studied provide the catalytic basis for many energy-related transformations, including solar-driven fuel production, fuel cells, and biomass conversion. The specific reactions under investigation include CO_2 reduction, alcohol oxidation and production, formate oxidation and production, CO reduction and other closely related reactions. The modular approach being developed derives from a consideration of the interactions between the active sites of enzymes and the protein matrix in which they are embedded, with an emphasis on function rather than structure. Our research involves thermodynamic and computational studies, design and synthesis of new catalysts, kinetic and mechanistic studies, and the integration of spectroscopic and electrochemical studies to develop a greater understanding of the interactions of the substrates with multiple sites of the catalysts. This modular energy-based approach is designed to provide rational approaches to electro-driven energy conversion reactions and other energy conversion reactions identified in the report "Basic Research Needs: Catalysis for Energy" (BES Workshop, Aug. 6-8, 2007).

Recent Progress

Studies of the First Coordination Sphere. One of the goals for the design of the first coordination sphere is developing a deeper understanding of the relationship between structure and the thermodynamics properties (homolytic bond dissociation energies, pK_a values, hydride donor/acceptor abilities, and redox potentials) of selected metal systems. For example, 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 $Et_2C{=}O$. This has led to a detailed thermodynamic study of the $CpW(CO)_2(IMes)H$ system as shown on the upper left-hand side of Figure 1. Similar thermodynamic studies have also been carried out for the molybdenum sulfur complex shown on the right of Figure 1, and for $[H_2M(diphosphine)_2]^{n+}$ systems (not shown). This thermodynamic information can be used to construct free energy landscapes such as the one shown on the lower left side of Figure 1, which depicts the relative energies of all of the species shown under the specified conditions. These free energy landscapes can be used to construct reaction profiles for catalytic and stoichiometric reactions of interest, which in turn allow for the determination of how changes in catalyst structure and reaction conditions will influence the desired reactivity. We have used this approach extensively in the design of molecular electrocatalysts for H_2 oxidation and production, and we are also applying this same

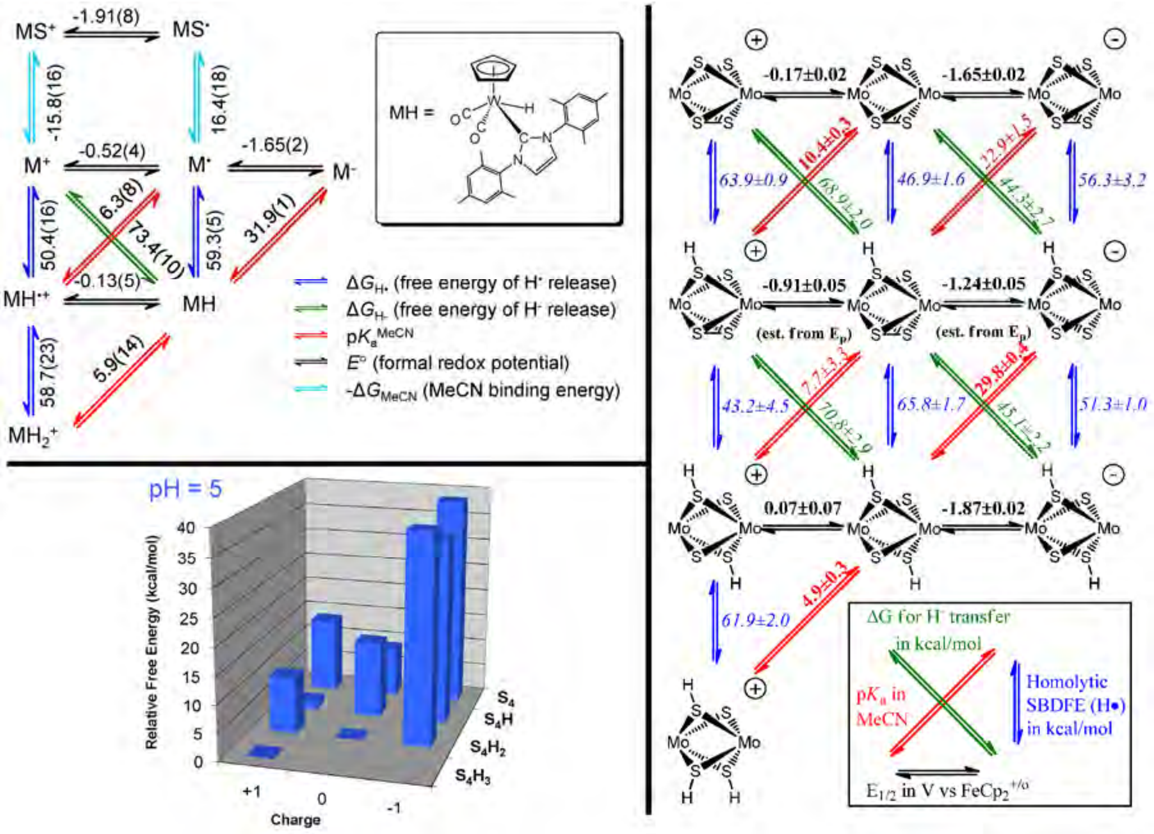

Figure 1. Thermodynamic scheme for the $CpW(CO)_2(IMes)H$ sytem (upper left) and the $[Cp^*Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ system (right). The lower left shows the free energy landscape derived at 1 atm H_2 for the Mo_2S_4 complexes.

approach to the development of electrocatalysts for CO_2 reduction, formate oxidation, and alcohol production/oxidation. These thermodynamic values can also be used to validate and evaluate different theoretical approaches for determining thermodynamic quantities.

Studies of the Second Coordination Sphere. The pendant N atom in the dithiolate bridge of the active site of [FeFe]-hydrogenase acts as a relay to facilitate the movement of protons between the distal iron atom and the proton conduction channel. This led us to undertake a series of studies of nickel, cobalt, and iron complexes with proton relays, and ultimately to the development of nickel catalysts that are very active for oxidation and production of H_2, with rates for H_2 production comparable to those for the [NiFe] hydrogenase enzymes. Incorporation of pendant bases has also been found to promote alcohol oxidation and formate oxidation. In addition, the presence of a second transition metal serving as a pendant Lewis acid promotes the rate of electocatalytic CO_2 reduction to CO.

Studies of the Outer Coordination Sphere (Stimulus-Controlled Catalysts).

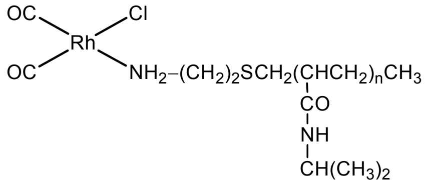

Figure 2. Stimulus-sensitive catalyst precursor, $Rh(CO)_2Cl(pNIPAAm)$.

To demonstrate the concept of using the outer coordination sphere to control catalyst activity, we have studied the product of the reaction of 4400 amu NH_2-terminated-oligo(N-isopropylacrylamide) (pNIPAAm polymer) with $[RhCl(CO)_2]_2$. The resulting complex, $Rh(CO)_2Cl(pNIPAAm)$ (shown in Figure 2), is soluble at low temperatures but precipitates above 32 ^{o}C. This abrupt solubility change is the result of a transition of the polymer from coil to globular. The catalyst structure was characterized using NMR, FTIR and XAFS. The catalytic properties of $Rh(CO)_2Cl(pNIPAAm)$ were probed by studying the hydrogenation of 3-buten-1-ol to butanol in water under 500 psi H_2 using our novel high-pressure PEEK (polyetheretherketone) cells and flow-through NMR system. At room temperature, the catalyst demonstrated 3000 turnovers per hour. At 40 ^{o}C, filtering the precipitated catalyst complex from the solution stops catalysis, and proves that the catalyst remains bound to the polymer. Moreover, redissolution of the filtered catalyst results in renewed catalyst activity, demonstrating the recoverability and reusability of the catalyst.

Future Plans

General Approach. Thermodynamic and kinetic studies of M-H and M-CO_2 bond cleavage/formation reactions for selected geometric platforms will be conducted to establish the characteristics of the first coordination sphere that control the homolytic *and* heterolytic solution bond dissociation free energies (SBDFEs) for these different platforms. Once an understanding of the energetics of the first coordination sphere is in hand, studies of the second coordination sphere will focus on the introduction of pendant bases or pendant Lewis acids in these complexes to enhance catalysis. Of particular importance will be the positioning of the pendant bases/acids with respect to the metal and substrate and matching of the energy requirements of the metal complex and the pendant base/acid to achieve the required activation of C-O and C-H bonds in the substrates. In parallel with research on the first and second coordination spheres will be investigations of the role of the outer coordination sphere in controlling catalytic reactions by the use of stimulus-responsive ligands. Initial studies in this area will focus on simple hydrogenation and hydroformylation reactions to develop the underlying principles. Once these principles have been established, incorporation of catalysts for multi-electron multi-proton processes will be undertaken.

Development of CO_2 Reduction/Formation Catalysts. We will pursue two potential pathways for CO_2 reduction, the CO pathway and the formate pathway. In the formate pathway the formation of a C-H bond is the predominant transformation that must take place. In this case we will explore the use of ligands with pendant amines to serve as proton donors/acceptors and metals capable of acting as hydride donor/acceptors to perform a concerted or stepwise transfer(s) of a hydride ligand and a proton between the complex and the substrate. An important aspect of this research is expected to be the careful matching of the hydride donor abilities of the metal and acidities of the protonated amine. Research on the CO pathway for CO_2 reduction will be guided by functional considerations suggested by the structure of the [NiFe] CO dehydrogenase enzyme. The important considerations are selective binding of CO_2 (as opposed to protonation) at the metal upon reduction of the metal center and providing an energetically accessible pathway for C-O bond cleavage. The former can be achieved by controlling the redox potentials of the catalysts, generating a metal centered radical that is stabilized more by CO_2 binding than protonation, and precisely positioning a Lewis acid in the second coordination sphere. C-O bond cleavage can be promoted by including a vacant coordination site in the first coordination sphere to facilitate water migration from C to the metal during C-O bond cleavage.

Development of Alcohol Oxidation Catalysts or Catalysts for Aldehyde/Ketone Reduction. We will use two strategies to achieve this goal. One is to use an increased understanding of the thermodynamic properties of tungsten and molybdenum dihydrogen or dihydride species studied previously by our group for ionic hydrogenations of ketones to guide the development of new catalysts capable of activating dihydrogen and sequentially transferring a proton and a hydride to a ketone or aldehyde. This will be coupled with electrochemical studies to allow extension to the development of electrocatalysts for aldehyde and ketone reduction. A second approach will involve the use of a metal hydride complex with a protonated pendant amine to transfer H_2 to a ketone, or for the reverse process, to oxidize an alcohol. This approach will be similar to a Noyori-type H_2 transfer reaction, but coupled with an electrochemical oxidation or reduction of the metal.

Studies of the Outer Coordination Sphere: Stimulus-Controlled Catalysts. Stimulus control of synthetic molecular catalysts will be achieved by attaching a catalytically active site to the peptides and polymers that are known to undergo well-defined structural changes upon application of an external stimulus. Such conformational changes are expected to result in large changes in the structure of the outer coordination sphere and in catalytic activities, providing external control of catalytic function. The changes in catalyst structure that regulate catalyst function will require the use of high pressure EXAFS studies in combination with high pressure and 2D NMR studies (up to 2000 psi) so that the catalyst function and structure can be studied under actual operating conditions.

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KC-03-02-01 L. Keith Woo

Organometallic Chemistry and Catalysis on Metal Surfaces

Graduate Student Erik Klobukowski
Postdoctoral Scholar Yibo Zhou
Contact Ames Laboratory and Department of chemistry, Iowa State University, Ames, IA 50011, kwoo@iastate.edu

Goal

The objective of this research is to gain a fundamental understanding of principles that underlie the catalytic activation of organic molecules on metal surfaces. A useful approach involves assessing how principles of organometallic chemistry may be useful guides for developing and optimizing reactions of organic molecules at metal surfaces.

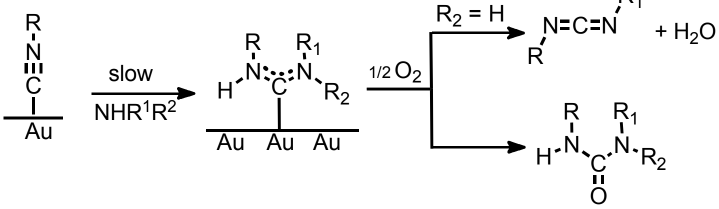
DOE Interest

Insights and advances in catalytic science provide critical means for addressing energy needs, reducing reliance on non-renewable resources, and developing sustainable approaches. Some of our current research has potential applications in providing more efficient processes for the production of important chemical feedstocks.

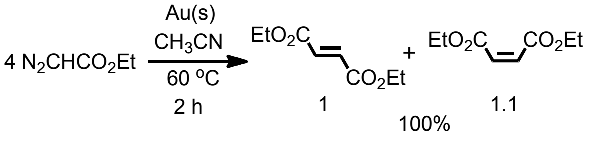
Recent Progress

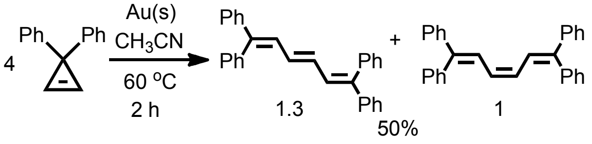
We have found that principles of homogeneous organometallic chemistry can be useful in guiding the development of catalytic processes on metal surfaces. For example, the formation of diamino carbene species on soluble gold complexes from reaction with isocyanides and amines also appears to occur at gold surfaces. As a result, micron-sized gold particles catalyze the reactions of isocyanides with primary and secondary amines under an atmosphere of O_2 to produce carbodiimides and ureas, respectively. Kinetic studies indicate that the reaction involves nucleophilic attack of the amine on an adsorbed isocyanide to form a diaminocarbene species bound to the gold surface (Scheme 1).[i] The details of the reaction with O_2 in the subsequent step have no simple precedents.

Scheme 1

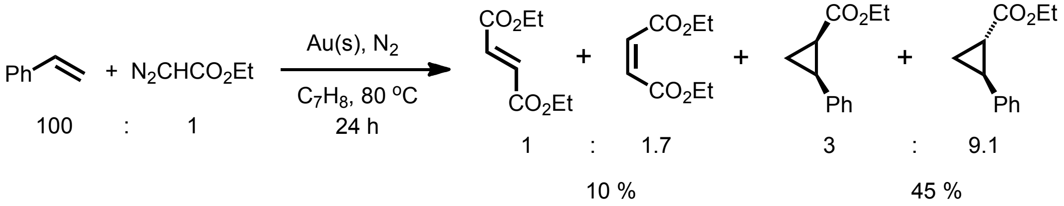


We have also found that the reactions of carbene precursors such as diazo compounds and diphenylcyclopropene produced coupled products that are consistent with the formation of reactive carbene species bound on gold.[ii] Similarly, gold powder catalyzes the cyclopropanation

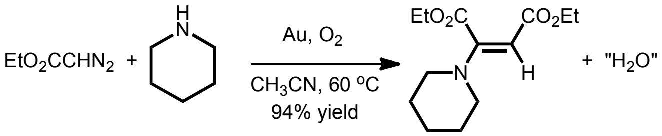




of olefins and diazo reagents in a manner analogous to well-known homogeneous processes. These results support the formation of reactive carbene species on bulk gold metal surfaces.



The chemistry of carbene precursors on gold surfaces was examined in more detail in the presence of added amines. The major products of these diazo reactions were unexpectedly enamines in good to excellent yields.[iii] These reactions are proposed to occur by initial formation of surface-bound R(H)C: carbene groups that are attacked by nucleophilic amines. The enamine products deviate substantially from those obtained in reactions catalyzed by homogeneous transition metal complexes and represent a new type of bulk gold-catalyzed reaction. Furthermore, the carbene coupling and cyclopropanation reactions of diazo reagents extend the range of bulk gold catalysis to reactions that are very different than the oxidative reactions reported previously. These results indicate that the investigation of the catalytic activity of bulk gold is producing novel results. The gold-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 unusually active and may be recycled.



Future Plans

In order to understand more fully the scope of catalysis on bulk gold and to examine potential mechanisms, we will explore a variety of additional reagents and reactions. Of particular interest are other oxidants that may be used in place of molecular oxygen. For example, alkyl hydroperoxides, peracids, iodosylbenzenes, and amine N-oxides are all readily available and easily monitored. These reagents are typically good oxygen atom transfer reagents and may favor a specific mode of reactivity.

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DE-FG02-07ER15843 **John F. Hartwig**

Chemistry of Complexes with Transition Metal-Heteroatom Bonds: Novel Insertion Chemistry and X-H Bond Activation

Postdctoral Research Associates: Zheng Huang, Jesse Tye, Jianrong Zhou
Graduate Students: Patrick Hanley, Cassaday Richers, Christo Sevov

Contacts: Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, IL 61801; jhartwig@illinois.edu

Goals

Under support of DOE, we have sought to discover new elementary reactions with which one can build new catalytic processes. During the past several years, we have been studying the chemistry needed to develop aminations of olefins and catalytic transformations of amines. In particular, we have been conducting studies to understand the factors controlling migratory insertions of alkenes into metal-amide and -alkoxo bonds and the N-H oxidative additions of amines and ammonia equivalents to the system we showed previously to add ammonia.

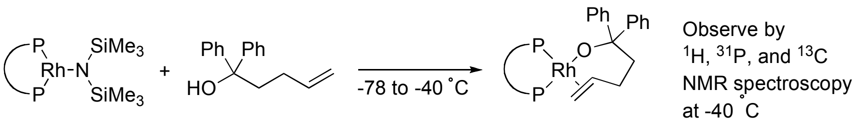
Potential Impact in Science and in Technologies of Interest to DOE

Billions of pounds of polyolefins, carboxylic acids, and aldehydes are prepared annually from alkenes by homogeneous catalysis. A large fraction of these materials are ultimately converted to amines. Thus, much energy, waste, and capital construction cost would be reduced if amines and other nitrogen containing chemicals could be prepared directly from alkenes. Unfortunately, amines and ammonia are often poisons to transition metal catalysts, and the cleavage of the N-H bond of an amine is challenging under neutral catalytic conditions because N-H bonds are only weakly acidic, and the electron pair leads to formation of Lewis acid/base adducts that are more stable than the complexes generated from N-H bond cleavage. Thus, our studies to understand the organometallic chemistry of N-H bond cleavage and reactions of amido complexes with olefins should lead to an ability to form amines directly from alkenes without the need to generate alcohols, acids, and other oxygenated compounds as intermediates.

Recent Progress

Olefin insertions into Rhodium Alkoxo Bonds

During the past year, we have focused on identifying systems that will allow an evaluation of the effect of the properties of the ancillary ligands on the rates of insertions of alkenes into rhodium-heteroatom bonds. To do so, we have studied intramolecular insertions of alkenes into rhodium-alkoxo bonds in complexes ligated by bisphosphines possessing a range of steric and electronic properties. Rhodium-alkoxido olefin complexes containing DPPF, DArPF (Ar = *p*-$CF_3C_6H_4$, *p*-$CH_3OC_6H_4$), Xantphos, DPEphos, DPPE, DPPP, DPPB, and BINAP as ancillary ligands were generated as shown in eq 9. Upon warming, products resulting from olefin insertion into the rhodium-alkoxo bond were observed (eq 10), and the rates for the insertion reactions were measured at 35 °C. The results from these studies show that reactions of complexes containing less electron-donating phosphines occur faster than those containing more electron-donating phosphines and those containing less hindered phosphines occur faster than those containing more hindered phosphines.



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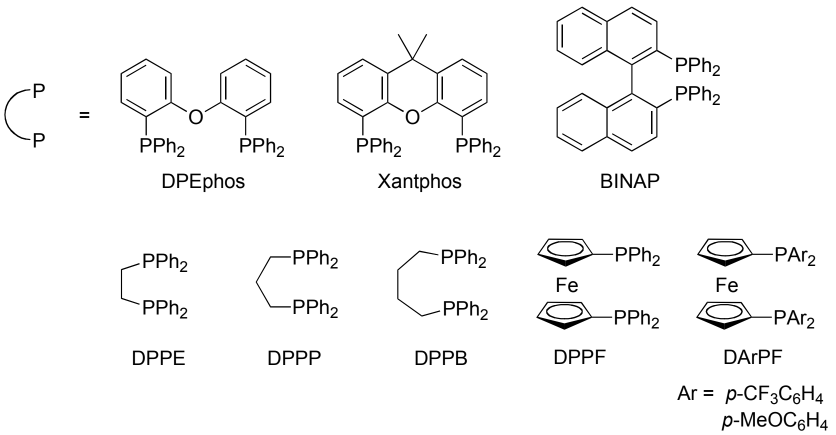

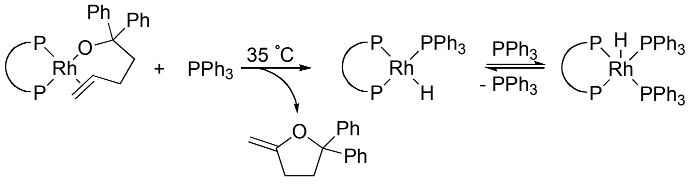

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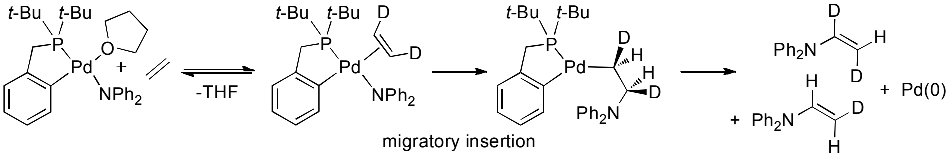
B.2. Olefin Insertions into Palladium-Amido Bonds

Unpublished computational studies by our group suggested that palladium complexes will undergo insertions of alkenes into metal-amido bonds more rapidly than the corresponding rhodium complexes, and a majority of the catalytic chemistry related to olefin insertions into amide and alkoxides has been conducted with palladium. Thus, we have sought to isolate discrete palladium-amido and -alkoxide complexes that insert alkenes to generate fundamental information about this new class of organometallic transformation.

During the past year, we prepared a series of palladium-diarylamido complexes containing a cyclometallated phosphine ligand and a coordinated THF. These complexes react with ethylene and octene to form enamine products from migratory insertion of the alkene into the metal-nitrogen bond. The mechanism of the reactions with alkenes occur by exchange of olefin for THF, as revealed by the positive order of the reaction in alkene and inverse order in the concentration of THF. A *syn*-aminopalladation that would result from migratory insertion was revealed by the stereochemistry of the enamine product resulting from reaction with *cis*-ethylene-d_2. The reactions of these amido complexes were sensitive to the electronic properties of the diarylamido group. The complex containing the more electron-donating amido ligand reacted nearly two orders of magnitude faster than the complex with the least electron-donating amido group.

Because the insertion occurs by replacement of the THF by alkene, we sought to prepare a three-coordinate arylpalladium amide lacking bound THF. Such a complex could bind alkene to form a detectable amido-olefin complex. Such a three-coordinate THF-free species was isolated from a synthesis of the amido complex in aromatic solvents. Addition of ethylene at -100 °C provided evidence for an ethylene amido species. In particular, the addition of $H_2{}^{13}C{=}{}^{13}CH_2$ to the three-coordinate amido complex at -100 °C generated a new complex with a ^{13}C NMR resonance in the range of alkenes bound to Pd(II). At -65 °C this complex reacted to form the enamine product and Pd(0), and the rate constant for this process at this temperature corresponded to a $\Delta G^{\ddagger}$ of 16 kcal/mol.



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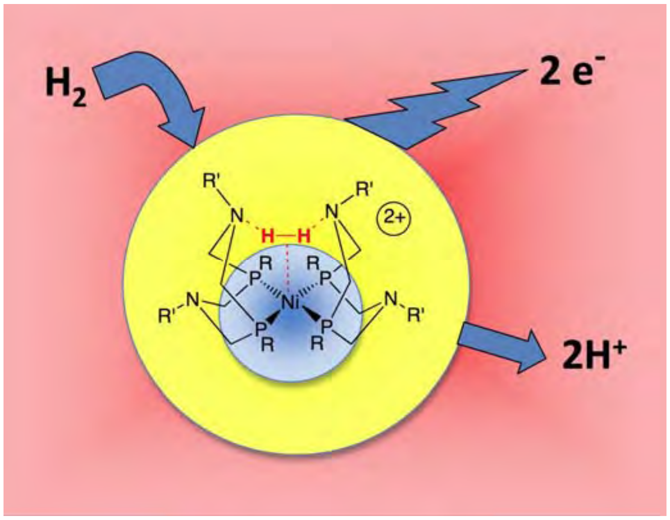
Overview of The Center for Molecular Electrocatalysis

R. Morris Bullock* and Daniel L. DuBois
Pacific Northwest National Laboratory, Richland, WA 99354
morris.bullock@pnl.gov

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a vital role in future energy storage and energy delivery systems. The Center for Molecular Electrocatalysis will address fundamental challenges in understanding how molecular electrocatalysts function, and will use this knowledge to rationally design new classes of molecular electrocatalysts. Experimental and theoretical studies include inorganic synthesis, ligand design, mechanistic studies, electrochemical measurements, determination of thermochemical values for metal hydride complexes, and evaluation of catalytic activity.

Electrocatalytic processes involving multi-proton and multi-electron redox reactions are pervasive in energy science. Our focus is on the production of hydrogen, oxidation of hydrogen, reduction of oxygen, and reduction of nitrogen. A unique approach in this Center is a focus on proton relays, which are functional groups (typically amine bases) that play a crucial role in the delivery of protons to (or from) the active site of molecular catalysts. We seek to understand, predict, and control the intra- and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes. Catalysts containing proton relays developed by researchers at PNNL exhibit activities for hydrogen production comparable to those of the NiFe hydrogenase enzymes used in Nature. The prevalence in energy science of reactions that require controlled movement of protons and electrons presages a large scope for the roles of proton relays.



$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O$$

$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3$$

The Center for Molecular Electrocatalysis was started in 2009. Michel Dupuis (PNNL) directs the theory/computational efforts. Jim Mayer (University of Washington) directs the studies on reduction of oxygen. Bruce Parkinson (University of Wyoming) oversees the electrochemical experiments, and Sharon Hammes-Schiffer (Pennsylvania State University) carries out theoretical studies on proton-coupled electron transfer.

DE-FG02-09ER16014 **T. Brent Gunnoe**

Development of Transition Metal Catalysts for the Functionalization of Carbon-Hydrogen Bonds: Fundamental Studies of Catalytic Hydroarylation of Olefins

Postdocs: Brandon Quillian
Students: Bradley McKeown, Evan Joslin, Max Friedfeld, Nicholas Foley
Collaborators: Cundari, T. R.; Petersen, J. L.
Contact: Department of Chemistry, University of Virginia, Charlottesville, VA 22904, tbg7h@virginia.edu

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 or hydroalkylation of carbon-carbon multiple bonds.

DOE Interest

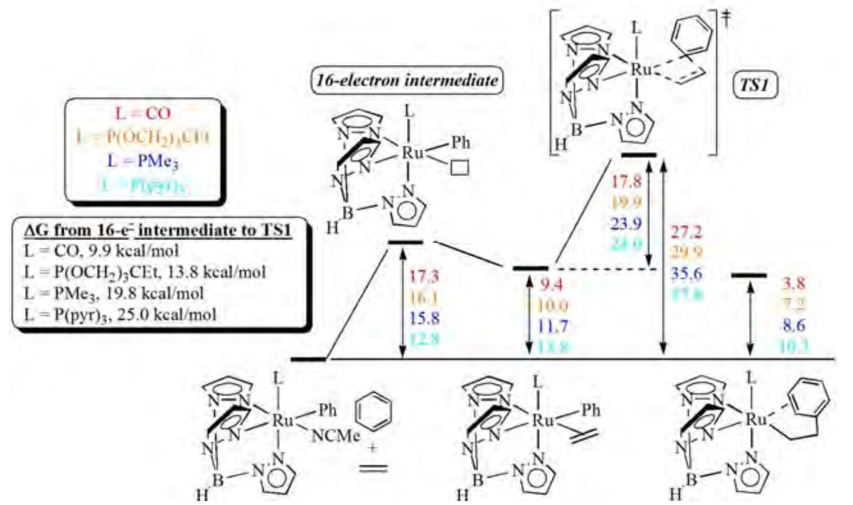
The conversion of hydrocarbons derived from fossil resources into higher value materials is a foundation of the chemical industry. Processes for primary carbon-carbon bond forming steps using basic hydrocarbon building blocks are often inefficient and energy intensive, and the development of more efficient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

Recent Progress

TpRu(L)(NCMe)Ph Catalysts. One goal of this research is to develop a detailed understanding of structure/activity relationships for catalysts that mediate the hydroarylation of olefins. In this project, we seek to understand how variation of ligand set, including steric and electronic properties, metal identity and metal oxidation state impact important reactions inside and outside the catalytic cycle. Previously, we reported that TpRu(CO)(NCMe)Ph is among the most active non-Friedel-Crafts catalysts for the hydroarylation of olefins using unactivated substrates. More recently, we studied the impact of steric and electronic profile of TpRu(L)(NCMe)Ph catalyst precursors by varying the ligand L including L = CO, $P(pyr)_3$ (pyr = *N*-pyrrolyl), $P(OCH_2)_3CEt$ and PMe_3,.

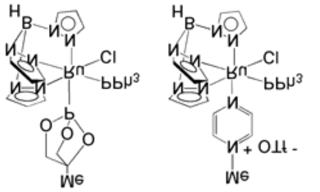
These efforts have allowed us to establish a framework to understand catalysis with the TpRu(L)(NCMe)Ph systems. *Inter alia*, the following salient points were elucidated: 1) increasing electron donor ability of L facilitates the overall rate of benzene C-H activation from TpRu(L)(NCMe)R systems with an overall $\Delta\Delta G^{\ddagger} < 1$ kcal/mol for the series of L = CO, PMe_3, $P(pyr)_3$ or $P(OCH_2)_3CEt$; 2) the mechanism of C-H activation is likely a σ-bond metathesis type reaction in which there is a Ru-H interaction in the transition state; 3) for TpRu(L)(η^2-C_2H_4)Ph complexes, the rate of olefin insertion decreases as the donor ability of L is increased with a calculated $\Delta\Delta G^{\ddagger} = 6.1$ kcal/mol between the CO and PMe_3 systems, which results in olefinic C-H activation competing with olefin hydroarylation; 4) increasing the steric profile of L can increase linear/branched ratios for catalysis with α-olefins. These studies suggest that adjusting the donor ability of L for TpRu(L)(NCMe)Ph catalysts has a more substantial impact on the rate of olefin insertion than the rate of benzene C-H activation. This prompted us to focus new catalyst design on systems that facilitate olefin insertion rather than systems that have a lower activation barrier for aromatic C-H activation.

We have used cyclic voltammetry to assess Ru(III/II) potentials for the series of TpRu(L)(NCMe)Ph systems studied to date and have found correlations between the redox potentials and important features of catalysis. We plan to exploit these relationships by preparing new catalysts based on d^6 complexes that exhibit d^5/d^6 redox potentials similar to TpRu(CO)(NCMe)Ph. For example, recently we have prepared the TpRu systems shown in Scheme 2, which will serve as precursors to pre-catalysts of the type TpRu(L)(NCMe)Ph.



Scheme 1. Calculated free energies (kcal/mol) for catalytic cycle of ethylene hydrophenylation by TpRu(L)(NCMe)Ph (□ indicates vacant coordination site).

Catalysts Based on Pyrazolyl-alkanes. Access to Ru(II) systems with charge neutral pyrazolyl alkane ligands will allow us to: a) access Ru(II) catalysts that are less electron rich than TpRu(CO)(NCMe)Ph, b) prepare cationic Ru(II) systems that match the electron density of TpRu(CO)(NCMe)Ph by incorporating phosphite or phosphine ligands, and c) explore the impact of cationic charge on catalysis. We have demonstrated that the cationic Ru(II) system [EpRu(CO)(NCMe)Ph][BAr'$_4$] (Ep = 1,1,1-tris-pyrazolylethane) catalyzes the hydrophenylation of ethylene; however, the strongly coordinated NCMe ligand and low solubility in hydrocarbon solvents dramatically limits catalyst efficiency. Recently, we have prepared a variant of the Ep ligand with a silyl ether group and coordinated the ligand to Ru. Electrochemical studies suggest that [Sp*Ru{P(OCH$_2$)$_3$CEt}Ph]$^+$ {Sp* = (^{t}Bu)Me$_2$SiOCH$_2$C(pz)$_3$; pz = pyrazolyl} should have similar electron density to {TpRu(CO)Ph}. Starting from Sp*Ru(PPh$_3$)Cl$_2$, we have prepared Sp*Ru{P(OCH$_2$)$_3$CEt}Cl$_2$, which we will use as a precursor to [Sp*Ru{P(OCH$_2$)$_3$CEt}Ph]$^+$.



Scheme 2. Systems that will be used to prepare TpRu(L)(NCMe)Ph catalysts.

Pt-based Catalysts. We have initiated studies of catalytic olefin hydroarylation using Pt(II) catalysts supported by bipyridyl (bpy) ligands. The bpy ligands provide a method to vary electron donor ability (via substitution at the 4/4'-positions) and study the impact on catalyst activity and other properties. These studies complement the ongoing efforts with Ru(II) systems and provide a comparison of

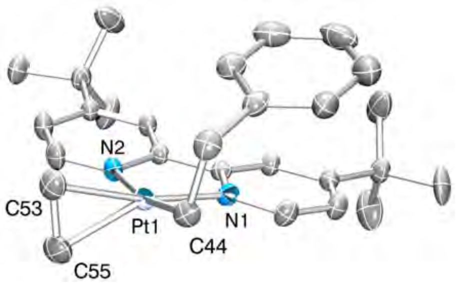


Figure 1. ORTEP of [(^{t}bpy)Pt(η^2-C_2H_4)(CH_2CH_2Ph)][BAr'$_4$], which is the proposed resting state for catalytic hydrophenylation of ethylene.

structure/activity relationship for d^6 and d^8 catalysts. We anticipated that rates of olefin insertion would be less dramatically influenced with less π-basic late transition metals, and preliminary data are consistent with the notion. The Pt(II) system $[(^t\text{bpy})\text{Pt}(\text{NC}_5\text{F}_5)\text{Ph}]^+$ (^{t}bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) is an active and relatively robust catalyst for the hydroarylation of olefins, and we have delineated several mechanistic details as well as begun to elucidate the influence of bpy donor ability by preparing $[(^x\text{bpy})\text{Pt}(\text{L})\text{Ph}]^+$ (^{x}bpy = nitro and methoxy analogs).

Future Plans

Objective 1. Determine whether TpRu(L)(NCMe)Ar {L = $[\text{NC}_4\text{H}_4\text{NR}]^+$, PF_3 or $\text{P(OCH}_2)_2\text{(O)CMe}$} catalysts exhibit similar activity and enhanced longevity relative to TpRu(CO)(NCMe)Ar systems and provide selectivity for the hydroarylation of α-olefins.

Objective 2. Determine the impact on catalysis using a Ru^{II} catalyst with reduced electron density relative to TpRu(CO)(NCMe)Ph in addition to matching the electronic structure of TpRu(CO)(NCMe)Ph with closely related cationic variants to discern the impact of cationic charge. Here, charge neutral Ru^{II} systems that possess κ^3-pyrazolyl-alkane ligands and a Ru-halide bond will serve as precursors to cationic catalysts.

Objective 3. Study catalyst precursors that possess structures outside the six-coordinate d^6 motif to determine if they exhibit similar structure/activity properties to the Ru^{II} (and related) systems and if they provide an entry into oxidative olefin hydroarylation chemistry. Here, we will initially probe catalysis with Pt^{II} and low-coordinate Ru^{II} systems (the latter systems have not been discussed herein, see publication #6 below for examples of complexes to be studied).

Publications (2008 – 2010)

1. "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)
2. "Chemistry Surrounding Group VII Complexes that Possess Poly(pyrazolyl)borate Ligands" Lail, M., Pittard, K. A., Gunnoe, T. B.* *Adv. Organomet. Chem.* **2008**, *56*, 95-153.
3. "Aromatic C-H Activation and Hydrophenylation of Ethylene by $\text{TpRu}\{\text{P(OCH}_2)_3\text{CEt}\}(\text{NCMe})\text{Ph}$" Foley, N. A., Ke, Z., Gunnoe, T. B.*, Cundari, T. R.*, Petersen, J. L. *Organometallics* **2008**, *27*, 3007-3017.
4. "Hydroarylation of Unactivated Olefins Catalyzed by Pt(II) Complexes" McKeown, B. A., Foley, N. A., Lee, J. P., Gunnoe, T. B.* *Organometallics* **2008**, *27*, 4031-4033.
5. "Chlorination of Boron on a Ruthenium Coordinated Hydridotris(pyrazolyl)borate (Tp) Ligand: A Caveat for the Use of $\text{TpRu(PPh}_3)_2\text{Cl}$" Foley, N. A., Abernethy, R. J., Gunnoe, T. B.*, Hill, A. F., Boyle, P. D., Sabat, M. *Organometallics* **2009**, *28*, 374-377.
6. "Six-, Five- and Four-Coordinate Ruthenium(II) Hydride Complexes Supported by *N*-Heterocyclic Carbene Ligands: Synthesis, Characterization, Fundamental Reactivity and Catalytic Hydrogenation of Olefins, Aldehydes and Ketones" Lee, J. P., Ke, Z., Ramírez, M. A., Gunnoe, T. B.*, Cundari, T. R.*, Boyle, P. D., Petersen, J. L. *Organometallics* **2009**, *28*, 1758-1775.
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Catalysts" Foley, N. A., Lee, J. P., Gunnoe, T. B.*, Cundari, T. R.* *Acc. Chem. Res.* **2009**, *42*, 585-597.

Wednesday Evening Session

The Electrocatalyzed Conversion of Carbon Dioxide and Water to Alcohols

Andrew B. Bocarsly
Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

Concerns about the environmental impact of rising atmospheric CO_2 concentrations have led to a variety of carbon sequestration strategies. Most approaches involve "hiding" carbon dioxide in geologic formations or photosynthetic conversion in vegetation. Much less effort has been directed toward "chemical mitigation" of CO_2. That is the transformation of carbon dioxide to into value added organics

With regard to this latter strategy, we have proposed the synthesis of simple alcohols as a target for a chemical mitigation strategy. Although the electrochemical conversion of carbon dioxide to methanol is a known process, the thermodynamically up hill nature of the process (690kJ/mole) coupled with the large activation barrier(s) associated with this 6e-/6H $^+$ reduction make conversion of CO_2 to methanol, without the further generation of CO_2 at the point of power generation, a challenging problem (1). One can consider various non-fossil fuel energy sources for this conversion; however, this only becomes possible if the presently reported system overpotentials (typically ~1V) can be reduced to several hundred millivolts. Thus, key to a successful process is the development of a stable catalytic system that is selective for the desired product(s).

We have previously reported the pyridinium catalyzed electrochemical reduction of CO_2 to methanol at certain electrodes with ~30-50% faradaic efficiency and only ~200 mV overpotential (2). At illuminated p-GaP photocathodes we find that faradaic efficiencies approach 100% and that the process can be run at a several hundred millivolts underpotential (3), allowing for the purely light driven reduction of carbon dioxide to methanol.

We have evaluated the chemistry of interest using a variety of electroanalytical techniques along with spectroscopic analysis and molecular structure/energy calculations using density functional theory (DFT) via the Gaussian 03 software package. Our electroanalytical evaluation of this reaction unambiguously indicates that the observed reduction involves a mediated charge transfer process, which is initiated by the one electron reduction of protonated pyridine (pyrH$^+$) to form a pyridyl free radical (pyrH•). It is also quite clear that this initial process is rate limiting and is followed by a surface sensitive set of reactions to produce formic acid via a carbamate type intermediate species. Once formic acid has formed, we find that a second pyrH• mediated charge transfer mechanism reduces this species to formaldehyde with close to 100% faradaic efficiency. A final set of pyrH• catalyzed reactions reduces formaldehyde to methanol. This final process is sufficiently efficient that formaldehyde can only be detected in the electrochemical reactor using mass spectroscopy. That is, what appears to be the smooth molecular catalysis of CO_2 to methanol is in fact, three highly efficient reactions, each catalyzed by the pyrH• species that stepwise produces methanol via a $CO_2 \rightarrow$formate$\rightarrow$formaldehyde$\rightarrow$methanol pathway.

Perhaps of more long term importance is the observation that certain substituted pyridines introduce the formation of carbon-carbon bonds generating predominately at this point isopropanol. The mechanism of this reaction is unknown at this point, however, it appears to follow a one-electron, free radical, path similar to that implicated for the formation of methanol.

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Low Oxidation State Catalysts for Oxidation Reactions: Overcoming the Seeming Dilemma and Realizing the Advantages

Roy A. Periana, Scripps Energy Laboratories, Scripps Research Institute, Jupiter, FL 33458
e-mail: rperiana@scripps.edu

Oxidation catalysts are typically based on the highest oxidation states of a particular metal complex, e.g., $Os^{VIII}O_4$, $Ru^{VIII}O_4$, $Mn^{VII}O_4^-$, etc. This seems consistent since the strongest "oxidants" should most efficiently catalyze "oxidation" reactions. However, this reasoning only holds if the rate determining steps in the reaction mechanisms involve reactions, such as hydrogen atom abstraction or outer-sphere electron transfer, that can correlate with redox potentials. However, since these reactions typically involve free-radicals or transition states with radical character, these types of reactions are not amenable to selective generation of primary oxidation products such as alcohols from alkanes. In this presentation, we will show that, counter intuitively, lower oxidation state catalysts are preferred for catalyzing the conversion of alkanes to alcohols. This is because such catalysts are most effective at catalyzing coordination reactions that operate by heterolytic CH bond cleavage. However, a seeming dilemma to this strategy of using lower oxidation state metal complexes to catalyze oxidation reactions is the thermodynamic instability of these catalysts in the presence of oxidants required for high yield conversion of the alkanes to alcohols. We will present strategies to overcoming this seeming dilemma

Changing Paradigms in the Chemical Sciences

Nancy B. Jackson

President-elect, American Chemical Society, 2010

Sandia National Laboratories, PO Box 5800, MS 1378, Albuquerque, NM 87185

How has the public gotten their money's worth from your research? This was the question we were asked to address by Congress when energy legislation included a request for the U.S. National Academies to study the output of catalysis research funded by the Department of Energy, Basic Energy Sciences. This talk will address some of the outcomes of that study as well as examine the potential effects that the question, when asked more frequently, could have on chemical research. Non-biomedical chemical research – such as catalysis and energy-related research - is most vulnerable to changes in public opinion. What can the American Chemical Society do? What can individual scientists do? What can universities and national laboratories do to convey the value of chemical research?

Thursday Morning Session

Cascade Catalysis and Homogeneous Metal Catalysts

Gerard van Koten and Bert Klein Gebbink

Debye Institute, Organic Chemistry and Catalysis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands (g.vankoten@chem.uu.nl)

Natures ability to compartmentalise its catalytic sites allows for multi-step reaction sequences with minimal side-product formation and minimal side effects from other catalytic sites. Active site isolation is key to the stability of enzymes, and has been particularly difficult to mimic using non-natural catalysts. Non-natural catalysts are essential for a large range of chemical transformations, which natural systems just cannot facilitate, and which homogeneous catalysts can. Homogeneous catalysts demonstrate the selectivity and activity desired for industrial fine chemical synthesis, and present trends in this field are moving towards the development of multi-step, one-pot processes where low solvent and salt waste is generated, and energy efficiency is required to produce a cost-effective end-product.[1] However, these one-pot cascade, tandem, or domino catalysed reaction sequences rely on catalyst, substrate and solvent compatibility as well as on catalyst stability and the possibility to compartamentalise the catalytic species (*e.g.* by binding these to suitable (in)soluble supports or by using stable catalysts that can catalyse different reactions[2]).

In this lecture various types of support will be discussed. Initially we explored the use of carbosilane dendrimers as chemically inert supports which had pincer-metal catalysts attached to their periphery. [3] Recent studies make use of supports which have very rigid core-shell structures.[4] The synthesis of these soluble supports with up to twelve catalytic sites at their periphery requires only a few steps. They have sizes amounting to 3.5nm. Experiments showed that these catalysts can be used in a continuous manner applying a membrane reactor (with Prof. D. Vogt, Eindhoven University) without detectable metal or ligand leaching.[4]

Most recent studies concentrate on the application of the immobilization of pincer-metal catalysts to nanosize supports via non-covalent binding.[5] In this way a number of catalytic species become linked to a nanosize support in an one-step procedure. This support can provide new properties to the catalyst, e.g. makes it water-soluble or puts the catalytic sites in a chiral surrounding.[5]

Finally, the partial inhibition of a lipase with a pincer-metal catalyst (see X-ray)[6] produced a hybrid catalyst/racemization material for the kinetic resolution of racemic alcohols.

Proof-of-principle of these approaches will be discussed and will be put in the perspective of closing the gap between homogeneous and heterogeneous catalysis and the possibility to compartimentalize homogeneous catalysts in a multicomponent catalyst system.

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Christine M. Thomas

Early/Late Heterobimetallic Complexes Linked by Phosphinoamide Ligands: Rational Tuning of Redox Potentials and Capacity for Small Molecule Activation

Graduate Students: Bennett P. Greenwood, Wen Zhou, Jonathan Wesley Napoline

Undergraduate Students: Benjamin G. Cooper '11, Vinay G. Setty '12, Daniel J. Graham '10, Vijay G. Setty '12, Usman Y. Hameedi '12, Alia H. Bluestein '10

Collaborators: Bruce M. Foxman (Brandeis)

Contacts: Brandeis University, 415 South Street, MS 015, Waltham, MA 02454; thomasc@brandeis.edu

Goal

To examine fundamental aspects of metal-metal interactions in early/late heterobimetallic complexes and ultimately utilize the nature of these interactions to access small molecule activation processes under mild conditions.

DOE Interest

Renewable energy strategies necessitate the development of catalysts that can utilize either solar (photocatalysts) or electrical (electrocatalysts) energy to transform naturally abundant small molecules into clean value-added fuels in an energy-efficient and environmentally benign manner. Towards this goal, complexes which link an early metal and a late metal are systematically being examined to assess (1) the effect of metal-metal interactions on redox behavior and (2) the ability of the highly polar metal-metal bonds in these species to facilitate σ bond activation processes such as those involved in activation of small molecule such as H_2, CO_2, and CH_4.

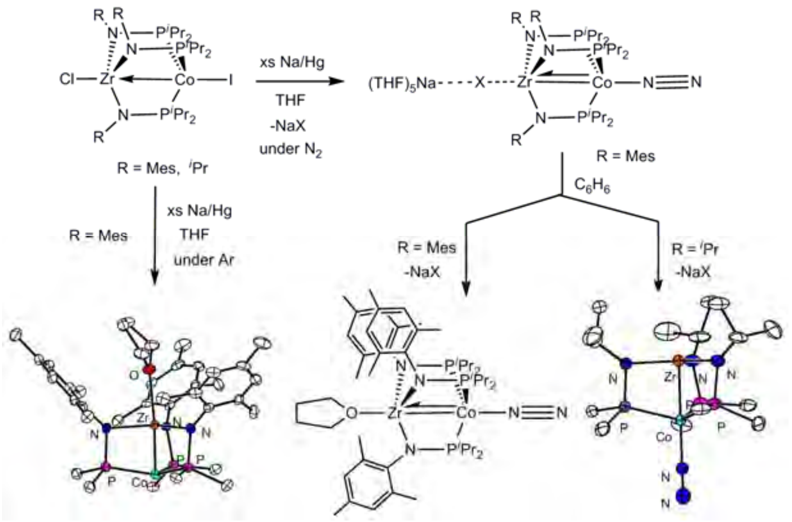
Recent Progress

Effect of Metal-Metal Bonds on Redox Potential: A series of Co/Zr heterobimetallic complexes supported by phosphinoamide ligand derivatives has been synthesized and the redox behavior of these compounds has been examined using cyclic voltammetry. It has been found that the metal-metal interaction results in a 0.8 – 1.0 V shift to milder reduction potentials as well as enhanced reversibility as compared to monometallic analogues [1].

Coordinatively Unsaturated Species Featuring Metal-Metal Multiple Bonds. Chemical reduction of these Co/Zr heterobimetallic complexes leads to highly reduced species that readily bind dinitrogen and feature metal-metal multiple bonds [2]. In addition to unusually short Co-Zr distances (2.14 Å – 2.36 Å), the dative nature of the Co→Zr bonds result in an effective *trans* influence from Co to Zr, leading to complexes featuring unusual trigonal monopyramidal coordination geometries at Co and Zr (Scheme

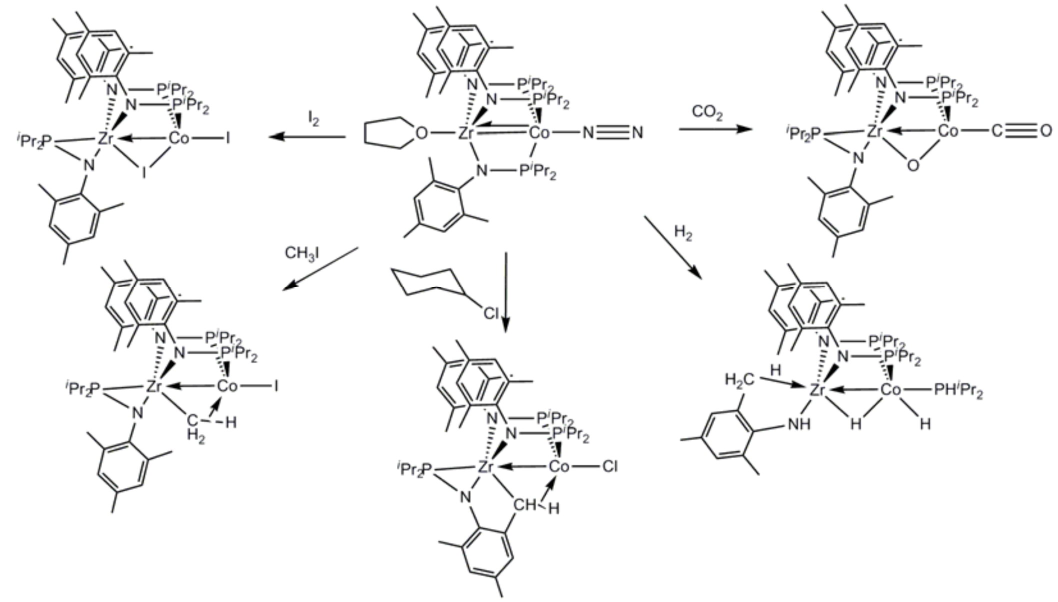
1). These complexes are primed for small molecule activation activity as a result of their (i) highly reduced and electron-rich nature, (ii) coordinative unsaturation featuring open coordination sites and/or weakly bound ligands, and (iii) highly polar metal-metal multiple bonds.

Scheme 1



Reactivity of Co/Zr Heterobimetallics Towards Small Molecules and σ Bond Activation. The reactivity of the coordinatively unsaturated, reduced heterobimetallic Co/Zr complexes is under investigation. Some preliminary results regarding the reactivity of the representative complex $(THF)Zr(MesNP^{i}Pr_2)_3Co(N_2)$ are shown in Scheme 2. Notably, it has been shown that these metal-metal multiply-bonded complexes are highly active towards the oxidative addition of X-X and C-X bonds (X = Cl, Br, I). In addition, $(THF)Zr(MesNP^{i}Pr_2)_3Co(N_2)$ reacts readily activates two molar equivalents of H_2, although this is accompanied by sacrificial cleavage of the H-H bond. In addition, the highly polar nature of the metal-metal bond in these complexes allows facile addition of CO_2 across the Co-Zr bond, leading to a terminal Co-CO and a bridging O^{2-} moiety.

Scheme 2



Future Plans

Functionalization of small molecules and catalysis. Continue examination into the reactivity of the reduced Co/Zr heterobimetallic complexes. Examine methods to incorporate sigma bond activation activity into useful catalytic cycles.

New metal-metal combinations. Expand metal-metal combinations to other areas of the periodic table, including changing Group IV early metal to Group III, Group V, or Group VI metal and changing the Co atom to Fe, Ni, Mn, or Ni.

Synthesis of N-(phosphinomethyl)amide ligands. Design new, more flexible ligands capable of accommodating a larger range of transition metals, as described above, and allowing reversible metal-metal bond formation. Such ligands are anticipated to be less sterically-encumbered and allow for more reactivity at the metal-metal bond.

Publications (2008-2010)

None have acknowledged the grant thus far.

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DE-AC05-76RL0 1830 **Wendy Shaw**

Enhancing Hydrogen Production and Oxidation Catalysts with Proton Channels

Fundamental Sciences Directorate, Pacific Northwest National Laboratory
Richland, WA 99354; wendy.shaw@pnl.gov

The objective of this research is to incorporate a rationally designed proton channel into well-studied nickel phosphine hydrogen production and oxidation catalysts for rate enhancement. Proton channels are essential for the rapid rates of proton reduction or hydrogen oxidation observed in hydrogenase enzymes, enzymes which are widely studied for their potential impact on energy and fuel storage. Small molecule catalysts are notably unable to match these rates. However, recent work has shown rate enhancements of three to four orders of magnitude for hydrogen production and oxidation catalysts by placing a fixed proton relay in the synthetic Ni-phosphine hydrogenase mimic. Based on these observations, providing a proton channel, consisting of multiple proton relays, to and from the active site may be an essential characteristic necessary to further enhance the activity of synthetic analogs. Building on these small molecule mimics, computer aided design will be used to guide the incorporation of structured peptide chains as proton channels. Synthesis and mechanistic studies, combined with more detailed computational studies will be used to provide a molecular level understanding of proton channels, revealing insights into how they can enhance homogeneous catalysts, as well as how they function in enzyme systems. In the long term, if successful, the enhanced rates afforded by the proton relay system could allow these catalysts, made of inexpensive metals, to compete with and replace expensive Pt catalysts in fuel cells.

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

Hydrosilylation Catalysts of Nickel and Carboamination of Aldimines and Alkynes with an Easy-to-Make Titanium Catalyst.

Additional PI's: Dongwhan Lee
Postdocs: Jiyoung Jung and Marlena Washington
Contact: Department of Chemistry, Indiana University, 800 E. Kirkwood Ave.,
Bloomington IN 47405; mindiola@indiana.edu

Goals

Prepare hydrosilylation catalysts for reduction of the carbonyl group using cheap transition metals such as Ni, and which also allow for expansion of the degree of functional group tolerance. We also want to explore the mechanism of a reaction that involves the carboamination of aldimines with alkynes by an easy-to-prepare titanium catalyst. Our studies in this area also expand this methodology to the formation of highly modular α,β-unsaturated imines, in particular monomers that can be readily polymerized or decorated to function as sensors for several analytes or metal ions.

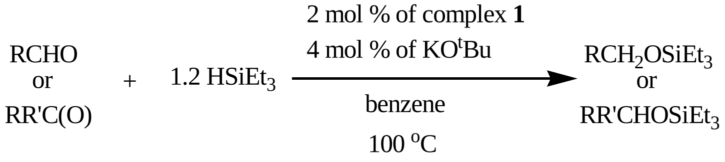
DOE Interest

The reduction of the carbonyl functionality, specifically the aldehyde and ketone groups, to alcohol via hydride transfer is an important transformation in organic synthesis. More importantly, reducing the carbonyl group followed by protection of the alcohol moiety would appeal from a synthetic standpoint if such a substrate is being used for subsequent multistep synthesis. Consequently, metal catalyzed hydrosilylation reactions constitute a practical protocol in synthetic organic chemistry because both the reduction and the protection steps are performed in a single, atom efficient fashion. Traditionally, catalytic hydrosilylation of the carbonyl functionality has been employed with precious, heavy metals ranging from Re, Rh, Ru, to Ir. Our studies focus on the use of cheap and late transition metals such as Ni and Co for hydrosilylation catalysis. We also are studying carboamination reactions promoted by easy-to-make titanium catalysts, and which allow for incorporation of unusual functional group for further transformations such as polymerization. Our studies allow for fundamental understanding of how C=N and C=C bonds are catalytically formed while C=N bonds broken but also provides an energy efficient route to novel and highly conjugated α,β-unsaturated imines. These new organic archetypes offer an excellent opportunity to study their photophysical properties and ability to detect various analytes such as CN^- or metal ions. Our route to these interesting moieties will readily establish their use for polymer formation and ion detection.

Recent Progress

Nickel Hydrosilylation Catalysts: Our group has reported a Ni(II) precursor using amino phosphine chelating ligands, $[(PN)Ni(\mu_2\text{-}Cl)]_2$ (**1**) (Scheme 1) that was capable of conducting the hydrosilylation of ketones and aldehydes, utilizing Et_3SiH as the hydride source. In these studies we

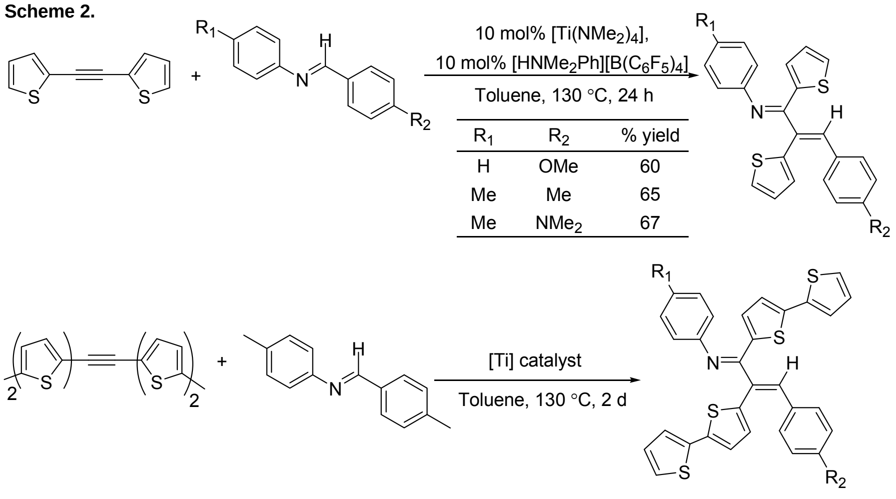
Scheme 1.



also detected a transient nickel-hydride as the active species mediating the catalytic hydrosilylation reaction, via a series of independent reactions using various hydride sources. We our now expanding this methodology to Co(II) catalysts as well as exploring Co(II) and Ni(II) boryl complexes as candidates for borylation chemistry.

Carboamination Catalysis: We discovered that protonolysis of the commercially available titanium reagent $Ti(NMe_2)_4$ with $[NHMe_2Ph][B(C_6F_5)_4]$ gives rise to a highly reactive precatalyst, $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$, useful in the carboamination of of aldimines and alkynes. Since our catalyst is an early transition metal it is tolerant to thiophene, dithiophene, and borane substituted alkynes (Scheme 2). Therefore, we can incorporate redox active sites into the α,β-unsaturated framework using a catalytic approach that can be modified readily at the aldimine or alkyne groups.

Scheme 2.



R_1	R_2	% yield
H	OMe	60
Me	Me	65
Me	NMe_2	67

Future Plans

Expand Hydrosilylation Catalysis to Co(II) and Fe(II) Complexes:

We are currently exploring Fe(II) and Co(II) complexes supported with aminophosphine ligands, N-(2-$^iPr_2$-4-methylphenyl)-2,4,6-triisopropylanilide and N-(2-$^iPr_2$-4-methylphenyl)-2,4,6-trimethylanilide as catalysts for hydrosilylation and borylation chemistry. Our goal will be to prepare Co(II) and Fe(II) complexes having a PN and a hydride ligand, and then explore their reactivity towards carbonyl containing groups as well as aromatic and aliphatic C-H bonds. Likewise, we will prepare Co(II) and Fe(II) boryl complexes in low-coordination environments.

Electropolymerization of α,β-Unsaturated Imines:

Having prepared the α,β-unsaturated imines shown in Scheme 2 we will conduct electropolymerization reaction in hopes of preparing polymeric material that can serve as sensor for analytes. Since the the α,β-unsaturated imines are highly modular we will explore imines having donor and acceptor groups since this will promote charge transfer within the organic framework.

Development of more Efficient Carboamination Catalysts:

Although we have reported a facile entry to carboamination catalysts using a combination of commercially available reagents such as $Ti(NMe_2)_4$ and $[HNMe_2Ph][B(C_6F_5)_4]$, we want to further expand this methodology to more efficient titanium(IV) and vanadium(V) catalysts that do not lose their ancillary ligands in the process of metal imide formation.

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Catalytic C–H Functionalization: Synthesis of Intermediate Analogs and Tuning the Redox Properties of New Catalysts

John F. Berry
Department of Chemistry, University of Wisconsin – Madison, Madison, WI 53706
Email: berry@chem.wisc.edu

Insertion of carbene and nitrene species into C–H bonds, catalyzed by metal-metal bonded compounds such as dirhodium tetraacetate, is a powerful synthetic method in organic chemistry. Despite the widespread use of this methodology, fundamental questions remain about the mechanism of C–H functionalization. To gain insight into proposed multiply-bonded Rh–Rh=CR_2 and Rh–Rh=NR intermediates, we present results on the synthesis, characterization, and extraordinary electronic structure of related M–M≡N nitrido compounds. Also, the synthesis and properties of new dirhodium catalysts will be presented. By utilizing redox non-innocent resorcinol-based dicarboxylate ligands, it is possible to tune the redox properties of the catalysts. This effect is used to test the hypothesis that the first step in catalyst degradation involves oxidation of the catalyst from the Rh_2^{4+} to the Rh_2^{5+} state.

Thursday Evening Session

From hydrogenase mimics to noble-metal free hydrogen-evolving electrocatalytic nanomaterials

V. Artero,* P.A. Jacques, P. D. Tran, S. Canaguier, A. Le Goff, B. Jousselme, N. Guillet, S. Palacin, M. J. Field and M. Fontecave

Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), Université Joseph Fourier (Grenoble)
and Centre National de la Recherche Scientifique (CNRS), France
e-mail: vincent.artero@cea.fr

As far as hydrogen/water interconversion is concerned, a number of technological solutions such as those developed in proton-exchange-membrane fuel-cells or electrolyzers are based on the powerful catalytic properties of platinum metal. But this scarce and expensive metal itself is not a sustainable resource and its replacement by low cost and readily available materials is a requisite for these technologies to become economically viable. A competitive alternative to platinum should be found in living micro-organisms metabolizing hydrogen thanks to hydrogenases. Catalysis in hydrogenases only requires base-metal centres (nickel and iron) and we will show how their active sites can be used as an inspiration for the design of new synthetic catalysts for hydrogen production and oxidation (1,2).

Then, we will show how the combination of such a bio-inspired approach with nanochemical tools, via the covalent attachment on carbon nanotubes of a nickel-bisdiphosphine mimic (3) of these active sites, results in a nickel-based cathode nanomaterial with remarkable performances under the strongly acidic conditions required in the expanding proton exchange membrane (PEM) technology. Hydrogen indeed evolves from aqueous sulphuric acid solution with very low overvoltages (<20 mV) and exceptional stability (> 100000 turnovers). Interestingly, this Pt-free catalyst is also very efficient for hydrogen oxidation under the same conditions with current densities similar to those observed for hydrogenase-based materials (4).

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DE-FG02-09ER16069 **Guy Bertrand**

Transition-Metal-Catalyzed Hydroamination of Non-Activated Carbon-Carbon Multiple Bonds with Ammonia

Postdocs: Rei Kinjo (50%) and Jean Bouffard (50%)
Student: Gael Ung
Contacts: University of California, Riverside, CA 92521-0403; guy.bertrand@ucr.edu

Goal

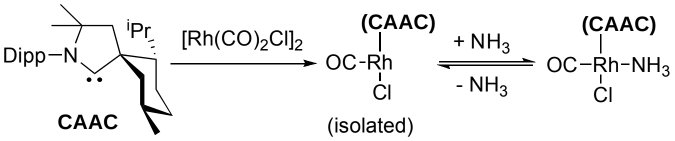
The development of efficient homogeneous catalysts allowing for the Markovnikov and anti-Markovnikov hydroamination of unactivated carbon-carbon multiple bonds with ammonia.

DOE Interest

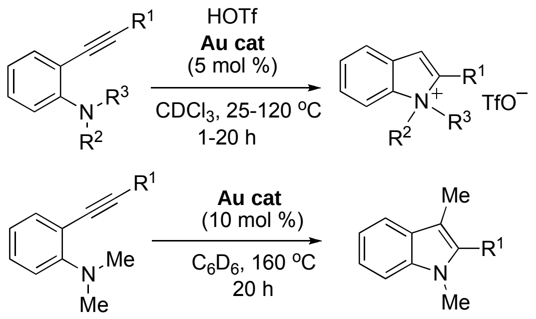
Nitrogen-carbon bonds are ubiquitous in products ranging from chemical feedstock to pharmaceuticals. Consequently, the so-called hydroamination reaction, the addition of an N-H bond across a carbon-carbon multiple bond, a process, which ideally occurs with 100% atom economy, has been widely studied. Various catalysts have been found to promote this chemical transformation, although many limitations still remain; one of the most prominent is the use of NH_3 as the amine partner. In fact, the utilization of ammonia in catalytic olefin hydroamination was listed among the ten greatest challenges for catalytic chemistry over a decade ago, and it remains unsolved today. More broadly speaking, apart from a few heterogeneous processes, examples of transition metal catalyzed functionalization of NH_3 are rare. The importance of these challenges is readily understandable since more than 100 million metric tons of NH_3 are produced per year, and the production of amines is similarly huge.

Recent Progress

Transition metals, which can activate amines, usually react with ammonia to afford inert Lewis acid-base complexes. We have shown that cyclic (alkyl)(amino)carbenes (CAACs) prevent the coordinative saturation of gold(I) centers by NH_3, but also make the coordination of NH_3 to rhodium reversible. We have already shown that CAAC gold complexes indeed catalyze the Markovnikov addition of ammonia to non-activated alkynes and allenes, giving rise to important nitrogen derivatives such as primary enamines, imines, allyl amines, and amines. These reactions constitute an ideal initial step for the preparation of simple bulk chemicals, as well as rather complex molecules, as we have already shown by the synthesis of a variety of heterocycles.



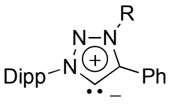
During the course of our mechanistic studies of the gold catalyzed hydroamination reaction, we discovered serendipitously two novel catalytic reactions, namely the hydroammoniumation and methylamination of alkynes [1]. We have briefly explored the scope of the hydroammoniumation reaction, and found that aryl and alkyl groups are



tolerated on the alkyne, and that the cyclization process occurs under milder conditions when a weaker basic amine was used. For the methylamination reaction, using 10 mol% of a 1/1 mixture of (CAAC)AuCl/KB(C_6F_5)$_4$, 2-alkynyl-N,N'-dimethyl-benzenamines are transformed into 2,3-disubstituted indoles in good to excellent yields after 20 h at 160 °C. This rearrangement tolerates aryl, as well as alkyl substituents on the alkyne.

It is important to note that most the reactions described above are performed at high temperature (up to 200 oC). This is a good indication of the very high thermal stability of our catalysts. We believe that this is due to the strong σ-donor properties of CAACs. Moreover, these complexes are not very sensitive to moisture, and have proven remarkably resistant to oxidation. This is largely due to the presence of strong carbon-metal bonds, and therefore other types of carbon-based L ligands are highly desirable.

We have recently found a new family that we named “mesoionic carbenes (MICs)”[2,3], since no reasonable canonical resonance forms showing a carbene can be drawn without additional charges. Importantly, these species are readily available, and can be prepared in large quantities. 1,2,3-Triazoles were obtained in up to 83% yield by the Cucatalyzed alkyne-azide cycloaddition of aryl azide and arylacetylene (CuAAC, "click chemistry"). The preparation and purification of aryl azides can be cumbersome, and present safety risks when performed on large scale. Therefore, the one-pot conversion of aniline to the desired aryl azide, followed by in-situ CuAAC was found to be especially convenient for the synthesis of MIC precursors. Alkylation with methyl or isopropyl trifluoromethanesulfonate afforded the corresponding triazolium salts in moderate to excellent yields. A simple deprotonation with either potassium bis(trimethylsilyl)amide or even potassium *tert*-butoxide in an ethereal solvent affords the corresponding MICs as very stable compounds.



MIC

MICs possess an ensemble of properties that portend to their utility. The synthesis of their precursors is short and efficient from readily available starting materials, yet modular and thus amenable to a wide variety of potential analogues. The lack of a dimerization pathway is predicted to allow for the preparation of comparatively unhindered MICs. We have already found that their donor properties are greater than those of NHCs and therefore good candidates as ligands for NH_3-hydroamination catalysts.

Future Plans

Having in hand a variety of carbon based L ligands, we plan to prepare both gold and rhodium complexes and to test their catalytic activity for the hydroamination of alkynes and allenes, but also of alkenes. Moreover, beside NH_3, we will test the hydroamination reaction using hydrazine, another difficult case. In fact, we have already preliminary results, which indicate that CAAC gold complexes are active in the presence of H_2NNH_2.

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

Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

Students: Guang Zhu, Keliang Pang, Daniela Buccella, Aaron Sattler, Wesley Sattler
Contact: Department of Chemistry, Columbia University, New York, NY 10027;
parkin@columbia.edu.

Goals

The specific objectives and research goals of the research performed during the present grant period 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 include: *(i)* coordination chemistry of molybdenum relevant to hydrodenitrogenation, *(ii)* cleavage of a C–C bonds of aromatic ring systems, and *(iii)* the conversion of transition metal carbonyl complexes into isocyanide compounds that have applications as catalysts for organic transformations.

Research Plan and Progress

1. Mechanisms Pertinent to Hydrodenitrogenation: Ring Fusion Promotes Access to η^4-Coordination, Oxidative Addition of Dihydrogen and Hydrogenation of Aromatic Nitrogen Compounds

Hydrodenitrogenation (HDN) is the important industrial process by which nitrogen containing impurities are removed from crude petroleum feedstocks and fuels. Although HDN is typically performed by using molybdenum based catalysts, the coordination chemistry of molybdenum relevant to HDN has not yet been established. Therefore, we have initiated a series of studies to define the coordination mode preferences of molybdenum with heterocyclic aromatic nitrogen compounds. For example, we have demonstrated that $Mo(PMe_3)_6$ reacts with phenazine (PhzH) to give $(\eta^6\text{-}C_6\text{-PhzH})Mo(PMe_3)_3$, $(\mu\text{-}\eta^6,\eta^6\text{-PhzH})[Mo(PMe_3)_3]_2$ and $(\eta^4\text{-}C_4\text{-PhzH})_2Mo(PMe_3)_2$, each of which displays previously unknown coordination modes for phenazine. A comparison of $(\eta^6\text{-}C_6\text{-PhzH})Mo(PMe_3)_3$ with the anthracene (AnH) and acridine (AcrH) counterparts, $(\eta^6\text{-AnH})Mo(PMe_3)_3$ and $(\eta^6\text{-}C_6\text{-AcrH})Mo(PMe_3)_3$, indicates that oxidative addition of H_2 is promoted by incorporation of nitrogen substituents into the central ring. Furthermore, comparison of $(\eta^6\text{-}C_6\text{-PhzH})Mo(PMe_3)_3$ with the quinoxaline (QoxH) analogue, $(\eta^6\text{–}C_6\text{–QoxH})Mo(PMe_3)_3$, indicates that ring fusion also promotes oxidative addition of H_2. Comparison of the mononitrogen quinoline (QH) and acridine compounds, $(\eta^6\text{-}C_6\text{-QH})Mo(PMe_3)_3$ and $(\eta^6\text{-}C_6\text{-AcrH})Mo(PMe_3)_3$, which respectively possess two and three fused six-membered rings, exhibit a similar trend, with the former being inert towards H_2, while the latter reacts rapidly to yield $(\eta^4\text{-}C_4\text{-AcrH})Mo(PMe_3)_3H_2$. Ring fusion also promotes hydrogenation of the heterocyclic ligand, with $(\eta^6\text{-}C_6\text{-AcrH})Mo(PMe_3)_3$ releasing 9,10-dihydroacridine upon treatment with H_2 in benzene at 95˚C. Furthermore, catalytic hydrogenation of acridine to a mixture of 9,10-dihydroacridine and 1,2,3,4-tetrahydroacridine may be achieved by treatment of $(\eta^6\text{-}C_6\text{-AcrH})Mo(PMe_3)_3$ with acridine and H_2 at 95˚C.

2. Carbon–Carbon Bond Cleavage of an Unstrained Aromatic Ring

Of considerable interest, we have also discovered that the tungsten complex $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ cleaves an aromatic C–C bond of quinoxaline, a transformation that is of considerable significance in view of the general difficulties associated with breaking C–C bonds by oxidative addition. The cleavage is accompanied by dehydrogenation, thereby resulting in the overall conversion of quinoxaline to an *ortho*-di(isocyanide)benzene derivative, namely $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$. The chelate ring that results from insertion of tungsten into the aromatic nucleus contains only 7 atoms, a ring size that is unprecedented for chelating isocyanide compounds, which otherwise typically possess large ($\geq$ 12 member) rings due to the tendency of the M–C–N–R motif to adopt linear geometries. The ability to isolate a chelating isocyanide compound with a 7-membered ring may be attributed to the fact that its mechanism of formation involves insertion of the tungsten center into the aromatic nucleus. Similar insertion reactions are also observed for the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 6-methylquinoxaline and 6,7-dimethylquinoxaline.

3. Synthesis of Transition Metal Isocyanide Compounds from Carbonyl Complexes

The ability to tune the steric and electronic properties of isocyanide ligands (RNC) by modifying the substituent on nitrogen has been of considerable benefit in the application of transition metal–isocyanide complexes as catalysts for organic transformations. Despite their widespread use, however, the majority of transition metal isocyanide complexes feature rather simple substituents on nitrogen, a reflection of the paucity of readily available commercial isocyanide compounds. The development of the catalytic applications of transition metal isocyanide compounds would be facilitated by new synthetic methods that do not require the use of the isocyanide as a reagent and, in this regard, we have discovered a straightforward method to convert a carbonyl compounds into its isocyanide counterpart.

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, carbon–carbon bond cleavage and new methods of synthesizing transition metal catalysts for organic syntheses.

Future Plans

Future studies will focus on *(i)* establishing details concerned with the reactivity of molybdenum and tungsten compounds towards heterocyclic sulfur and oxygen compounds with respect to determining mechanisms of hydrodesulfurization and hydrodeoxygenation, *(ii)* establishing the mechanism of the C–C bond cleavage reaction of quinoxaline by performing a computational analysis, and *(iii)* evaluating catalytic applications of transition metal complexes with chiral isocyanide ligands synthesized from achiral carbonyl complexes.

Publications (2008 – 2010)

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7. “Temperature Dependent Transitions Between Normal and Inverse Isotope Effects Pertaining to the Interaction of H–H and C–H Bonds with Transition Metal Centers.” Gerard Parkin *Acc. Chem. Res.* **2009**, *42*, 315-325.
8. “Multiple Modes for Coordination of Phenazine to Molybdenum: Ring Fusion Promotes Access to η^4-Coordination, Oxidative Addition of Dihydrogen and Hydrogenation of Aromatic Nitrogen Compounds.” Aaron Sattler, Guang Zhu, and Gerard Parkin *J. Am. Chem. Soc.* **2009**, *131*, 7828-7838.
9. “Synthesis of Transition Metal Isocyanide Compounds from Carbonyl Complexes *via* Reaction with $Li[Me_3SiNR]$.” Wesley Sattler and Gerard Parkin *Chem. Commun.* **2009**, 7566-7568.
10. “Cleaving Carbon–Carbon Bonds by Inserting Tungsten into Unstrained Aromatic Rings.” Aaron Sattler and Gerard Parkin *Nature* **2010**, *463*, 523-526.
11. “Metal–Metal Bonding in Bridging Hydride and Alkyl Compounds.” Gerard Parkin *Structure and Bonding* **2010**, *136*, 113-145.

Friday Morning Session

Persuading CO_2 to be Useful

P. G. Jessop
Queen's University, Department of Chemistry, Kingston, Ontario, Canada, K7L 3N6.
e-mail: jessop@chem.queensu.ca

Carbon dioxide, which is famous as an environmentally-problematic waste product, can be used to help chemical reactions and processing in economically and environmentally sensible ways. This presentation will describe recent research on the use of reactions of CO_2 for making value-added products and for facilitating separations. These two topics illustrate two divergent strategies for making use of this waste gas; is it better to permanently fix the CO_2 so that the carbon atom ends up in the product molecule, or is it more advisable (economically and environmentally) to develop processes that temporarily bind CO_2 and then release it again?

The environmental benefit of the first strategy, permanently fixing the CO_2, seems clear, but in fact it is not. In many cases, the reagents that are required for CO_2 fixation are high-energy materials, the synthesis of which was energetically costly. There are, however, many cases of economically valuable products that can be prepared from CO_2. The conversion of ketones and CO_2 to chiral β-hydroxycarboxylic acids by a combination of base-promoted carboxylation and Ru-catalyzed asymmetric hydrogenation will be described as an example (*1*).

The second strategy, temporarily binding the CO_2 and then releasing it again, seems environmentally counterproductive. However, if the temporary use of the CO_2 makes the process consume less energy and raw material, then the use of CO_2 is economically and environmentally beneficial, even if the CO_2 is released at the end of the process. The majority of the presentation will focus on some very simple reactions of CO_2 that have the potential to save energy and materials.

Carbon dioxide can be used as a trigger, in the presence of water or an alcohol, to switch a neutral amine or amidine into a bicarbonate or alkylcarbonate salt. If the equilibrium is roughly balanced, then flushing the system with inert gas or air will remove the CO_2 and switch the charged compound back into a neutral amine or amidine. This simple switching process can be incorporated into many molecules to render them "switchable", resulting in many practical advantages for reactions and separations.

Switchable solvents, meaning liquids that can be reversibly switched from one form to another, were envisioned to be solutions to the practical conundrum called "Murphy's Law of Solvents", which states that "The best solvent for any one process step is bad for the next step." We wanted to design solvents that would meet the needs of one process step and could then be modified, *in situ*, to meet the needs of the subsequent step. We have developed three different kinds of switchable solvents (Figures 1, 2, and 3).

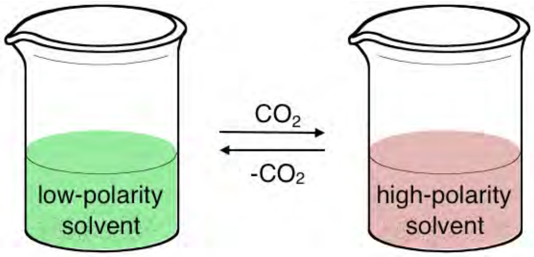

Figure 1. "Switchable-polarity solvents". These solvents have low polarity until they are exposed to an atmosphere of CO_2, at which point they change into high-polarity ionic liquids. The polarity difference is large enough that many solutes are soluble in only one form of the solvent. The process is reversed by removal of the CO_2 from solution.(*2-4*)

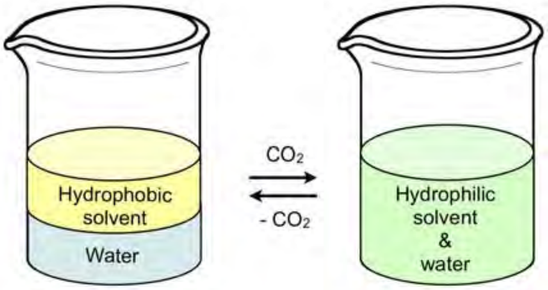

Figure 2. "Switchable-hydrophilicity solvents" are liquid solvents that are normally so hydrophobic that they have very little miscibility with water and form a biphasic mixture when mixed with water. However, when exposed to CO_2, these solvents become very hydrophilic and completely miscible with water. Therefore these solvents can behave like hexane but be easily removed, by extraction with carbonated water, without distillation (*5*).

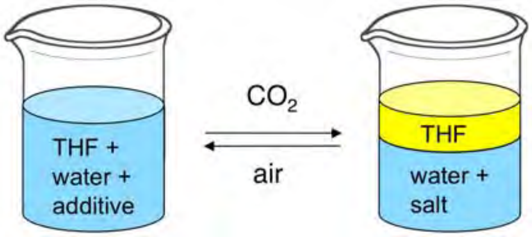

Figure 3. "Switchable water". An aqueous solution of an uncharged additive has an ionic strength of zero and is miscible with THF. However, after CO_2 is introduced, the additive changes to a salt, raising the ionic strength, and forcing the THF out of solution. This represents a reversible method for "salting-out" of organic compounds from water (*6*).

Reactions and post-reaction separations in switchable solvents have been achieved, and related work is ongoing (*2-4, 7*). However, alternative uses of switchable solvents have been found, including as easily reversible CO_2-capture agents.(*8*)

Switchable solutes are solutes that can be reversibly switched from hydrophilic to hydrophobic. In a biphasic mixture of water and an organic solvent, a switchable solvent can be made to partition selectively in an aqueous phase (in the presence of CO_2) and then into the organic phase (in the absence of CO_2) (*9*). This has applications in catalysis (*10*).

Switchable surfactants (Figure 4) are surfactants that can be switched between a surfactant form and a demulsifier form (*11*). The application of CO_2-triggered switchable surfactants to separations and emulsion polymerizations will be described.

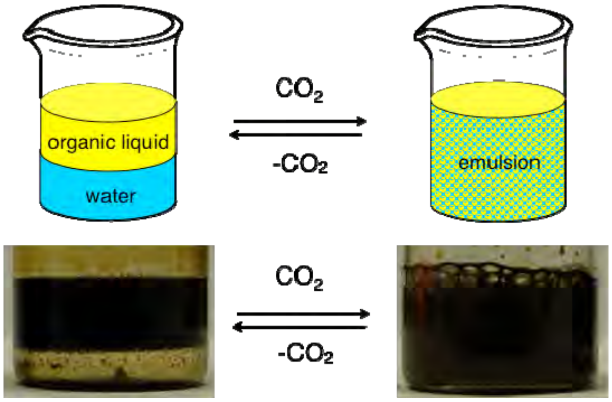

Figure 4. A switchable surfactant is a molecule that reversibly switches from one form that stabilizes an emulsion to another form that does not stabilize the emulsion. We have developed switchable surfactants that respond to the presence and absence of CO_2.

In summary, the application of CO_2 as a trigger for switchable chemicals seems to be a flexible approach that offers new possibilities for facilitating chemical reactions and separations.

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

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

Students: Theodor Agapie, Smaranda Marienescu, Jeffrey Byers, Suzanne Golisz, Steve Baldwin, Ian Tonks, Ted Weintrob
Collaborators: Sara Klamo (Dow), Hans Brintzinger (University of Konstanz)

Contacts: Department of Chemistry, California Institute of Technology, Pasadena, CA 91125; bercaw@caltech.edu

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 precatalysts based on complexes of 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 Precatalysts for Olefin Polymerizations with Group 4 and 5 having Bi- and Tridentate Pincer Ligands. We have undertaken a major project to explore synthetic routes to semi-rigid, nonmetallocene catalysts for olefin polymerization and other transformations. Recognizing that *ansa*-metallocenes have provided the most important framework for single-site catalysts for α-olefin polymerization with tacticity control, we have developed a semi-rigid ligand, LX_2-type pincer ligand family (L = pyridine, furan, thiophene, pyrazole; X = phenoxide, anilide) that has some of the same advantageous features of *ansa*-metallocenes. We have examined the performance of Ti, Zr, Hf, and V complexes as propylene polymerization precatalysts and prepared a variety of tantalum compounds.

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. Preliminary experiments reveal that an imido iron complex is obtained by treatment of the THF adduct with azides, and that rapid intramolecular C-H activation follows.

Structural Studies of Zirconium Hydride Adducts with Alkylaluminums. In collaboration with Hans Brintzinger from the University of 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.

Future Plans

Preparation of New Group 4 and 5 Transition Metal and Iron Complexes with New Di- and Tridentate Ligands. New experiments are planned that are intended to further probe and expand the scope of catalysis with early transition metal-based single site catalysts, and to investigate new types of catalytic transformations, *e. g.* catalytic additions of HX (X = SiR_3, AlR_2, BR_2, NR_2) to multiple carbon-carbon bonds. The major focus of the new projects will concern the synthesis of new generations of these LX_2-type pincer ligands, having X ligands that are stronger π donors (X = anilide, thiophenolate and phospha-anilide, as opposed to X = phenoxide), that we anticipate will be more stereorigid and enforce C_s or C_2 symmetry, due to improved π bonding and or more ring strain for S and P donors. Catalysts with stronger pincer ligand π-bonding should therefore provide a more predictable catalyst structure. In this regard they should more closely resemble metallocene catalysts. The structures of these new (LX_2)Ta-imido/amido and -*tris*(imido) compounds will provide evidence for stronger Ta-X π-bonding, as compared with the known *bis*(phenolate)pyridine analogs. Moreover, stereoselective propylene polymerizations are expected for the group 4 alkyl precatalysts.

Intramolecular C-H activation in the metallation of benzene-linked bis(phenolate)bis(benzyl) complexes of Ti, Zr, and Hf. Precatalysts based on bis(benzyl) derivatives of Ti, Zr, and Hf having a benzene-linked bis(phenolate) were found to cleanly eliminate an equivalent of toluene with formation of a dimeric, catalytically inactive complex with a metallated benzene. Isotopoic labeling studies indicate that for Ti, this straightforward, concerted σ-bond metathesis elimination of toluene by abstraction of hydrogen from the 2-position of the benzene-1,3-diyl linker by a benzyl group is not coccuring. Studies of the mechanisms of these transformations are currently underway.

Structural Studies of Zirconium Hydride Adducts with Alkylaluminum and Investigations of their Activities in Functioning Olefin Polymerization Systems. Synthetic, structural and exploratory polymerization studies of cationic alkylaluminum-complexes zirconocene hydrides will be completed, including studies of the roles of the most prevalent species in functioning catalytic systems. Rates of initiation and propagation in propylene polymerizations are being measured by NMR.

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

Direct Partial Oxidations Using Molecular Oxygen

Additional PIs:	Karen Goldberg (U. Washington)
Graduate Students:	Brian J. Boro, Raymond B. Lansing, Agnes Mrutu, Marie V. Parkes, Nancy E. Bush (New Mexico) Gregory R. Fulmer, Christopher J. Semiao (Washington)
Undergraduate Student:	Alexandra Herndon (Washington)
Collaborators:	Richard P. Muller (Sandia National Laboratories), Eileen N. Duesler (New Mexico)
Contact:	Richard A. Kemp, Department of Chemistry and Chemical Biology - MSC03 2060,1 University of New Mexico, Albuquerque, NM 87131; rakemp@unm.edu Karen I. Goldberg, Department of Chemistry, Box 351700, University of Washington, Seattle, WA 98195-1700; goldberg@chem.washington.edu

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 various oxidation reactions with O_2 that cannot be catalyzed by known heterogeneous systems, as well as investigating those systems that require "activated" oxygen sources such as peroxides for reaction. 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 O_2 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. Computational studies of the fundamental steps of the proposed pathways are also being carried out and these investigations are proving important in choosing and modifying our experimental targets.

DOE Interest

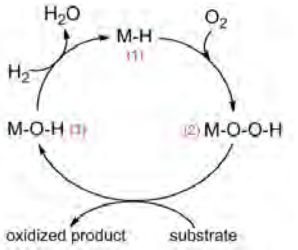
Significant reduction of energy usage in industrial-scale catalytic processes goes to the heart of the interests of DOE. As well, elimination of reaction steps in multi-step routes in order to prepare functionalized products directly is also of importance. More effective atom-efficient reaction chemistry 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 addresses 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

Our working model of the proposed catalytic cycle is illustrated in **Figure 1**. Recently, the two sub-teams have focused on synthetic methodology designed to expand both the range of ligands and metals utilized from our initially-studied $(PCP)^{t\text{-}Bu}$Pd-H system (PCP = $2,6\text{-}C_6H_3(CH_2PR_2)_2$). Our synthetic efforts have two major desired outcomes - to produce transition metal hydrides that react with molecular O_2, and to prepare new homogeneous metal complexes capable of delivering O atoms to organic substrates selectively. In the recent PCP-ligand work we have prepared a large number of new transition metal complexes based on Ni, Pd, and Pt. Generally, these species are initially formed as the metal halides, and must be converted into the metal hydrides (M-H, species 1 in **Figure 1**) prior to reaction with O_2 to form M-OOH (species 2). We have found this hydride conversion is not straightforward using any of these metals, as each system requires an extensive study to determine which hydride source can effectively convert the M-X bond to a M-H bond. This work culminated in a paper in *Inorganic Chemistry* that discussed the effects of various hydride reagents used, and we also filled a void in structural Ni-H pincer chemistry. In related synthetic work, the variety of PCP-Pd complexes produced covered a large span, including sterically- and electronically-modified arms on the PCP ligands, and anthracene as a new ligand backbone. We have also greatly expanded the number of well-characterized PNP Ozerov-type ligands, including increasing the number of asymmetric types of $^{R}PNP^{R'}$ ligands. We are also exploring novel, hemi-labile PCO ligands with various Group 10 metals, primarily Pd. Notably, the ^{tBu}PCO ligand has been observed to coordinate in a tridentate fashion like its PCP analogue, as well as in a bidentate PC binding mode, thus supporting our hypothesis that the "O-Pd" bond would be more labile than the "P-Pd" bond.

Figure 1. Proposed Catalytic Cycle for Preparing Partially Oxidized Species



In almost all of these cases, we were able to prepare not only the M-X precursors, but also the M-H species, although in some cases (*e.g.*, highly electronegative groups on P arms) we were not able to produce the hydride. All of the M-H complexes prepared have been treated with O_2 to attempt to prepare M-OOH (species 2), and many of the resulting hydroperoxides have been characterized fully by NMR spectroscopy. Overall, more than 20 M-X or M-H complexes have been structurally characterized by X-ray crystallography, as have several M-OOH complexes formed by the direct insertion of O_2 into the M-H bonds under mild conditions. These O_2 reactions have varied in complexity. In general, it appears that Ni tends to give a mixture of products, while Pd tends to give only one M-OOH species.

Additionally, we have prepared Group 10 compounds containing multidentate carbene CNC ligands. Unfortunately as was found with many of the PCP compounds investigated in this project, the conversion of the M-X species to M-H has been problematic. Changing the reducing ability of the hydride reagent over a wide range led to either no reactivity, or complete dissociation of the ligand from the metal. Using Ni and Ag salts, we have discovered an unprecedented *trans*-metallation reaction in which the CNC carbene is transferred to a Ag^+ ion from a Ni complex! This is very surprising in that it is well-known that Ag carbenes can act as reagents to transfer carbenes from Ag^+ ions to other metals. While the exact mechanism for this intriguing reaction is unknown, the reaction may be driven by the formation of the $Ag_7(NO_3)_7(CNC)_2$ product, a previously-unknown 3D Ag-coordination cluster.

Reaction and Mechanistic Chemistry

The M-OOH species described above are effective at transferring an O atom to inorganic substrates, such as R_3P. However, it has proven much more difficult to selectively transfer the O atom to organic substrates. The difficulty in O transfer is interesting as we have shown that $(PCP)^{t\text{-}Bu}$Pd-OOH and other MOOH complexes undergo thermal loss of an O atom to form the corresponding hydroxide complexes M-OH. We continue to screen all new M-OOH complexes that are prepared for their reactivity with olefins and other organic substrates. In addition, we are examining two new routes for epoxidation/O-atom transfer. We have proposed an intramolecular H^+-assisted mechanistic route to transfer the β-O atom to an organic substrate, and we are preparing compounds with the potential to engage in this pathway. We have shown computationally that this alternative mechanism should be more energetically-favorable. An additional pathway under investigation for epoxidation involves the oxidation by oxygen of metal β-hydroxy alkyls and metalloxetanes.

Future Plans

- Determine the structure/property relationships between the ligands attached to the metal and the reactivity to a) form a hydroperoxide, and b) transfer an O-atom;
- Evaluate new M complexes with particular ligand modifications to promote alternative H^+-assisted mechanistic pathway to transfer O-atoms to organic substrates and β-hydroxy alkyl/metalloxetane routes to epoxides; and
- Examine Cu-based (Cu/CuO cycle) heterogeneous catalysts for epoxidation.

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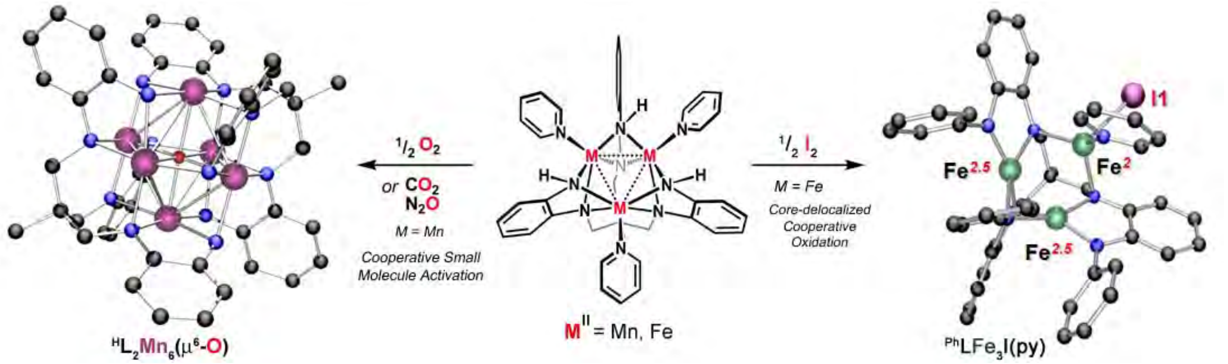
Name: Theodore A. Betley
Rank: Assistant Professor, Harvard University (July 2007)
Address: 12 Oxford Street
Cambridge, MA 02138
Phone: (617) 496 - 9944
Fax: (617) 496 - 3792
E-mail: betley@chemistry.harvard.edu

Title: **New methods for small molecule activation**

Abstract: Multi-electron transformations in biology (e.g. nitrogen fixation, water oxidation) are effected using polynuclear metalloenzymes. To gain insights into the utility of polymetallic reaction center designs, we have set out to synthesize ligand architectures that permit the inclusion of multiple metal centers in the same proximal space. Our new ligands feature multiple metal binding sites without sacrificing control of the steric and electronic control about the individual metal ions. A family of 3*d* trimetallic complexes have been synthesized using these templates. The new complexes were characterized by X-ray diffraction, electrochemistry, UV-vis, Mössbauer, and SQUID, revealing rich redox chemistry and complex magnetic phenomena. Simple chemical oxidation exhibit a variety of oxidation products, including both site-isolated and core-distributed oxidation patterns. We will finish by describing our efforts to use these polymetallic platforms to effect multi-electron chemical transformations.



Poster Presentations

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

Oxo Catalysts for the Conversion of Lignocellulosic Biomass

Postdoc: Dr. Guodong Du and Dr. Michael J. Zdilla
Students: Rex Corbin, Jeanette Cessarich, Isaac Corn, and Erin Smith
Contact: Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907; mabuomar@purdue.edu

Goal

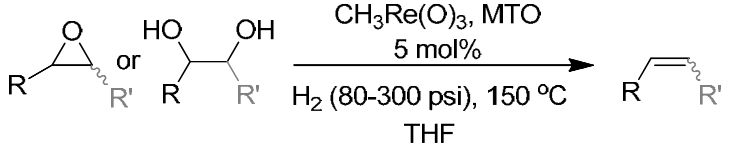
Develop metal oxo catalysts for the deoxygenation reactions of biomass-derived compounds. Define the kinetics and mechanisms of **D**iol-to**A**lkene **Re**action (DARe).

DOE interest

As petroleum resources diminish and their environmental footprint can no longer be ignored, the utilization of biomass resources into liquid fuels as well as high value-added organics (chemical feedstock) is a major research objective. One of the major obstacles in utilizing biomass is the challenge of removing oxygen atoms from carbohydrates and polyols to increases the energy content and decrease the boiling point. A desirable catalytic system would utilize dihydrogen, tolerate water and air, operate under relatively mild conditions, and give good selectivity. Our approach has been to develop catalysts for the **D**iol-to-**A**lkene **Re**action (DARe) because alkenes are valuable feedstock and they can easily be transformed to longer hydrocarbon chains via olefin metathesis. The fundamental chemistry we are studying in combination with quantitative kinetics will provide the foundation for future designs and use of catalysts in biomass conversions.

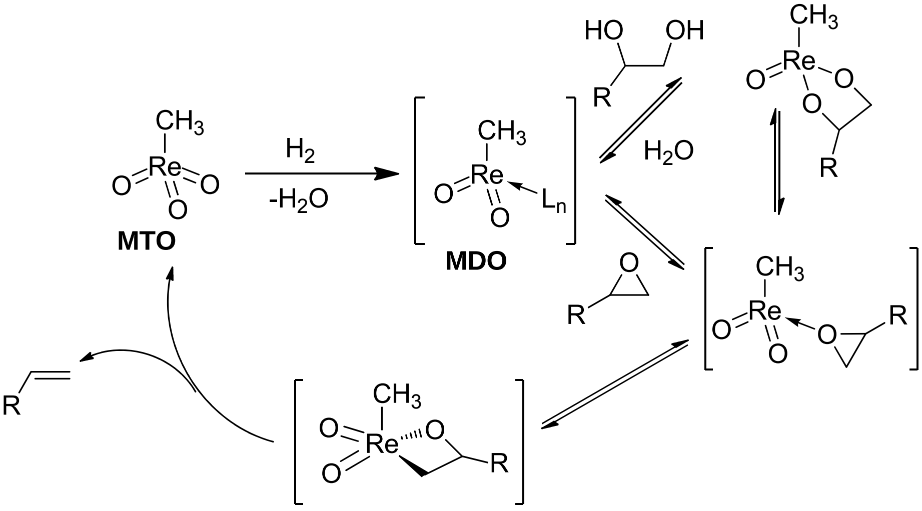
Recent Progress

***D**iol-to-**A**lkene **Re**action (DARe) Catalyzed by MTO*: Catalytic epoxidation and dihydroxylation of alkenes is a well studied and widely used reaction in organic synthesis. The reverse reaction, deoxygenation of epoxides and diols, is much less developed. Less than a handful of catalysts have been reported in the literature which use stoichiometric phosphines as O-atom acceptors. We have discovered that MTO catalyzes the conversion of epoxides and diols to alkenes (DARe) with dihydrogen under reasonable conditions (150 °C and 80-300 psi), Equation 1.



(1)

MTO is effective for aliphatic, cyclic, and aromatic epoxides with high selectivity for olefins. It also gives good yields of alkene (60-70%) with cyclic *cis* diols. The remaining mass balance in these instances is isomerization to the *trans* diol, which does not react further. However, aliphatic diols require 300 psi of H_2, and under these conditions the resulting alkene is hydrogenated by MTO to the alkane. Therefore, 1,2-hexandiol affords hexane rather than 1-hexene. Based on our initial mechanistic studies we propose the mechanism in Scheme 1. The reaction of MTO with H_2 is novel because previous experimental and computational studies have claimed that MTO is not reduced by dihydrogen.



Scheme 1. DARe catalyzed by MTO.

So far the MTO catalyst has not been very effective with biomass-derived compounds. The biggest obstacle has been charring of polyols in the presence of the MTO catalyst. For example, erythritol and 1,4-anhydroerythritol give only 25% yield of 2,5-dihydrofuran and tetrahydrofuran (THF) in the ration 5:1.

Future plans

Kinetics of DARe and characterization of relevant intermediates: Study the reactions kinetics, characterize the rhenium intermediate, and characterize the MTO-H_2 reaction. Based on lessons learned from the MTO system, we will investigate other rhenium and molybdenum oxo complexes and extend the Diol-to-Alkene Reaction (DARe) to biomass-derived carbohydrates and polyols

Molybdenum complexes with redox-active ligands: Synthesize molybdenum complexes containing redox active diimine ligands and explore their reaction chemistry with carbohydrates and polyols. These complexes could open the door to new paradigm in catalysis featuring cooperative redox between the metal and ligand. In other words, the ligand can act as an electron reservoir.

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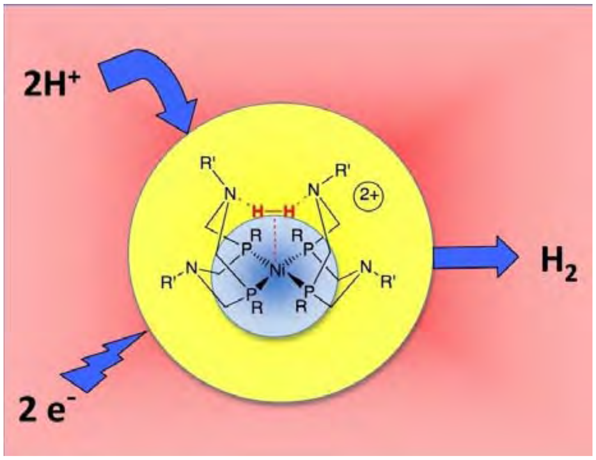
The Center for Molecular Electrocatalysis **Aaron M. Appel**

Utilization of Proton Relays in Electrocatalysts for Hydrogen Production

Lead PI: Morris Bullock and Dan DuBois
Postdoc: Uriah Kilgore
Contact: Pacific Northwest National Laboratory, Richland, WA 99354; aaron.appel@pnl.gov



For hydrogen production, the transfer of protons to the metal center is a crucial and often rate-limiting step for molecular electrocatalysts. The use of proton relays has been shown to improve proton transfer, increase catalytic rates, and decrease overpotentials. This has been demonstrated using nickel complexes of cyclic diphosphine ligands which contain two positioned pendant amines, $\mathrm{Ni}(\mathrm{P}^{\mathrm{R}}{}_{2}\mathrm{N}^{\mathrm{R'}}{}_{2})_{2}{}^{2+}$. Variation of the ligand substituents results in large changes in the rates and operating potentials for the catalysts. Additionally, the use of different acids and conditions results in remarkably different catalytic rates. For complexes with R = phenyl and R' = *para*-substituted phenyl, the potentials of the $\mathrm{Ni}^{2+/1+}$ and $\mathrm{Ni}^{1+/0}$ couples show significant dependence on the *para*-substituents, indicating effective communication between the *para*-substituents and the metal center. When R = phenyl and R' = benzyl, the strength of the acid used has been found to change the catalytic mechanism: using *p*-bromoanilinium as the acid ($\mathrm{p}K_a = 9.4$) reduction occurs first, followed by protonation; using *p*-cyanoanilinium ($\mathrm{p}K_a = 7.0$), protonation occurs before reduction. While both acids lead to catalytic hydrogen production, the overpotentials are remarkably different (240 mV vs 50 mV, respectively). The difference in the catalytic mechanisms and the corresponding thermochemical implications will be presented.

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

Control of Hydrogen Release and Uptake in Condensed Phases

Additional PIs: Greg Schenter
Postdoc: Avery Luedtke
Collaborators: Shawn Kathmann Nancy Hess, Herman Cho, John Linehan, Abhi Karkamkar, Don Camaioni, Roger Rousseau, Mark Bowden; Thomas Proffen and Luc Daemen (LANSCE), Bill David (RAL), Sario Cantelli (La Sapienza), Russ Hemley (CIW), Wendy Mao (Stanford)
Contacts: Pacific Northwest National Laboratory, POB 999 – MS K2-57, Richland, WA 99352; tom.autrey@pnl.gov

Goal. The objective of our research is to expand fundamental insight into hydrogen activation in molecular complexes that will provide the basis for developing rational approaches in catalysis design and small molecule activation. We propose that: (i) bi-functional – ambiphilic centers – comprised of electron-rich and electron-poor sites, provide an environment for heterolytic activation of molecular hydrogen into protonic and hydridic characteristics and (ii) environmental factors such pressure or nanoscale effects and interfacial interactions enhance kinetics and modify thermodynamics of molecular crystals offering an alternate approach to "frustrated Lewis acid/base pairs. This work has wide ranging implications in catalysis for energy storage and energy storage materials as well as alternative approaches to catalytic activation of small molecules. We use DOE user facilities at LANSCE for neutron and APS for synchrotron experimental studies. Work at PNNL focuses on experimental NMR and Raman spectroscopy using computational molecular dynamics to provide insight into understanding the complex phenomena.

Current research focuses on the relationship between structure and dynamics in bifunctional molecular complexes. Steric, electronic and dynamical properties control the equilibrium between dative bonding and hydrogen activation in ambiphilic complexes composed of Lewis acid/base pairs. We combine experimental and computational approaches to gain fundamental insight into properties that control kinetics and thermodynamics of the heterolytic activation of hydrogen, eq 1 and the competing molecular transformations, eqs 2, 3. The fundamental insight gained in these studies will provide a basis for an approach to the rational design of new catalysts.

$$R_3N\rightarrow BX_3 \ + \ H_2 \quad \Leftrightarrow \quad [R_3NH]^+[HBX_3]^- \qquad (1)$$

$$R_3N\rightarrow BX_3 \quad \Leftrightarrow \quad [NR_3BX_2NR_3]^+[BX_4]^- \qquad (2)$$

$$R_3N\rightarrow BX_3 \ + \ [R_3NH]^+[HBX_3]^- \quad \Leftrightarrow \quad [NR_3BX_2NR_3]^+[BX_4]^- \qquad (3)$$

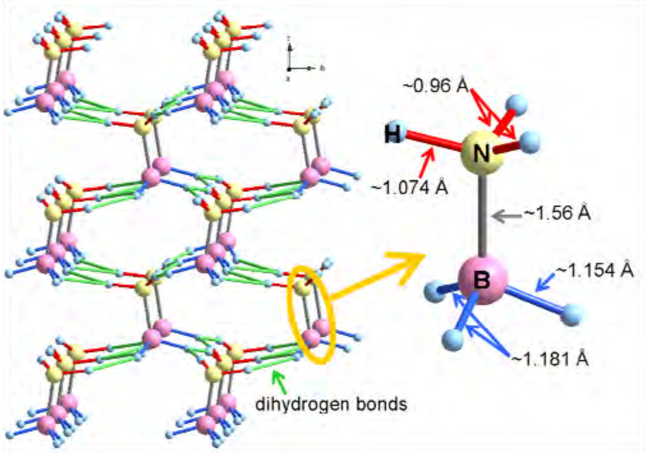
DOE Interest. The US DOE has issued recent workshop reports for *Basic Research Needs: Catalysis for Energy* and *Basic Research in Hydrogen Storage* calling for novel approaches for rational catalyst design and new breakthroughs in novel materials for energy storage in chemical bonds. Our research uses 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".

Recent Progress. The classical parent donor–acceptor complex composed of a borane Lewis Acid and an amine Lewis base $R_3N\rightarrow BX_3$ has been a focus of our research. Addition of molecular hydrogen to these Lewis acid/base pairs results in the formation of protonic $NH^{\delta+}$ and hydridic $BH^{\delta-}$ Our work integrates experimental and molecular modeling tools to develop a description of the long-range, average or static structure of a crystalline 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, $NH_3 \rightarrow BH_3$, $[NH_4][BH_4]$, $[NH_3BH_2NH_3][BH_4]$ and can be readily extended to other studies of complex condensed matter systems. Specifically where the substituent's X and R on the borane Lewis acid and amine Lewis base, (eqs 1-3), are varied to provide an approach to modify the catalytic nature of the Lewis acid/base pairs for small molecule activation.

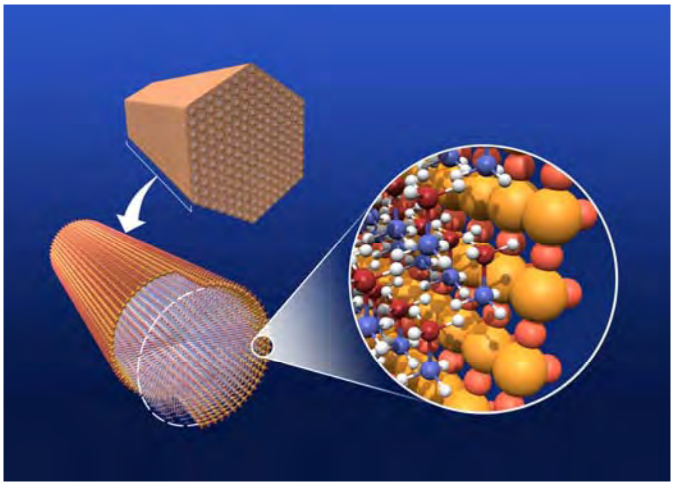
A few examples of recent results are summarized below. A more complete description is provided in the publications listed.

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	^2H NMR, QENS	NMR, XAFS

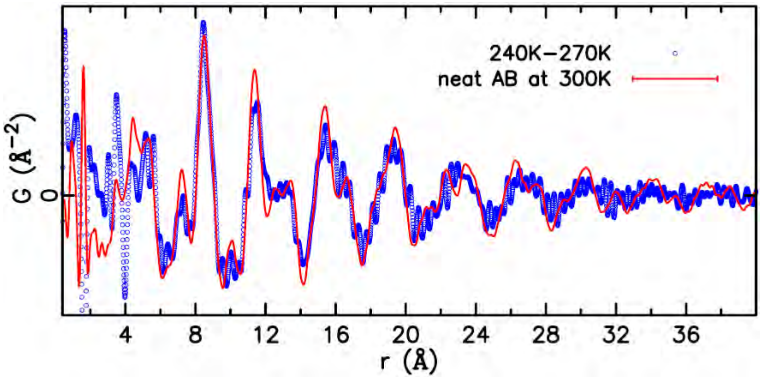
Average Structure: The *structure of the orthorhombic phase of AB* obtained from Rietveld analysis of the Neutron Powder Diffraction (NPD) data acquired at LANSCE data was measured from 10 - 275 K to compare with dynamics modeling. Figure on right shows the connectivity of the hydrogen bonding network in the molecular crystal at 200 K. (H atom shown in white, B in magenta and N in yellow). Modeling shows the H is extremely dynamic and accounts for the large thermal ellipsoids observed in the neutron powder diffraction data obtained for $^{11}BD_3ND_3$. The results of this work were recently published in the J. Phys Chem. A. 2009 DOI: 10.1021/jp900839c.



Local Fluctuations: *The phase transition in the parent Lewis acid/base complex $NH_3 \rightarrow BH_3$ was studied using Anelastic spectroscopy and differential scanning calorimetry to determine the characteristics and kinetics of the order-disorder phase transition.* The orthorhombic to orientationally disordered tetragonal phase transition at 222.4 K was determined from a measure of the temperature dependence of the vibration frequency and elastic energy dissipation in a polycrystalline sample of ammonia borane. The time constant for the phase transition under isothermal conditions shows the life time for the orthorhombic to tetrahedral transition is on the order of 900 seconds at 2220 K. Lower temperature dynamical measurements show that there two dynamically processes occurring on the kilo-hertz time scale that corresponds to the rotational hopping rates observed by ^2H dynamical NMR line shape analysis. This work was recently published in the J. Phys Chem. C. 2009, 113, 5872.

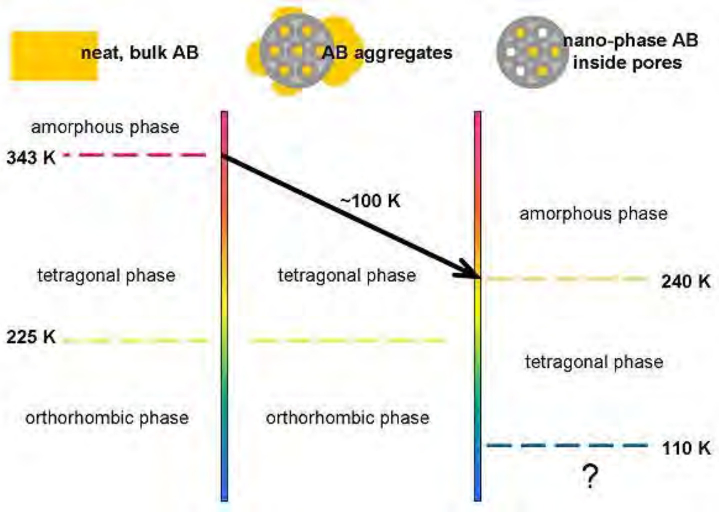


Complex Phenomena: XR-PDF experiments at the *Advance Photon Source* (ANL) was used to study the diffraction patterns for ammonia borane embedded in the mesoporous silica, MCM-41, across a temperature range from 80K to 300K. The work showed that nanophase ammonia borane held within the confined spaces of the mesoporous silica looses crystalline character at much lower temperatures, above 240K, and does not undergo the expected structural phase change at 225K. The PDF experiments show that trapping AB in MCM-41 destabilizes the molecular crystal at temperatures above 240K and stabilizes its high-temperature disordered tetragonal phase even at much lower temperatures than would be expected. The PDF analyses of the data, coupled with previously available results of xenon-129 nuclear magnetic resonance spectroscopy, provides the first insight into how the nanostructure ammonia borane complex may be destabilized to enhance the catalytic nature of Lewis acid/base pairs towards activation of hydrogen. Interfacial interaction in nano-scaffolds may provide an alternate approach to the development of *Frustrated Lewis Pairs*.



Furthermore, the research has wide ranging implications that demonstrates the prowess of PDF analysis of x-ray powder diffraction data for the determination of soft materials—compounds containing light elements—trapped within heavy mesoporous materials. Conventional crystallographic diffraction techniques are insufficient to characterize such guest species with limited long-range order.

This work recently published in the *J. Am. Chem. Soc.* 131(38):13749-13755. DOI: 1021/ja904901d, was highlighted in the APS Final Report.



The phase diagram of bulk and nanophase ammonia borane. When heated, bulk ammonia borane undergoes an orthorhombic to tetragonal phase transition at 225K and becomes amorphous above 343K. However, confined nanophase ammonia borane does not undergo the phase transition at 225K. Instead, it remains in the tetragonal phase from 110K to 240K. Amorphization of nanophase ammonia borane occurs at a much lower temperature, 240K, than bulk ammonia borane.

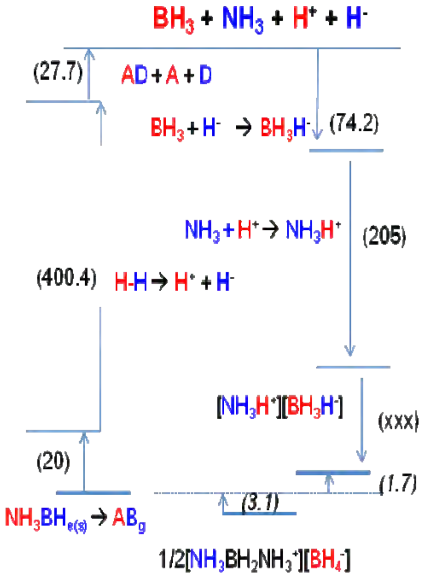
Future Plans

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 the activation of small molecules. *Specifically, we seek to develop a better understanding of molecular processes in materials that have alternating electron-rich and electron-poor sites, such as Lewis acid/base pairs, capable of the heterolytic activation of molecular hydrogen.* Priority will focus on understanding the interplay between structure and dynamics and how external environments can modify the kinetics and thermodynamics in Lewis acid/base pairs for the activation of small molecules in catalytic processes:

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 H_2 release from AB. A study of the structure and dynamics of this proto-typical Lewis acid/base pairs will provide insight into the catalytic nature of hydrogen activation. The thermodynamics will determine the equilibrium distribution between the dative pair and the ionic pair, eq 1.



As shown in the adjacent figure, a thermodynamic cycle illustrates the components of the molecular system that must be evaluated to determine the final equilibrium between the dative bonded Lewis acid/base pair with molecular hydrogen and the ionic salt with the heterolytically activated molecular hydrogen. Our previous work has shown that nano environments and interfacial interactions can destabilize the crystalline phase of AB providing an external handle to modify thermodynamics and kinetics. We will focus on modification of the substituents on the Lewis acid and base components to further understand the activation of small molecules in catalytic transformations. This fundamental knowledge will provide insight to impact the catalytic transformation of small molecules such as hydrogen for fuel cell power, conversion of carbon dioxide to methanol and nitrogen to ammonia.

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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

Graduate Students and Postdoctorals: S. Althaus, P. Kalita, E. Klobukowski, K. Manna, S. Nedd, E. Szajna-Fuller, C.-H. Tsi, K. Yan
Collaborators: B. Trewyn, O. Pestovsky, D. Liu, I. Slowing, T. Kobayashi, H.-T. Chen

Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, IA 50011-3111
bakac@ameslab.gov, vsylin@iastate.edu, marek@ameslab.gov, sadow@iastate.edu, kwoo@iastate.edu

Goal

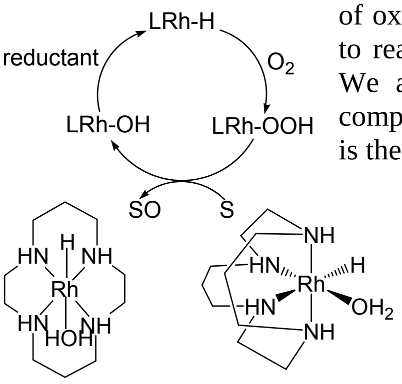
Discover new catalytic principles in solutions and on surfaces. Develop new catalysts and specific catalytic systems for targeted reactions that are important to the missions of the DOE, such as catalytic conversions of biomass, utilization of molecular oxygen, and selective transformations involving C-O, C-H and C-N bonds. Develop new synthetic methods for the preparation of mesoporous oxide catalysts with well-defined pore/particle morphology and fully characterized catalytic surfaces with unique and tailored properties.

DOE Interest

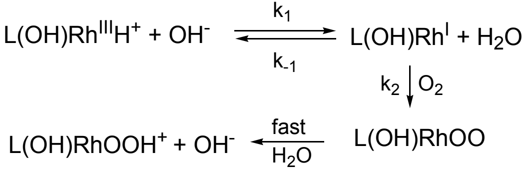
Our research addresses homogeneous activation of molecular oxygen, catalytic chemistry on bulk metal surfaces, design of new ligands and catalytic systems that function in both homogeneous and 3D environments, and design, synthesis and application of functionalized mesopores in catalysis. This work combines 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.

Recent Progress

(1) Oxygen activation by transition metal complexes. Superoxo and hydroperoxo metal complexes are generated by coordination and stepwise reduction of molecular oxygen at metal centers in the early stages of oxygen activation. Hydroperoxo complexes have been shown in the past to react with a variety of substrates by electron and oxygen atom transfer. We are currently developing catalytic oxidations based on hydroperoxo compounds as active oxidants. One of the crucial steps in the catalytic cycle is the generation of a hydroperoxo complex from molecular oxygen. A facile route to such complexes involves insertion of oxygen into metal-H bonds. The reaction between O_2 and both *cis* and *trans*-$L^1(H_2O)RhH^{2+}$ in neutral and alkaline aqueous solutions is unusually facile and generates the corresponding hydroperoxides in less than one second under ambient conditions. Detailed kinetic investigation showed that the reaction takes place by a direct OH^- attack at the hydride site of the hydroxo form, i. e. $L^1(HO)RhH^+$:



trans-L^1RhH^{2+} *cis*-L^1RhH^{2+}

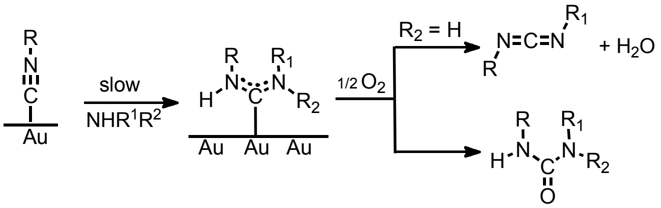


A widely accepted mechanistic picture for the self-reactions of $ROO^{\bullet}$ radicals involves head-to-head dimerization, dissociation of O_2 and formation of organic products. The inorganic analogues, i. e. superoxometal complexes $LMOO^n$ are more persistent and show little tendency to engage in second-order self-reactions. We have, however, observed a fast cross reaction between one such complex, $Cr_{aq}OO^{2+}$, and acylperoxyl radicals. Selectively labeled species, $RC(O)^{16}O^{16}O^{\bullet}$ and $Cr_{aq}{}^{18}O^{18}O^{2+}$, generated $^{16}O^{18}O$ quantitatively, and provided strong evidence for a tetraoxo intermediate, $RC(O)^{16}O^{16}O^{18}O^{18}OCr^{2+}$. This appears to be the first documented example of such a reaction involving an inorganic superoxo complex.

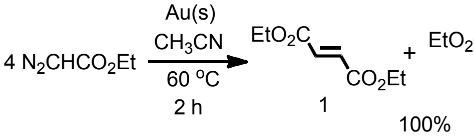
$$RC(O)^{16}O^{16}O^{\bullet} + Cr_{aq}{}^{18}O^{18}O^{2+} \rightarrow {}^{16}O^{18}O + \text{products}$$

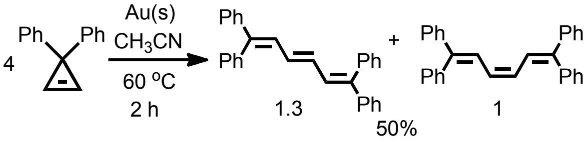
(2) Organometallic chemistry and catalysis on bulk gold metal. Micron-sized gold particles catalyze the reactions of isocyanides with primary and secondary amines under an atmosphere of O_2 to produce carbodiimides and ureas, respectively. Kinetic studies indicated that the reaction involves nucleophilic attack of the amine on the adsorbed isocyanide to form a diaminocarbene bound to the gold surface (Scheme 1). The details of the reaction with O_2 in the subsequent step have no simple precedents.

Scheme 1

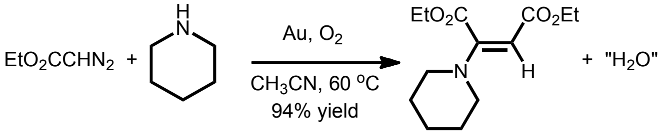


The reactions of carbene precursors such as diazo compounds and diphenylcyclopropene produced coupled products that are consistent with the formation of reactive carbene species bound on gold.

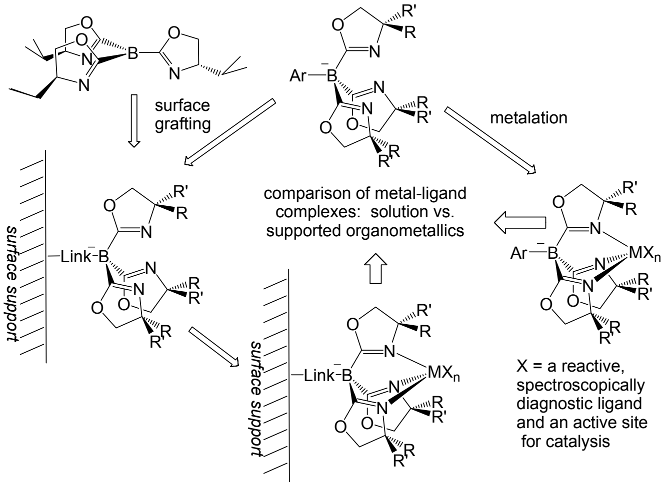




The chemistry of carbene precursors on gold surfaces was examined in more detail in the presence of added amines. The major products of these diazo reactions were unexpectedly enamines in good to excellent yields. These reactions are proposed to occur by initial formation of surface-bound R(H)C: carbene groups that are attacked by nucleophilic amines. The enamine products are very different than those obtained in reactions catalyzed by homogeneous transition metal complexes and represent a new type of bulk gold-catalyzed reaction. These results indicate that the investigation of the catalytic activity of bulk gold is producing novel results. 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.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.



(3) Boron-bridged oxazolines and silylmethyl ligands for solution-phase and surface chemistry. We are interested in transition metal complexes that maintain similar coordination geometries under homogeneous and surface-supported conditions, allowing rational preparation of well-defined surface catalytic sites. Our approach involves synthesis of a new family of 2-oxazolinyl-borane and borate ligands. This ligand family is spectroscopically rich, containing B, C, and N nuclei for solution phase and solid state NMR spectroscopy, as well as the IR active oxazoline motif that has $\nu_{C=N}$ responsive to metal center coordination. The B-Surface linkage insulates the catalytic active site from the surface, allowing ligand-based control over coordination environment. Furthermore, the oxazoline unit provides oxidation- and hydrolysis-resistant donor groups and a racemization-resistant stereocenter for stereoselective applications, and this feature allows an additional level of three-dimensional control.



X = a reactive, spectroscopically diagnostic ligand and an active site for catalysis

Our recent efforts have involved coordination chemistry of tris(oxazolinyl)phenylborate ligands as well as the reactivity of their transition metal compounds. Tris(oxazolinyl)borate iridium(I) compounds react with strong electrophiles such as MeOTf by *N*-methylation of an oxazoline rather than oxidative addition. Furthermore, the oxygen atom in the oxazoline group can act as a donor group for hard metal cations such as lithium, giving structures that are 'arrested' salt metathesis intermediates. Aluminum compounds catalyze lactide ring opening polymerization, as do the bis(oxazolinyl)borate compounds derived from the addition of trimethylaluminum and bis(oxazolinyl)phenylborane.

In order to facilitate surface characterization of reactive organometallics, we have also prepared rare earth (Yb(II) and Y(III)) and alkaline earth metal (Ca(II)) compounds containing the tris(dimethylsilyl)methyl ligand. The spectroscopically-active SiH moieties in this ligand forms agostic interactions in coordinatively unsaturated compounds, and we have studied solid state and solution phase spectroscopic properties of these compounds. Additionally, the β-agostic interactions change the reactivity of these groups in comparison to aliphatic hydrocarbyl ligands, such that the SiH groups are the nucleophilic sites rather than the carbon bonded to the electropositive metal center.

(4) New synthetic route to mesoporous mixed oxide catalysts. The feasibility of a new synthetic method has been demonstrated in the synthesis of a mesoporous calcium silicate mixed oxide material for the transesterification reaction in biodiesel synthesis. 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 method is also useful for the synthesis of a mesoporous aluminum silicate (Al-MS) material in which the aluminum atoms are tetrahedrally coordinated and stable up to at least 400 °C. The double resonance ^{27}Al-^{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 mesoporous aluminosilicate shows excellent catalytic reactivity for the Claisen rearrangement of allyl phenyl ether.

Remarkable new capabilities of solid-state NMR spectroscopy were achieved 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. The technique yielded well resolved two-dimensional (2D) ^{13}C-^{1}H HETCOR spectra of surface-bound species under natural abundance within minutes. The first ^{15}N-^{1}H spectrum of surface species was acquired, also without isotope enrichment.

Future work

Base-catalyzed insertion of O_2 into metal-hydrogen bonds. Now that we have discovered first examples of this type of reaction, we plan to explore other metal hydrides to determine the generality of this chemistry and to prepare other hydroperoxo complexes as active oxidants in catalytic oxidations with molecular oxygen. Stoichiometric oxidations by oxygen atom transfer from hydroperoxides have been documented, which leaves the reduction of hydroxo products to hydrides as the next major challenge in making the reaction catalytic.

Oxidations Using Fe Catalysts. As we have shown in our earlier work on Fe(IV) in aqueous solutions, the oxidation of substrates such as alcohols and aldelhydes takes place in parallel one-electron and two-electron reactions. The catalysis is thus largely precluded, because one-electron pathways generate Fe(III) which is not converted to Fe(IV). Only two-electron path, which generates Fe(II), can be incorporated into a catalytic cycle. We will explore the reaction of Fe(II) with ozone in acetonitrile as a source of Fe(IV) that may be better equipped for two-electron processes in view of the greatly changed thermodynamics. Early preliminary results suggest that two-electron chemistry indeed domonates in this acetonitrile.

Mechanistic probes with atom transfer oxidants. In order to understand more fully the scope of catalysis on bulk gold and to examine potential mechanisms, we will explore a variety of additional reagents and reactions. Of particular interest are other oxidants that may be used in place of molecular oxygen. For example, alkyl hydroperoxides, peracids, iodosylbenzenes, and amine N-oxides are all readily available and easily monitored. These reagents are typically good oxygen atom transfer reagents and may favor a specific mode of reactivity.

Characterization of Silica-grafted oxazolinylborato organometallics. We are currently applying state-of-the art solid state NMR techniques for the characterization of silica-grafted compounds. Our grafting methods involve Si-O-B interactions, so we are developing NMR methods to prove this interaction, define the catalytic surface loading, and probe the metal-ligand interactions. The reactivity of surface and solution compounds will be compared, particulary in bond activation reactions.

Influence of the mesopore environment on catalyst selectivit 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.

Cooperative catalysts. 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. 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.

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Bart M. Bartlett

Structure-Properties Relationship Studies in Compositionally Complex *n*-doped Titanates: Toward the Photooxidation of Water

Students: Tanya Breault and Joseph Yourey
Contacts: University of Michigan, Department of Chemistry
930 N. University Avenue, Ann Arbor, MI 48109
bartmb@umich.edu

Goal

Develop solution-based sol-gel and electrodeposition routes to control dopant levels in *n*-type titanates for high charge-carrier mobility towards photocatalytic water splitting.

DOE Interest

Studying structure-properties relationships in compositionally complex transition metal oxides is critical for developing photocatalyts capable of splitting water into its constituent elements, hydrogen and oxygen for solar fuel production. Doping mid-to-late transition metals such as manganese into the titanate structure shifts the electronic absorption from the ultraviolet to visible part of the electromagnetic spectrum, vital for the goal of solar energy conversion. However, magnetic order present on the lattice limits charge-carrier mobility in the oxides of the inexpensive first-row transition metals. Synthetic control of both dopant concentration *and* dopant ion dispersion on lattice sites of crystalline materials is required for the rational design of more efficient (i.e.—high photoconductivity) semiconducting oxides.

Recent Progress

Sol Gel Synthesis of Mn-doped $SrTiO_3$: *n*-doped $SrTiO_3$ thin films can be prepared from the soluble precursors $Mn(acac)_3$ (acac = acetylacetonate), $Sr(CH_3CO_2)_2$ and $Ti(OBu)_4$ from aqueous/organic mixtures under acidic conditions. Heating the precursor mixture in acetic acid at 60 ºC results in a homogeneous aqueous solution that is cast onto an FTO conducting glass substrate. After spin coating the resulting solution at 2000 rpm and annealing at 600 ºC for 6 h, perovskite crystalline films result, evidenced by powder X-ray diffraction in Figure 1.

Sol Gel Synthesis of Mn-doped TiO_2: Doping 10% Mn into TiO_2 in a similar fashion as described above results in redish-brown amorphous films. However, structural information can be garnered by annealing the prepared solutions in Pt crucibles. Microcrystalline powders having the anatase structure result when samples are annealed between 500 and 650 ºC, but the rutile forms at temperatures ≥ 700 ºC. Scanning electron microscopy shows rough surface films with a thickness of ~ 250 nm in these films, illustrated in Figure 2.

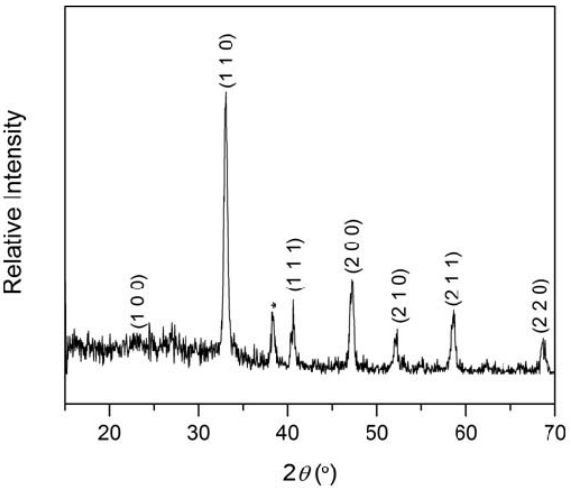

Figure 1. pXRD pattern of $SrTiO_3$:Mn thin films. The *'ed peak results from the FTO substrate.

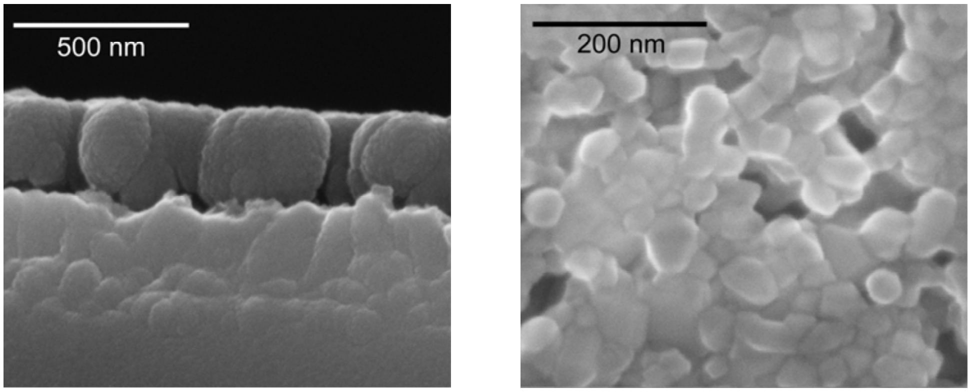

Figure 2. Cross-sectional (left) and top-down (right) SEM micrographs of amorphous TiO_2:Mn (10% Mn doping) on an FTO substrate.

Photoconductivity Measurements: The perovskite thin film described above shows a shift in the ligand-to-metal charge transfer band (LMCT) band from 380 nm in pure $SrTiO_3$ (UV) to a band having a shoulder at 410 nm (blue-violet), illustrated in Figure 2. The bathochromic shift in the absorption of $SrTiO_3$:Mn can be rationalized by the fact that the Mn 3d band is lower in energy than the Ti 3d band due to Mn being more electronegative than Ti. This results in decreasing the onset potential of current flow from 1.0 V (vs. Ag/AgCl) in the dark to 0.6 V under 100 mW/cm^2 illumination using a Xe/Hg lamp with a 410 nm cutoff filter, illustrated the inset of Figure 3a. Films prepared from a 20% Mn solution show enhanced photoelectrochemical properties. Most important, these photoconductivity experiments are performed in a potassium phosphate buffered electrolyte solution *at pH 7* with a Pt cathode. In the TiO_2:Mn films, we note that much lower dopant concentration is needed, with the highest current densities observed at 5% Mn, shown in Figure 3b.

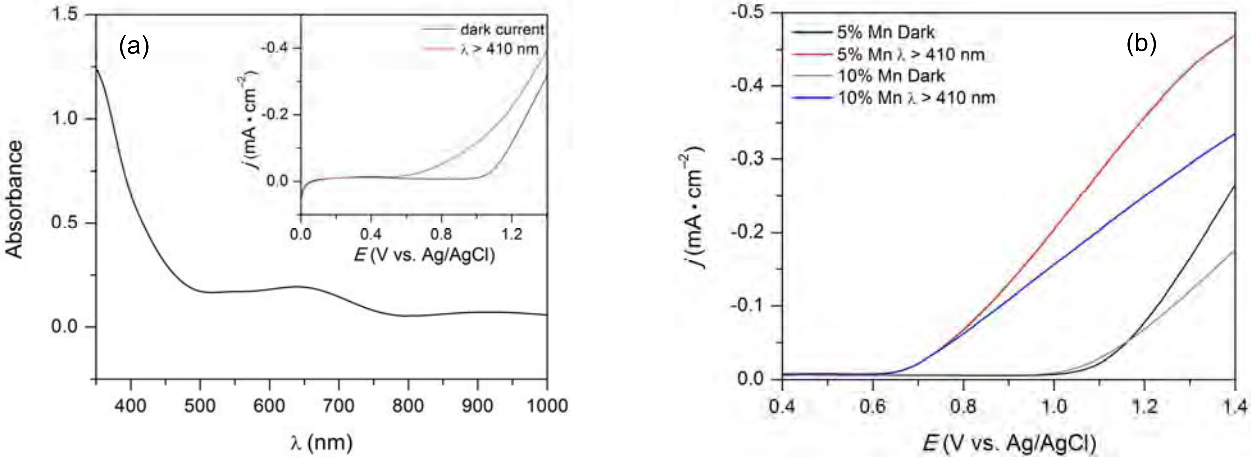

Figure 3. a) Electronic absorption spectrum of a $SrTiO_3$:Mn crystalline film with 80:20 Ti:Mn. ***Inset.*** *I-V* curve of the film in a pH 7 buffered solution. b) *I-V* curve of TiO_2:Mn at 5 and 10% Mn concentration.

Future Plans

Quantifying O_2 Formation in Water Photooxidation Studies: The next step in this work is quantifying the efficiency of our cells. Incident photon to current efficiency (IPCE) can be measured using monochromatic light with our existing set-up. Then, quantum yield (QY) can be determined by measuring O_2 production at the surface of our photoanodes by fluorescence spectroscopy. We have a custom-built cell in our laboratory to probe both IPCE and QY.

Electrochemical Deposition of Higher Surface Area Films: The films prepared by sol-gel processing are rough surface films. We aim to prepare materials with similar compositions thorugh electrodeposition methods. The key questions is can we achieve higher surface areas as well as control morphology to decrease the charge-carrier diffusion length, thereby increasing chemical efficiency (quantum yield)?

Magnetization Study of Domain Ordering in Doped Films: The aim of this study is to address Mn dispersion throughout the crystal lattice. By probing magnetism, we can understand if the compositions result in materials having highly localized electrons or Mn-rich domains that form a new valence band. Ti^{4+} is d^0, therefore it contributes nothing to the magnetic moment of the compound. However, Mn^{4+} is paramagnetic, and the moment under saturation magnetization directly probes the number of interacting spins in this superparamagnetic system at low dopant levels. Magnetism, in conjunction with X-ray photoelectron spectroscopy can provide significant insight into the electronic structure of *n*-doped thin films.

Reduction of CO_2 into Fuels via Lewis Acid-Activated, Multielectron Transformations

Louise A. Berben
University of California, Department of Chemistry, Davis, CA 95616
email: laberben@ucdavis.edu

The combination of Lewis acidic centers to activate and bind CO_2 at low overpotentials, in conjuction with a source of multielectron reducing equivalents is being investigated.
The multi-electron reduction of CO_2 into simple products such as formate, formaldehyde and methanol, or into the most basic C-C coupled products such as ethanol remains a challenge in developing renewable sources of fuel and chemicals.[i,ii,iii] Electrocatalysis,[iv] as a method for the reduction of CO_2 is particularly appealing because the energy and electrons required to cycle a photocathode:electrocatalyst system can be harnessed from sunlight.

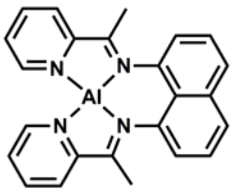

Figure 1. Structure of (naphimpy)Al.

In one approach, we are investigating a redox-active ligand (naphimpy = naphthaline diiminepyridine) in conjuction with a Lewis acidic reaction center (Figure 1). Catalysts obtained by chelation of Lewis acidic metal centers, will be used to activate and bind CO_2. In conjunction with the reducing equivalents stored in the ligands, both activation and reduction of CO_2 will be achieved. We have shown that the ligand naphimpy can be accessed in multiple oxidation states thus supplying multielectron reducing equivalents to a bound CO_2 molecule.

In a second approach we are investigating Lewis acidic sites tethered to catalytically active electrode and photoelectrode surfaces to lower observed overpotentials and modify product compositions.

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DE-FG02-02ER15368 **C. Jeffrey Brinker**

Catalytic and Transport Behaviors of Model Porous and Composite Nanostructures

Students: Shisheng Xiong, Adam Wise
Collaborators: Ying-Bing Jiang (UNM), Darren Dunphy (UNM), George Xomeratakis, UOP, S.Moghaddamand M. Shannon (UIUC)
Contacts: 1001 University Blvd SE Suite 100, Albuquerque, NM 87106; cjbrink@sandia.gov

Goal

Combine self-assembly, interfacial assembly and atomic layer deposition to create model, highly ordered porous or composite thin film nanostructures. Systematically control pore size, shape, and chemistry to reveal new nanoscale transport phenomena in gas and liquid media. Prepare ordered nanoparticle/polymer or oxide composites with controlled nanoparticle spacing and arrangement and interfacial chemistries to test collective catalytic-, charge-, and energy transfer characteristics of model 2D and 3D systems.

DOE Interest

Improved membrane technologies are needed for many energy-related applications, including (but not limited to) CO_2 sequestration, biofuel purification, controlled oxidation, and hydrogen purification and separation. Also, new processing methods are required for producing robust 2D and 3D NP arrays on arbitrary substrates to investigate collective behavior between NPs for charge-transfer and catalytic applications (e.g. solar cells, solid-state lighting, electrocatalysis).

Recent Progress

An Inorganic-Organic Proton Exchange Membrane for Fuel Cells with a Controlled Nanoscale Pore Structure (collaboration with S. Moghaddam and M. Shannon (UIUC))- Proton exchange membrane (PEM) fuel cells are being extensively studied for applications in energy conversion and storage but their development has been impeded by problems related to the membrane electrode assembly (MEA). We recently demonstrated that a silicon-based inorganic-organic membrane offers a number of advantages over Nafion–the most widely used PEM in hydrogen fuel cells - including higher proton conductivity, lack of volumetric size change, and enhanced MEA construction capabilities. The proton conductivity is practically independent of humidity. The inorganic-organic structure is made by fabricating a silicon membrane with ~5-7 nm pores, self-assembly of a molecular monolayer and selective ALD deposition of a hydrophilic aperture at the pore entrances. ALD reduces the diameter of the pores to ~2 nm, ensuring hydration of the pores via capillary condensation and resulting in a proton conductivity 2-3 orders of magnitude higher than that of Nafion at low humidity. A MEA constructed with this inorganic-organic proton exchange membrane delivered an order of magnitude higher power density than that achieved previously with a dry hydrogen feed and an air-breathing cathode.

Integration of a Close-Packed Quantum Dot Monolayer with a Photonic-Crystal Cavity via Interfacial Self-Assembly and Transfer - Nanoparticle (NP) assembly into ordered 2- and 3-D superlattices has stimulated enormous recent interest as a means to create new artificial solids whose electronic, magnetic, and optical behaviors can be tailored by the size dependent properties of the individual NPs mediated by coupling interactions with neighboring NPs, suggesting applications in a diverse range of technologies including photovoltaics, sensors, catalysis, and magnetic storage. To date superlattice assembly has been demonstrated for monosized, binary, and even ternary systems, allowing development and interrogation of a range of collective behaviors: electron transport within 2- and 3-D arrays of Coulomb islands, Foster resonance energy transfer between superlattice monolayers in close proximity, switchable optical properties through regulation of NP d-spacing, and new magnetic behaviors based on binary superlattices. Superlattice fabrication is performed principally by droplet evaporation or convective assembly on an inclined plate. These techniques are often slow, restricted in the size and topography of the substrate, and result in van der Waals solids with limited mechanical behaviors. To address these issues we recently developed a general, rapid method to prepare large area, free-standing, NP/polymer monolayer superlattices by interfacial NP assembly within a polymer film on a water surface.

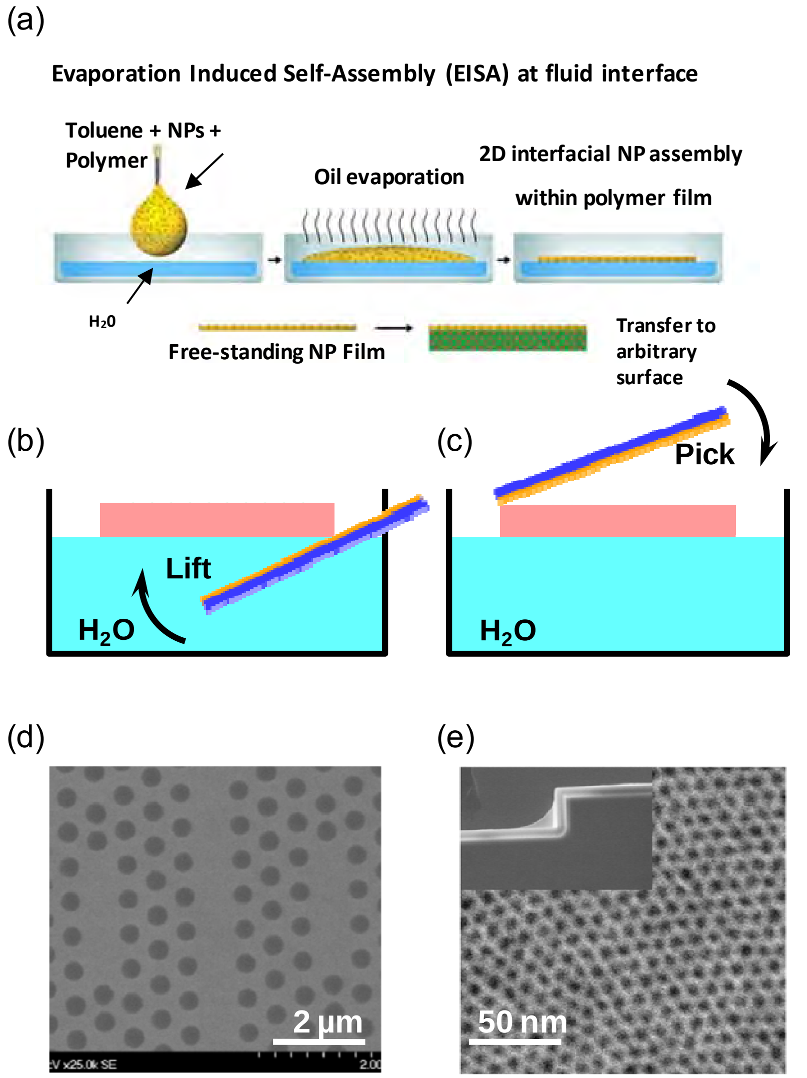

Figure 1 (a) Schematic diagram showing the formation of NP/polymer array by interfacial assembly. (b, c) A schematic representation of the film transfer process for the picking (b) and lifting (c) processes. (b) The QDs are in close contact with the cavity in the sample prepared by the picking process. (c) The QDs are about 20-nm away from the cavity in the vertical direction. (d) SEM picture of a photonic crystal device after coating with a PbS-P3HT composite monolayer film. (e) TEM picture of a monolayer of PbS-P3HT film.

Interfacial self-assembly provides a facile and fast method to assemble and transfer a large area NP array uniformly to a topographically complex photonic crystal surface. The transferred ultra-thin close-packed QD monolayer provides high density, extraordinary uniformity and robustness, and controllable film thickness. A seamless conformal interface between the QD monolayer and the photonic crystal microcavity is realized by either a 'picking' or 'lifting' transfer procedure (see schematic Figure 1). This allows optimal coupling between QDs and the photonic-crystal cavity, while relaxing the requirement of positioning individual QDs. Tuning the cavity resonance to the dot emission becomes unnecessary because the QD has a broad emission bandwidth. The uniformity and close proximity of the NP monolayer to the photonic crystal surface allows us to demonstrate an enhanced spontaneous emission of infrared quantum dots coupled to the defect cavity, while maintaining high Q.

To demonstrate the importance of having the QD array in close contact with the photonic crystal cavity, we compared the enhanced photoluminescence from samples prepared by the ‘picking’ and ‘lifting’ transfer processes. Fig. 2 shows a dramatic enhancement in photoluminescence from the cavity mode for the sample where the QD film is picked up by the photonic crystal (blue curve) versus the supported QD film prepared by lifting (red curve). The difference between the two photoluminescence measurements is consistent with the fact that the ‘picking’ process allows the QDs to be in close contact with the photonic-crystal cavity, providing better coupling to the cavity and thereby yielding a larger enhancement. In contrast, for the ‘lifting’ process, the coupling is dramatically reduced despite the QDs being separated by only 20-nm from the cavity in the vertical direction. The highest Q factor observed with this deposition technique is about 8000, for conditions where the polarization of the photoluminescence is perpendicular to the waveguide axis. To the best of our knowledge, this is the highest Q factor ever achieved using colloidal QDs coupled to a photonic crystal microcavity.

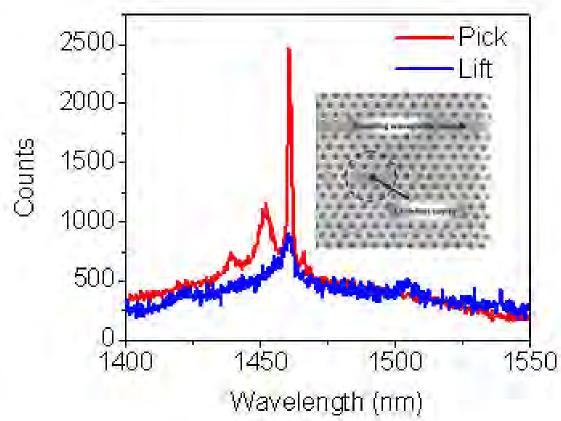

Figure 2 Comparison of PL signals from QD-cavity system prepared by a picking and lifting process. The inset denotes the region of excitation marked by a black dashed circle. This resonance is referred to as E_x resonance with its emission polarization parallel to the waveguide. The PL is collected by a spectrometer with a 300 g/mm grating and 50 um slit width.

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FWP ERKCC44 **A. C. Buchanan, III**

Organic Chemical Transformations at Interfaces

Additional PI: Edward Hagaman
Postdocs: Jian Jiao, Banghao Chen
Staff support: Michelle Kidder, J. Todd Skeen
Collaborators: Alan Chaffee (Monash University, Australia), Craig Barnes (University of Tennessee), Ariana Beste (University of Tennessee), Chris Jones (Georgia Tech), Robert Harrison (ORNL), Sheng Dai (ORNL), Steve Overbury (ORNL), Marvin Poutsma (ORNL), Ken Herwig (ORNL)

Contact: A. C. Buchanan, III, Chemical Sciences Division, Oak Ridge National Laboratory, Bethel Valley Rd., P.O. Box 2008, MS-6197, Oak Ridge, TN 37831-6197; buchananac@ornl.gov

Goal

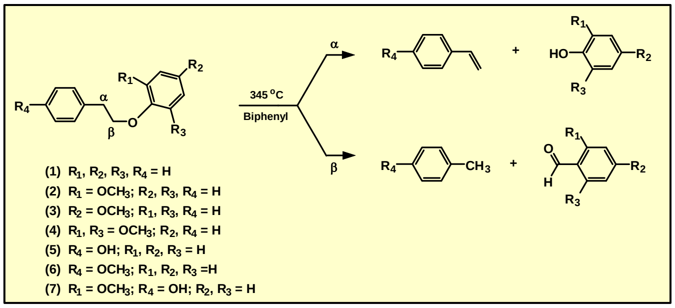
The objective of this program is to gain new fundamental understanding of the factors that control the chemical transformations for oxygen-containing organic molecules in homogeneous phases and at solid metal oxide interfaces.

DOE Interest

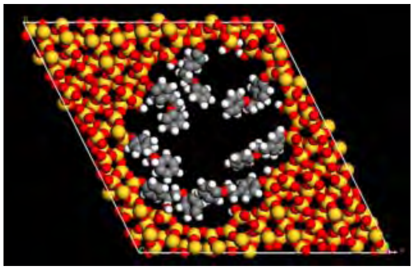
The organic molecules examined in this research are models for important functional groups present in lignocellulosic biomass, a renewable organic energy resource of interest as an alternative source of fuels and chemical feedstocks, and the mesoporous metal oxides studied are often used as catalysts or catalyst supports. The fundamental free-radical pathways associated with the thermochemical conversion of relevant oxygenated organic molecules are not well understood as opposed to hydrocarbon chemistry. Hence, this research provides fundamental, quantitative knowledge on reaction kinetics, mechanisms, product selectivities, and impact of metal oxide surface interactions that will contribute to advances in the design of innovative catalysts for the utilization of renewable resources as a sustainable source of fuels and chemicals.

Recent Progress

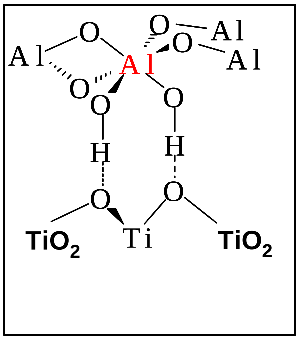
Substituent Effects on Phenethyl Phenyl Ether Pyrolysis (PPE): The impact of hydroxy and methoxy substituents on the pyrolysis at 345 °C of PPE, a model for the dominant β-aryl ether linkage in lignin, revealed that the novel rearrangement pathway involving the β-radical (an O-C phenyl shift) remains operative in the aryl substituted analogs with α/β-product selectivities ranging from 3.0 to 7.4. Reaction rates were much more strongly influenced by substituents on the aryl ether ring which can result in up to a 25-fold increase in rate. Interpretation of



these substituent effects is somewhat complicated since they impact multiple steps in the free-radical chain decay pathway. DFT computational studies have now provided some clarification on the origin of these effects. The increase in rate by methoxy substituents on the aryl ether ring has been correlated with the decrease in C-O bond dissociation enthalpies (M06-2X/6-311++G**) that control the rate of the initial unimolecular scission step that produces phenethyl and substituted phenoxyl radicals. For two *ortho*-methoxy substituents, the decrease in the BDE was a substantial 8.6 kcal mol^{-1}. Furthermore, calculation of rate constants for hydrogen abstraction by chain carrying benzyl and phenoxyl radicals (and their substituted counterparts) provided insight into polar and steric effects that impact overall product selectivities. Particularly significant was the discovery of the highly polarized transition state for hydrogen abstraction at the β-site by electrophilic phenoxyl radicals that facilitates this pathway. Calculation of rate constants was challenging due to the large number of low frequency modes (< 100 cm^{-1}) in the transition states that required the use of a semi-classical vibrational partition function to take into account anharmonic effects. Nevertheless, the rate constants used in a steady-state kinetic expression very successfully reproduced the overall α/β-product selectivities for PPE and substituents of the phenethyl aryl ring.



Impact of Pore Confinement on Chemical Reactivity: There has been considerable recent interest in understanding the effects of confinement of organic molecules in nanoporous solids on their chemical and physical properties as well as there chemical reactivity, including applications in organic synthesis and asymmetric catalysis. PPE was confined in mesoporous silicas by condensation of a phenol derivative with the surface silanols. The pyrolysis rate was found to increase slightly, but a significant change in the α/β-product selectivity was observed increasing to ca. 15 compared with a value of 5 when tethered to the surface of nonporous silica. Further studies involving changes in grafting density and tailoring the interface with additional tethered spacer molecules resulted in α/β-product selectivity values as high as 100. In conjunction with results from molecular dynamics (MD) simulations and quasi-elastic neutron scattering (QENS) studies, it appears that the rearrangement path involving the O-C phenyl shift is hindered by hydrogen bonding interactions with surface silanols and by steric congestion in the pores. Studies of the role of mesoporous silica-confined hydrogen donor molecules on the pyrolysis of surface-confined diphenylpropane molecules revealed that the pyrolysis rate was dependent on both the pore size and on the molecular orientation of the grafted hydrogen donor molecule. The dependence on molecular orientation was found to be different when the pyrolysis was conducted on the external surface of nonporous silica nanoparticles indicating an important role for surface curvature in bimolecular hydrogen transfer steps.



Solid-State NMR Spectroscopy: Solid-state NMR spectroscopy was used to explore the structure of complex metal oxides of interest as novel materials, catalyst supports, and separation media. As a recent example, ^{27}Al MAS and 3QMAS NMR have been used to study Al_2O_3/TiO_2 catalyst supports synthesized via excess-solution impregnation and surface sol-gel methods. Temperature and alumina loading level strongly affected the chemical states of aluminum oxide species observed.

Surface cations, $Al(H_2O)_6^{3+}$, a surface alumina monolayer, and disordered transitional aluminas (multi-layers) and α-alumina, coexist on the TiO_2 surface. Chemical shift and quadrupole coupling constants were obtained for the major species identified in 3QMAS experiments. Gold particle catalysts prepared from these supports calcined at 500 °C showed optimum catalytic activity in CO oxidation, and the smallest gold particle size. The highest catalytic activity was found for those catalyst supports that show by NMR the maximum monolayer type octahedral alumina on the titania surface.

Future Plans

- *Lignin Model Compounds:* Pyrolysis studies of oxygen functional group chemistry will explore important aliphatic hydroxyl substituents on PPE. Of particular interest is examining the potential role of intramolecular hydrogen bonding on the chemical transformations. Experimental studies will be coupled with theoretical investigations aimed at computing more accurate rate constants for key elementary steps. One new focus will be the important O-C phenyl shift step for the substituted $PhCH_2CH{\bullet}OPh$ radicals.
- *Pore confinement and Chemical Reactivity:* Studies of pore confinement effects will examine new substituted lignin models to examine the impact of substituents on product selectivity under confinement conditions. In addition, more acidic surfaces such as Al-MCM-41 will be investigated to explore competitive acid-catalyzed reactions. This research will be complemented by QENS studies of hydrogen bonding dynamics between the lignin models and the metal oxide surfaces coupled with MD simulations. This will provide insights into the nature of these interactions as a function of organic molecular structure, pore size, and surface acidity.
- *Solid-State NMR Spectroscopy:* Solid-state NMR investigations will probe new metal oxide structures focusing not only on key metal sites [e.g. Si, Al, V] but also on surface oxide structures probed by O-17 NMR coupled with isotopic labeling. In addition, our recent success in developing new microcoils capable of generating intense rf fields will be further developed, which may have great benefit in multiple quantum NMR experiments on solids that require excitation of broad resonances with MHz linewidths.

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Activation of H_2 by Non-Metals for Energy Storage in Chemical Bonds

Donald M. Camaioni, Abhi Karkamkar and Tom Autrey
Pacific Northwest National Laboratory, Catalysis Science Group, P.O. Box 999,
Richland, WA 99352
donald.camaioni@pnl.gov

We present preliminary results of a new Lab-Directed investigation into heterolytic splitting of H_2 by non-metal Lewis acid/Lewis base pairs. The development of H_2 activation in non-metal systems is in its early stages. Elucidation of structure-reactivity principles will stimulate development of molecular systems and materials that incorporate bifunctional, ambiphilic centers for small molecule activation. Our approach is to characterize the properties of Lewis pairs in solution and solid phase environments relevant to H_2 activation using a suite of experimental methods (NMR spectroscopy, calorimetry, x-ray and neutron scattering analyses) in combination with computational electronic structure methods (density functional theory and molecular orbital). Initial theory work has focused on calculations of the energies, barriers and pathways for hydrogen splitting by combinations of amines and BX_3 (X = H, F, Cl, Ar, OAr) compounds. Results for ammonia and BH_3, BF_3 and BCl_3 model Lewis acids will be compared and contrasted. Features unveiled in these calculations are leading us to explore combining these acid-base functionalities into molecular and supramolecular structures. Results of these calculations, our approaches to synthesizing target systems and experimental characterization of them will be highlighted.

Pacific Northwest National Laboratory operated by Battelle for the U.S. Department of Energy

Christopher J. Chang

Bioinspired Molecular Catalysts for Production of Hydrogen from Water

Co-PI: Jeffrey R. Long
Postdoc: Hemamala I. Karunadasa
Students: Julian P. Bigi, Curtis A. Wray
Contact: C. J. Chang, 532A Latimer Hall, University of California, Berkeley CA 94720-1460; phone: (510) 642-4704; email: chrischang@berkeley.edu; webpage http://www.cchem.berkeley.edu/cjcgrp

Owing to issues of climate change and accelerating global energy demand, the search for viable carbon-neutral sources of renewable energy is amongst the foremost challenges in science today. In this context, a major quest of renewable energy research is the search for efficient catalysts for the production of hydrogen from water that rely on cheap and earth-abundant elements. Here we report a new chemical platform to achieve this goal through the discovery of a well-defined molybdenum-oxo complex that catalytically generates hydrogen from water at neutral pH or even from seawater. Our work establishes that high-valent metal-oxo units can be exploited to create reduction catalysts that are robust and functional in water, a concept that has broad implications for the design of green and sustainable chemistry cycles.

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DE-FG02-05ER659 **Paul J. Chirik**

Understanding Nitrogen Fixation

Students: Donald Knobloch, Doris Pun, Scott Semproni

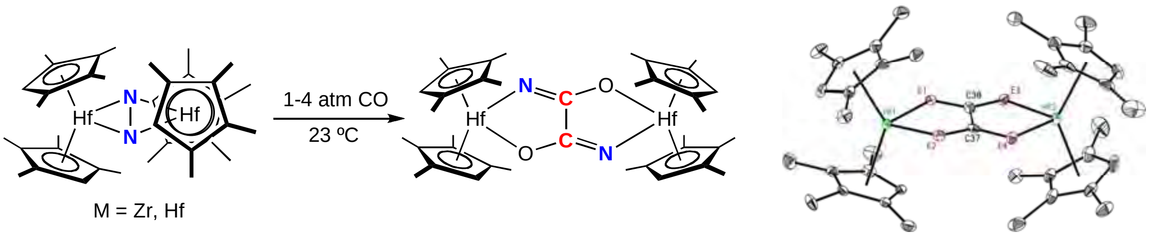
Contact: P. Chirik, G-50A Baker Laboratory, Cornell University, Ithaca, NY 14853
Phone: (607)254-4538; email: pc92@cornell.edu
Webpage: www.chem.cornell.edu/pc92

Goals

The purpose of our program is to explore fundamental chemistry relevant to the functionalization of atmospheric nitrogen (N_2). Specifically, we are interested in developing nitrogen-carbon bond-forming reaction given the widespread utility of this linkage in fertilizers, fine and commodity chemicals and pharmaceuticals. If successful, such methods may reduce the fossil fuel consumption and the domestic energy insecurities associated with industrial ammonia synthesis and hydrogen production. With DOE support, we have prepared and characterized a family of bis(cyclopentadienyl) zirconium and hafnium dinitrogen complexes that contain activated N-N bonds. Importantly, these molecules exhibit a rich N_2 functionalization chemistry including hydrogenation to ammonia, N-H bond formation via C-H activation and nitrogen-carbon bond formation using CO_2 and isocyanates as the carbon sources. Current and future efforts are directed toward expanding the scope of these reactions and developing practical routes to organic molecules using N_2 as a synthon.

Recent Progress

Our laboratory has recently discovered that treatment of our previously reported family of zirconocene and hafnocene complexes with side-on, activated dinitrogen ligands with carbon monoxide results in facile N-N bond cleavage with concomitant assembly of two N-C bonds and one C-C bond. This unique CO-induced N_2 cleavage reaction was initially discovered with a difficult to access *ansa*-hafnocene dinitrogen compound but has since been shown to be a general transformation for N_2 compounds of this type. As illustrated in the Figure below, carbonylation of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ occurs readily with 1-4 atm of CO at 23 ºC and cleanly furnishes the corresponding oxamadide product.



Having discovered a unique ligand-induced N≡N bond cleavage reaction that simultaneously forms both N-C and C-C bonds, we have been elaborating the functionalized core to nitrogen-containing organic molecules. Treatment of the zirconocene and hafnocene oxamidide complexes with Brønsted acids liberates free oxamide, an important fertilizer under exploration as an alternative to urea. Likewise, addition of various alkyl halides and triflates furnishes the corresponding 1,2-addition products derived from N-alkylation and provides routes to both symmetric and asymmetric N, N'-dialkyl oxamides. More recent work has demonstrated that carbon monoxide-induced N_2 cleavage can be coupled to dinitrogen hydrogenation as addition of H_2/CO mixtures furnishes zirconium and hafnium μ-NH, isocyanate compounds.

DOE Interest

The synthesis of ammonia, NH_3, from its elements, H_2 and N_2, via the venerable Haber-Bosch process is one of the most significant technological achievements of the past century. Our research program seeks to discover new ammonia independent pathways to nitrogen-containing organic molecules that disrupt the strong $N\equiv N$ bond in N_2 and create new, fundamental chemical linkages for the construction of molecules with application as fuels, fertilizers and fine chemicals. If successful, such routes would reduce fossil fuel demands and increase domestic energy security.

Future Plans

The discovery of CO-induced N_2 bond cleavage opens many new pathways for exploration of dinitrogen functionalization. Particular emphasis will be placed on preparing isotopically labeled derivatives as well as value-added heterocycles and amides of interest in organic synthesis and the fertilizer industry. As part of more long-term objectives, we will also examine the possibility of using CO as a trigger for N_2 cleavage and attempt to intercept μ-nitrido intermediates with various polar and non-polar reagents. Focus will also be devoted to developing constituent steps of catalytic cycles.

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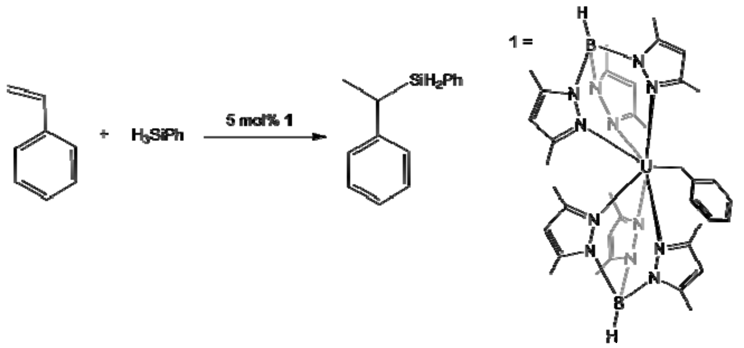
Homogeneous Catalysis using Uranium(III) Alkyl Species

Suzanne C. Bart* and Philip E. Fanwick
Chemistry Department, Purdue University
email: sbart@purdue.edu

Compared to transition metals, the organometallic chemistry of uranium is relatively unexplored. While alkyl complexes of uranium are known,[1] they are typically tetravalent, and some undergo decomposition via radical pathways.[2, 3] Our lab has explored the synthesis of uranium(III) alkyls to determine their comparative reactivity as well as their potential utility for catalytic chemistry. Recently, we have synthesized the uranium(III) alkyl complex, Tp*$_2$U(CH$_2$Ph) (**1**) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate), a rare example of a uranium(III) monoalkyl. Initial studies indicate that this complex catalytically hydrosilylates olefins. Studies with terminal alkynes have demonstrated that catalytic dehydrogenative silylation occurs. The characterization of the uranium complex, details of the catalytic chemistry, and a proposed mechanism will be presented.



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

Synthesis and Catalytic Chemistry of Yttrium and Lanthanide Metal Complexes

Students: Benjamin M. Schmiege, Elizabeth Montalvo, Justin R. Walensky, Michael K. Takase, Nathan A. Siladke, and Matthew R. MacDonald
Contacts: Department of Chemistry, 1102 Natural Sciences II,
University of California, Irvine, CA 92697-2025
Ph: 949-824-5174; FAX: 949-824-2210; wevans@uci.edu

Goal

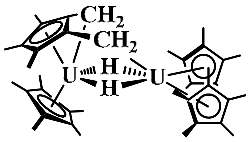
The objective of this research is to use the special properties of the f elements to advance chemistry in energy related areas. This project is oriented toward the discovery of reaction pathways that will provide the basis for new types of catalytic cycles and processes that, at present, are not under 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 are being pursued.

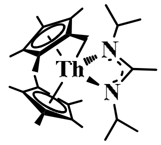
DOE Interest

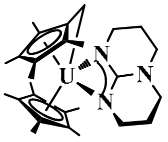
The elements with f valence orbitals, the lanthanides and actinides, are large, electropositive metals that represent extremes in the periodic table in terms of chemical and physical properties that can be used to identify a broader set of alternatives for addressing problems in energy utilization, transmission, 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

Although (η^5:η^1-$C_5Me_4CH_2$) tuck-in f element complexes were found to be key intermediates in alkyl C-H bond activation in the 1980's, it was not until 25 years later that the first crystallographic evidence of an f element tuck-in species was obtained in the form of the tuck-in tuck-over dihydride, $(C_5Me_5)U[\mu\text{-}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2](\mu\text{-}H)_2U(C_5Me_5)_2$, **A** (ref. 3). Now, in the past year, *three* new examples of f element tuck-in complexes have been synthesized that could be fully characterized by X-ray crystallography: $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)Th[^iPrNC(Me)N^iPr]$, **B** (ref. 11), $(C_5Me_5)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)U(hpp)$, **C** (ref. 14 describes precursor chemistry with the bicyclic guanidinate, hpp = $N_3C_7H_{12}$), and $(C_8H_8)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)U(THF)$, **D** (see next page). The new tuck-in complexes were generated by manipulation of traditional metallocene coordination environments with amidinate, guanidinate (hpp), and cyclooctatetraenyl ligands, respectively. These compounds provide an excellent set of complexes for investigating C-H activation reactivity with a single isolable tuck-in moiety.

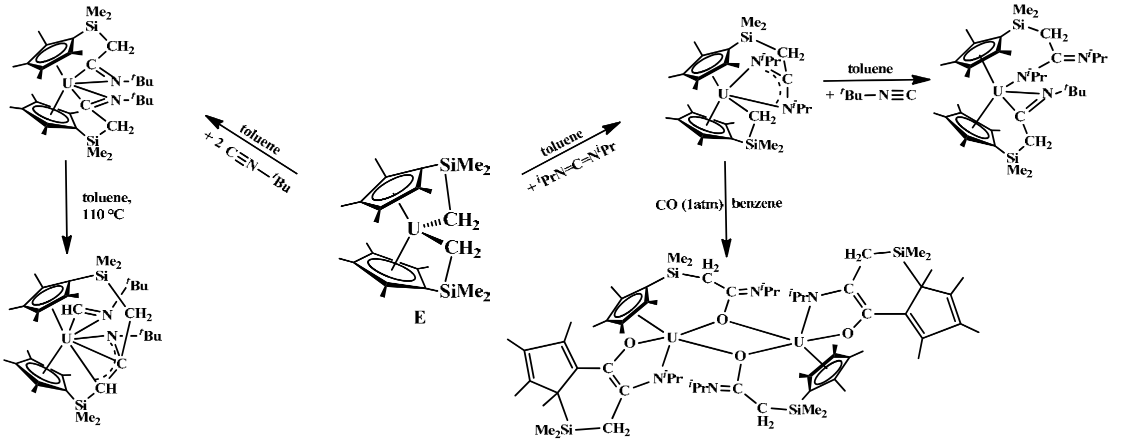
A: 

B: 

C: 

D: 

In addition, a double silyl tuck-in complex, (η^5:κ^1-$C_5Me_4SiMe_2CH_2$)$_2$U, **E** (ref. 16), has been isolated from a reaction involving two intramolecular C-H bond activation reactions. This complex will allow the study of U-C bond reactivity in a tethered environment that could lead to reactions not observable with conventional complexes. Preliminary studies of the insertion chemistry of **E** have shown that it will readily generate new U-(element) linkages that can be examined in tethered form. Unusual reactions originating from **E** are shown below.



Future Plans

The isolation of the new tuck-in and silyl-tuck-in complexes provides an opportunity to study actinide-(element) reactivity in complexes in which the reaction thermodynamics have been modified by the intramolecular tethering. The reactivity of these complexes will be pursued in attempts to define new reaction pathways that may be accessible under the proper conditions.

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Metal-Catalyzed Functionalization via Transient Covalent Attachment

Eric M. Ferreira* and Erin E. Stache
Colorado State University, Department of Chemistry, Fort Collins, CO 80523
email: emferr@mail.colostate.edu

Although tremendous developments have been made in the use of homogeneous catalysis toward synthetically useful applications, it is clear that many limitations still exist. A unique approach to the transition metal-catalyzed functionalization of unreactive bonds will be presented. This strategy involves the utilization of an organic compound that can act dually, featuring an acetalization component to temporarily attach to a substrate, and a ligating component to direct the metal to a specific site on the substrate. This tactic will rely on the design and optimization of ligand structure and reaction conditions to fully realize the desired process.

We will outline our latest efforts toward this overarching goal. Specifically, we have designed specific ligand scaffolds that feature a transacetalization component, based on amino amides and amino alcohols, capable of "docking" carbonyl-based compounds. Several of these ligands have been covalently attached to various aldehyde compounds, and the resulting molecules have been evaluated in palladium-catalyzed oxidative functionalizations. Early observations suggest the feasibility of this concept for directing site-specific reactivity, giving chemo-, regio-, and diastereoselective functionalization. Experimentation has also illustrated that substrate exchange processes are also possible with these structural motifs. It is anticipated that the design and establishment of catalytic systems that can impart this type of reactivity will eventually develop into extremely powerful and useful synthetic transformations that will impact the chemical community. Moreover, these studies will substantially deepen our understanding of several fundamental aspects of catalysis and reactivity that could have widespread implications in future reaction design.

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

Supported-Nanocluster Catalyst Formation Kinetic and Mechanistic Fundamental Studies

Postdocs:	Prof. Saim Özkar
Students:	Joe E. Mondloch; Ercan Bayram
Collaborators:	Prof. Anatoly I. Frenkel, Yeshiva University, New York, NY
Contacts:	Department of Chemistry, Colorado State University, Ft. Collins, CO 80523 phone: (970)-491-2541; Email: rfinke@lamar.colostate.edu web page: http://www.chm.colostate.edu/rgf/index.html

Goal

The primary goal of our DOE-funded program is to follow the kinetics, and establish the mechanism(s), of the historically difficult to follow, and hence relatively little studied and poorly understood, *nucleation* and *growth* of *supported nanocluster heterogeneous catalysts.*

DOE Interest

Studies of the kinetics and mechanisms of formation of supported-nanocluster heterogeneous catalysts address a major gap in our knowledge of this extremely important class of commercial catalysts. Nanocluster composition and size control of the resultant supported-nanoparticle catalysts are being emphasized in systems that involve formation of the supported catalyst *in contact with solution* that are, therefore, unusual. The significance and overall importance and impact of the proposed studies are that they address DOE's "Grand Challenge for catalysis science in the 21st century (of) understand(ing) how to design catalyst structure to control catalytic activity and selectivity".

Recent Progress

We published 11 papers in the 2008 to early 2010 period; the titles of those publications (which fall primarily under our just expired, 2006-2009 DOE grant) are detailed below and address their content. Relevant to our new, fall 2009 DOE renewal proposal of the above title ("*Supported Nanocluster Catalyst Formation Kinetic and Mechanistic Fundamental Studies*"), we published our first paper in that area, paper #11 below titled "Monitoring Supported-Nanocluster Heterogeneous Catalyst Formation: Product and Kinetic Evidence for a 2-Step, Nucleation and Autocatalytic Growth Mechanism of $Pt(0)_n$ Formation from H_2PtCl_6 on Al_2O_3 or TiO_2". This paper is of some significance in that it (i) provides proof of concept that the kinetic and other methods in our proposal do work, and (ii) addresses the supported nanocluster formation—and a number of issues that our studies uncover—in the classic precatalyst system of H_2PtCl_6 on oxides such as Al_2O_3 or TiO_2.

Future Plans

At present we are focusing on bringing to publication our initial studies of a better defined, "prototype" supported-organometallic to supported-nanoparticle system, Ir(1,5-COD)Cl/γ-Al_2O_3 plus H_2 to $Ir(0)_n$/γ-Al_2O_3. Those studies include demonstration of the first 7 or 8 attributes we define in that paper as being characteristic of a prototype system for supported-nanoparticle formation in contact with solution. After that, we plan to focus on the additional kinetic and mechanistic studies necessary to understand the particle-formation mechanism and its implications for how to control particle composition, size and shape en route to improved, higher selectivity, higher activity and longer lifetime supported-nanoparticle heterogeneous catalysts.

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DE-FG02-05ER15630 **Michel R. Gagné**

Oxidative Addition at Anomeric Centers in the Pursuit of Value–Added Fine Chemical Feedstocks from Cardboard and Potatoes

Postdoc: Lucas Zucarello, Colleen Munro-Leighton
Student: Stephen Andrews
Contact: Dept of Chemistry, UNC Chapel Hill, Chapel Hill NC, 27599-3290
mgagne@unc.edu

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.

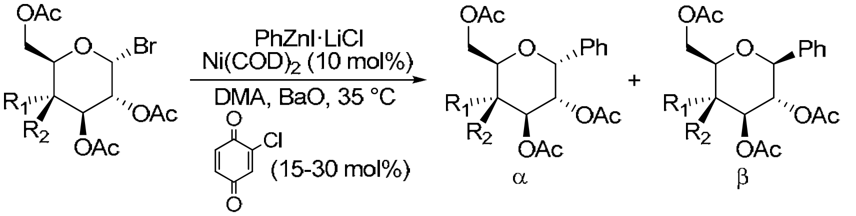
DOE Interest

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, etc.) 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.

As part of our long-term goal of developing methodologies for the conversion of poly-saccharide feedstocks into value added materials, we have been investigating various methods for activating the key anomeric linkage in sugars. The guiding notion is that this bond not only links the sugars together, but it is characterized by unique reactivity by virtue of its anomeric stabilization and the stereoelectronic effects that result. Learning to catalytically activate bonds at this center will provide the fundamental reactivity profiles that will eventually enable us to rationally design catalysts for their selective activation and subsequent conversion to modified, more useful structures. To this end, we have been investigating a number of approaches to their activation.

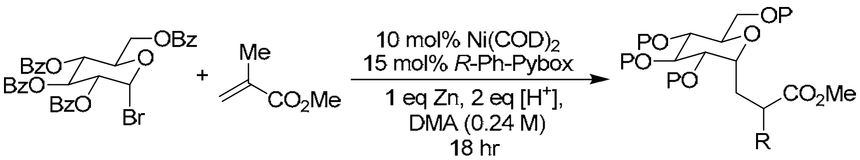
Recent Progress

Ni-catalyzed cross coupling reactions. We have previously reported a Ni-catalyzed Negishi cross-coupling approach to aryl *C*-glycoside synthesis, in which protected glycoside halides are coupled to aryl zinc reagents. This chemistry represents improvements in the field, taking advantage of mild reaction conditions, convenient glycosyl bromide substrates, avoidance of strong Lewis acids or toxic heavy metal activators, and facile preparation of the requisite aryl zinc reagents. Our first generation catalysts focused on terpy- or pybox-coordinated Ni catalysts, since these were found to satisfactorily catalyze the coupling of alkyl or aryl zinc reagent and glycosyl halides (the Negishi reaction) to yield biologically relevant *C*-glycosides. These original catalysts were limited to formation of β-*C*-aryl glycoside products. We previously reported that 2-chloro-1,4-benzoquinone was a useful ligand in that it provided the beta-stereoisomer of the carbohydrate in good yieldso. Use of galactosyl bromide results in an even more selective reaction. In the intervening time we have discovered that the ligand functions to oxidize the aryl zinc reagent and is reduced to the dianionic dihydroquinone. We are currently trying to understand this mechanism and the consequences of the this ligand effect, which seemingly acts on the zinc reagent to control the diastereoselectivity.



R_1	R_2	yield	α:β
OAc	H	69%	4:1
H	OAc	70%	95:5

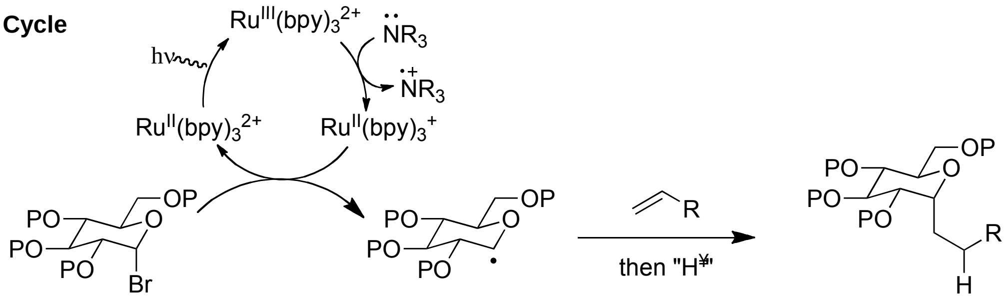
Ni-catalyzed reductive coupling reactions. In the previous funding cycle we developed a method for coupling electron-deficient alkenes with glycosyl bromides using nickel catalyst in the presence of a stoichiometric reductant and a proton source. Mechanistic studies indicated that the Ni-catalyst was activating the carbohydrate via a radical oxidative addition process and that the intermediate C1-radical was being intercepted by the electron deficient alkene (see below). This knowledge led us to consider the possibility that bone fide electron transfer mediators might be capable of converting light energy into useful reduction equivalents.



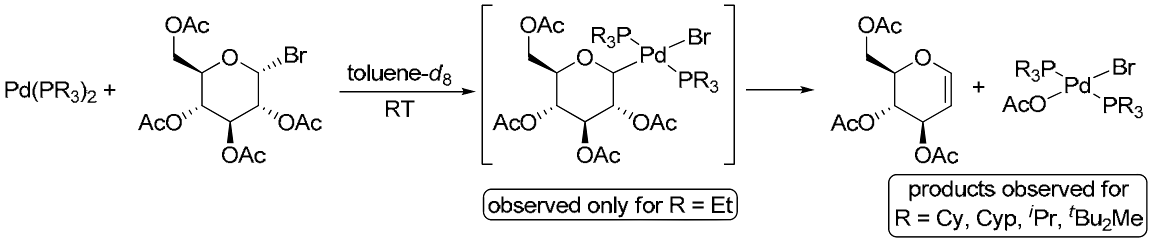
[H$^+$]	Yield	d.r.
NH_4Br	75%	1.6:1
^{i}Pr$_2$NEt·HBr	94%	2:1
^{i}Pr$_2$CHOH	80%	5:1

Light Mediated Reductive Coupling. As we explored the role of the metal catalyst toward greater diastereoslectivities, tris(bypridine)ruthenium(II) chloride emerged as a proficient light mediated catalyst. We have shown that simple compact fluorescent light bulbs provides an extremely efficient and inexpensive driving force for the mild generating of glycosyl radicals. These radicals can then be coaxed to react with electron-deficient alkenes to produce *C*-glycosides with perfect α-selectivity. The reaction requires *N*,*N*-diisopropylethylamine as the stoichiometric reducing agent and allows for the highest reported yield for coupling of glycosyl radicals with some common alkenes, including acrolein and methyl vinyl ketone.

Photoredox Cycle



Oxidative Addition to New Metal Systems. Investigation of alternate metal systems offered the possibility to broaden the reactivity available to carbohydrates. We have shown glycosyl bromides to undergo oxidative addition with *trans*-(PMe$_3$)$_2$Ir(CO)(Cl) in the presence of AIBN to give both anomers of the expected glycosyl Ir(III) complex, which have been characterized by X-ray crystallography. The observed selectivity for these reactions (1.3-5:1 α:β) are likely limited by the radical nature of the proposed mechanism. We have also demonstrated that (R$_3$P)$_2$Pd complexes react with glycosyl halides to give transient glycosyl Pd(II) oxidative addition products, which are susceptible to decomposition via protecting group elimination. For palladium complexes of most phosphine ligands attempted, only the decomposition products are observed at room temperature. The reactivity and structure of the transiently stable (-50°C) (PEt$_3$)$_2$Pd(glucosyl)(Br) is currently being examined.



Future Plans

Ni-Catalyzed Cross-Coupling. Having recently optimized reaction conditions for this catalysis, we plan to and investigate the scope of the α–selective arylation reactions with respect to arylzinc reagent and sugar substrate, including both protecting group and sugar identity.

Light Mediated Reductive Coupling. Current work in this area focuses on exploring the scope of reaction, including the electronic character of the olefin and the identity of the sugar. In addition, studying the role of the Hantzsch ester additive in the reaction mechanism as well as its impact on the yield could greatly enhance our understanding of this chemistry and lead to further improvement to the reactivity. The potential for applications of this catalysis to multi-step syntheses will also be explored.

New Oxidative Addition Systems. Continued investigation into promising reactivity with palladium(0) complexes and glycosyl halides will be a focus for the coming year. Choice of phosphine ligand appears to have a dramatic impact on both the initial oxidative addition step and the stability of the resulting Pd(II) complex. In addition, reactivity studies with new Pd(II) complexes including cross-coupling and insertions could result in new carbohydrate C1 functionalization reactions.

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Catalytic Activity and Mechanistic Insights Regarding High-Valent Metal-Oxo Corrolazines and Their Participation in Oxygen-Atom-Transfer and Hydrogen-Atom-Transfer Reactions

D. P. Goldberg,* K. A. Prokop, P. Leeladee
The Johns Hopkins University, Department of Chemistry, Baltimore, MD 21218
e-mail: dpg@jhu.edu

High-valent metal-oxo species are implicated as key intermediates in a wide range of catalytic oxidations. In particular, manganese- and iron-oxo species are proposed as the active oxidants in numerous synthetic (e.g. Jacobsen-Katsuki epoxidations) and biological (Cytochrome P450 hydroxylations) processes. The preparation of such species for direct interrogation is an important, yet challenging goal because of their typical inherent instability. Our group has taken a biomimetic approach to this problem wherein we have synthesized a modified porphyrinoid framework that we call corrolazine, designed to access high-valent iron-oxo and manganese-oxo complexes.[1] The manganese-oxo complex $(TBP_8Cz)Mn^V(O)$ (TBP_8Cz = octakis(4-*tert*-butylphenyl(corrolazinato)) was synthesized with the corrolazine platform, and provides a rare example of an isolable Mn^V-oxo complex. This complex was shown to catalyze the epoxidation of alkenes with a series of iodosylarene (ArIO) oxidants.[2] Mechanistic studies, however, pointed to a previously unknown oxo-metal-ArIO intermediate as the catalytically active oxidizing agent. An isoelectronic Mn^V-imido complex was shown to participate not in NR group transfer, but in a cross-over reaction where it catalyzes oxygen-atom-transfer via a parallel mechanism. The Mn^V-oxo complex was also shown to be a competent hydrogen atom abstraction agent with certain C-H substrates. Recent kinetic studies have revealed unprecedented rate enhancements (~10,000-fold) for hydrogen-atom-transfer (HAT) induced by the addition of anionic donors to the Mn^V-oxo complex. Density functional theory calculations provide a theoretical framework to understand these remarkable rate enhancements.[3] The mechanistic studies described can be related to the functioning of metalloenzymes such as Cytochrome P450, as well as provide information for designing new synthetic oxidation catalysts.

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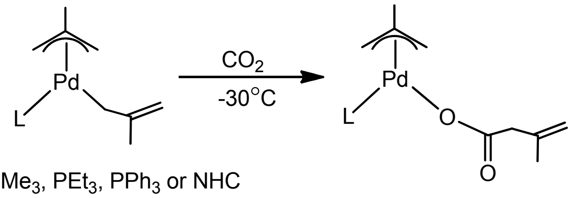
The Reaction of Carbon Dioxide with Palladium Allyl Bonds

Nilay Hazari

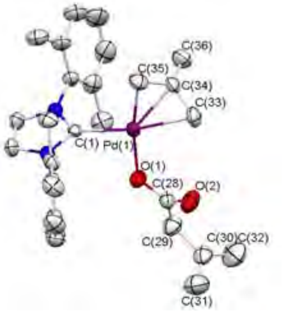
There has been significant interest in the transition metal catalyzed functionalization of CO_2 because this green house gas is potentially a readily available and inexpensive source of carbon in the synthesis of both commodity chemicals and complex organic molecules.[1] In particular the reactions of palladium allyl species with CO_2 to form palladium carboxylates have been suggested as a crucial step in several catalytic cycles. These include systems for the coupling of CO_2 with butadiene to form lactones,[2] the carboxylation of allyl stannanes[3] and allenes[4] and the carboxylative coupling of allylstannanes and allyl halides.[5] However, there has been little research investigating stoichiometric reactions of well defined palladium allyl complexes with CO_2 and the feasibility, scope and mechanism of this reaction remain unclear. In this presentation our current research in this area will be described.

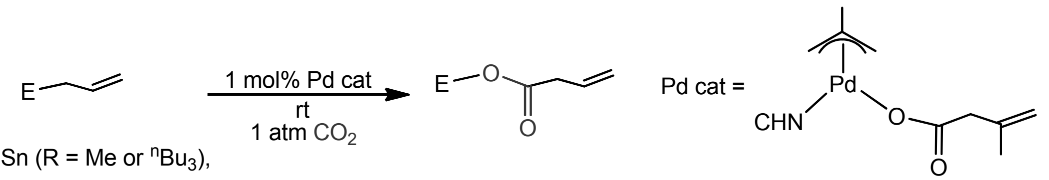
We have prepared a family of palladium allyl complexes of the type bis(2-methylallyl)Pd(L) (L = PMe_3, PEt_3, PPh_3 or NHC; NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene), which contain one η^1 and one η^3-2-methylallyl ligand. These complexes react rapidly with CO_2 at low temperature to form well defined palladium carboxylates, which have been fully characterized for the first time (Eq 1). Using a combination of computational and experimental techniques we have performed mechanistic studies on the carboxylation reaction. The coordination mode of the allyl ligand is crucial and whereas nucleophilic η^1-allyls react rapidly, η^3-allyls do not react. We propose that the reaction of η^1-palladium allyls with CO_2 does not proceed via direct insertion of CO_2 into the Pd-C bond but through nucleophilic attack of the terminal olefin on electrophilic CO_2 followed by a palladium mediated S_N2 reaction. Furthermore, the carboxylate products from the reaction of CO_2 with bis(2-methylallyl)Pd(L) are by far the most active catalysts reported to date for the carboxylation of allylstannanes with CO_2 (Eq 2) and are the first catalysts for the carboxylation of allylboron species.



(1)

L = PMe_3, PEt_3, PPh_3 or NHC
NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene



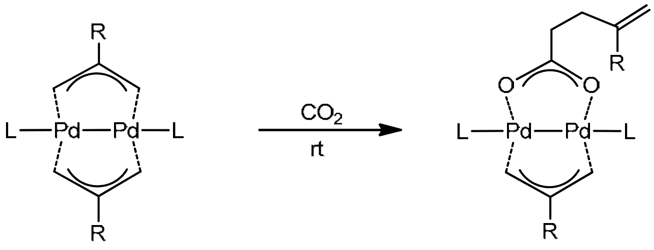


(2)

E = R_3Sn (R = Me or $^nBu_3$), $(OH)_2B$

NHC = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene

Alongside our work with monomeric palladium allyls, we have demonstrated that dimeric palladium(I) complexes with bridging allyl ligands also react with CO_2 (Eq 3). The reaction of these species with CO_2 occurs in hours at room temperature and the mechanism is currently being investigated but is believed to involve direct coordination of CO_2 to palladium.



(3)

L = PMe_3, PEt_3, PPh_3 or NHC
R = H or CH_3

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Grant Number DE-FG02-09ER16089 **Patrick L. Holland**

High-Spin Cobalt Hydrides for Catalysis

Postdoc: Ajdin Kavara
Graduate Student: Thomas Dugan
Collaborator: Thomas Cundari (Univ. North Texas)
Contacts: Department of Chemistry, University of Rochester, Rochester, NY 14627; holland@chem.rochester.edu

Goals

Explore the catalytic ability of low-coordinate cobalt complexes in small-molecule catalysis. Determine the mechanisms of organometallic transformations at metals with high-spin electronic configurations.

DOE Interest

Organometallic chemists have traditionally used catalysts with strong-field ligands that give low-spin complexes. However, complexes with a weak ligand field have weaker bonds and lower barriers to geometric changes, suggesting that they may lead to more rapid catalytic reactions. Developing our understanding of high-spin complexes requires the use of a broader range of spectroscopic techniques, but has the promise of changing the mechanism and/or selectivity of known catalytic reactions. These changes may enable the more efficient utilization of chemical resources. A special advantage of cobalt and iron catalysts is that the metals are more abundant and cheaper than those currently used for major industrial processes that convert unsaturated organic molecules and biofeedstocks into useful chemicals.

Recent Progress

Starting New Grant: This grant started in September 2009, and we have arranged the necessary manpower (Dr. Kavara starts May 2010) and equipment (delivery of EPR spectrometer expected in summer 2010) to ramp up the project.

Development of Unsaturated Cobalt Precursors: For the reasons described above, we anticipated that β-diketiminatocobalt complexes would be a fertile ground for reductive reactions. The literature on low-coordinate β-diketiminatocobalt complexes had been relatively undeveloped, consisting of part of one paper from our group, and one from Timothy Warren's group. Last year, we published three papers on cobalt chemistry, including novel paramagnetic N_2, alkyl, and hydride complexes. These have been characterized with X-ray crystallography, magnetic susceptibility, and NMR and IR spectroscopies. The cobalt(I) complex $[KLCoH]_2$ (Figure, left) is the first example of a three-coordinate transition metal with a hydride ligand. In addition, the cobalt(II) complex $[LCoH]_2$ undergoes [1,2]-addition to the double bonds of alkenes.

$[KLCoH]_2$

LCo

In an interesting development, we have learned that it is possible to isolate the surprising, *highly* unsaturated species $L^{tBu}Co$. Rather than being two-coordinate at cobalt, this high-spin cobalt(I) complex has "slipped" one of its imine donors to form an η^6 interaction with an arene (Figure, right). The "slipping" isomerization is reversible upon addition of donor ligands. Therefore, we anticipate that $L^{tBu}Co$ will be a fruitful starting material for small-molecule activation reactions and catalysis.

Catalytic Hydrogenation by Cobalt Complexes: $L^{tBu}Co$ and the hydride complexes catalyze the hydrogenation of cyclohexene at mild temperatures (60 °C). The scope and mechanism of the hydrogenation reaction are under study.

Future Plans

New Reactions of High-Spin Cobalt Complexes: The potential applications for $L^{tBu}Co$ as a stoichiometric reactant and and as a catalyst are many. We will focus on transformations of industrially important molecules, as well as biomass platform molecules.

Catalysis with High-Spin Cobalt Complexes: The mechanism of catalytic hydrogenation remains to be determined. We will endeavor to extend the catalytic [1,2]-addition ability to other unsaturated substrates.

Spectroscopy of High-Spin Cobalt(II) Species: Since the cobalt(II) species have an $S = 3/2$ spin state, they have rich EPR spectra that give information on the orbital occupation of the complex. These will be coupled with computational studies in order to outline the electronic structure determinants of reactivity in paramagnetic cobalt organometallic complexes.

Publications (2008-2010)

- K. Ding, A. R. Pierpont, W. W. Brennessel, G. Lukat-Rodgers, K. R. Rodgers, T. R. Cundari, P. L. Holland, "Cobalt-Dinitrogen Complexes With Weakened N-N Bonds," *J. Am. Chem. Soc.* **2009**, *131*, 9471-9472.
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Versatile New Hybrid Catalytic Materials for Selective Liquid and Vapor-Phase Reactions: Porous Phosphine Coordination Materials Consisting of Well-Defined Organometallic Species

Simon M. Humphrey

Department of Chemistry and Biochemistry, University of Texas at Austin, 1 University Station A5300, Austin TX 78712-0165; email: smh@cm.utexas.edu

Porous metal-organic coordination polymers constructed using organophosphine building blocks are unique examples of phosphine-abundant solid-state materials that are both thermally and chemically robust.[1,2] The so-called Phosphine Coordination Materials (PCMs) are crystalline solids, whose composition and structures are well understood. In essence, the PCMs provide regular phosphine-abundant surfaces that are ideal candidates for post-synthetic functionalization with noble metals in order to generate stable hybrid catalytic materials. Such modified materials contain well-defined single-site catalysts that mimic well known and industrially important phosphine-based organometallic complexes. There are several potential added benefits of the catalytic PCMs over their molecular counterparts, which include, size and shape-selectivity based on precise pore topology, ease of recovery, and the ability to function under both liquid and vapor-phase conditions. A suitable family of PCMs has already been prepared and is currently being investigated in the preparation of catalysts for both hydrogenation and oxidation chemistry. Our studies are also being extended to the incorporation of inherently chiral catalytic sites, using chelating bis(phosphines) for chiral catalysis.

In addition, the phosphine-abundant PCMs have the potential for selective growth of noble metal nanoparticles within the pores, by using molecular species as well-defined nucleation sites. It is hoped that this process may result in the template formation of very small nanoparticles with unusual and unique surface structures, based on using the parent PCMs as sacrificial ‘molds’, to form colloidal composites.

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

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

Students:	Ryan Reith, Brett Swartz, Ting Li, Meagan Evans
Postdocs:	Taro Tanabe
Collaborators:	Juventino García (UNAM, Mexico City) Odile Eisenstein, Dr. Eric Clot (Univ. Montpellier)
Contact:	Dept. of Chemistry, University of Rochester, Rochester, NY 14627 phone: (585)275-5493; Email: jones@chem.rochester.edu webpage: http://www.chem.rochester.edu/faculty/faculty.php?name=jones 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, chloroalkanes, ketones, and acetylenes, and (3) C–C bond activation in aryl-alkynes, aryl-nitriles, and allyl-nitriles, (4) carbon-fluorine bond activation with zirconium. We have made progress in each of these areas, as described below.

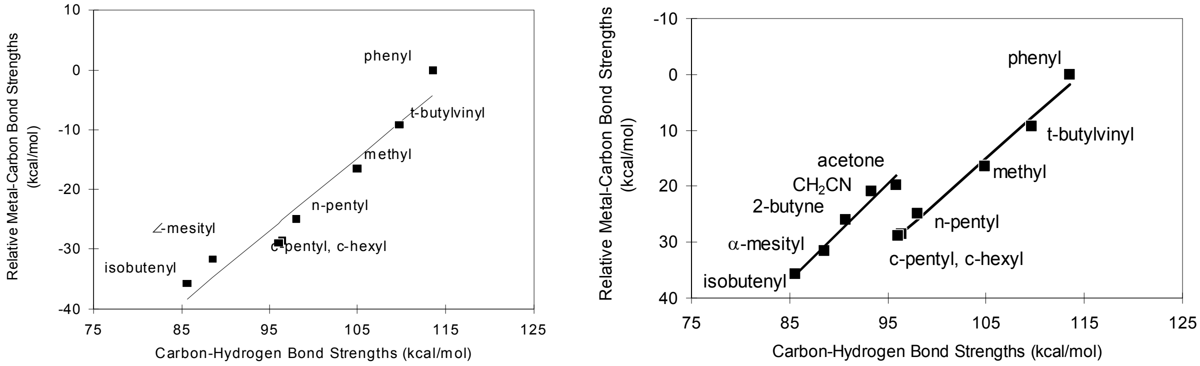
Significant Recent Achievements and Results

The accomplishments of the current year include: (1) measurement of relative metal-carbon bond strengths for a variety of substituted hydrocarbons, demonstrating the importance of resonance anion stabilization in strengthening M-C bonds; (2) a complete experimental and theoretical study of C-CN bond cleavage in benzonitrile; (3) energetics of C-H bond activation of fluorinated aromatic hydrocarbons both by theory and experiment, establishing a quantitative basis for the "ortho-fluorine effect"; (4) C–C bond activation selectivities in asymmetric acetylenes; and (5) solvent effects and activation parameters in the competitive cleavage of C-CN and C-H bonds in 2-methyl-3-butenenitrile using nickel(0).

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

C–H Bond Activation:

Using the [Tp'Rh(CNneopentyl)] scaffold, we have used kinetic measurements to determine relative metal-carbon bond strengths for a variety of substituted hydrocarbons. The new data shows the importance of alkyl groups for which resonance anion stabilization is present. In these ligands, the increase in the ionic component to the metal-carbon bond increases the strength of the bond. New alkyl groups studied that support this hypothesis include cyanomethyl ($-CH_2CN$), 2-butynyl ($-CH_2C\equiv CCH_3$), and C-enolate ($-CH_2C(=O)CH_3$). These combine with the earlier studied α-benzyl and allyl groups, which fell distinctly off the trendline joining 'normal' hydrocarbons (alkyl, aryl, and vinylic C-H). This effect can be dramatically demonstrated by looking at a plot of M-C vs. H-C bond strengths (Figure 1). The resonance contribution to the bonding adds about 10 kcal/mol to the M-C bond strengths. A thorough thermodynamic analysis has been performed to justify this hypothesis.



Old analysis: *New analysis:*

Figure 1. Prior published trend in M-C vs H-C bond strengths (left). New dual correlations with added resonance-stabilized data (right).

We have also examined C-H activation in a series of fluoroaromatics using the [Tp'Rh(CNneopentyl)] fragment. Kinetic competition and reductive elimination studies allow the determination of relative M-aryl^F bond strengths, and a plot of this data shows a linear correlation with a slope of 2.15. In collaboration with Eric Clot and Odile Eisenstein, we have prepared a similar plot with calculated relative M-C bond strengths. The agreement between the experimental and theoretical plots is uncanny (Figure 2)!

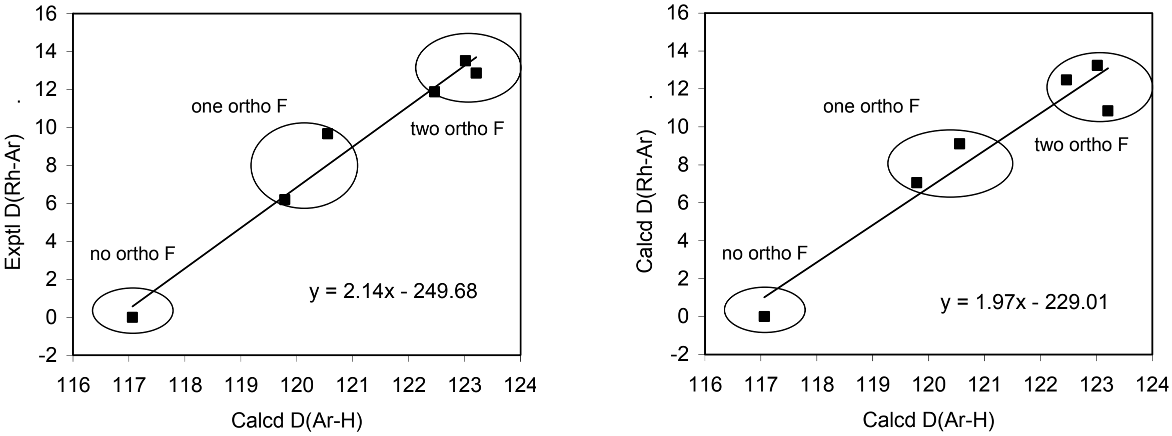


Figure 2. Plots of M-aryl^F vs. H-aryl^F bond strengths. Experimental (left) and theory (right).

C–C Bond Activation:

We have finished a complete experimental and theoretical study of the mechanism of cleavage of the C-CN bond in benzonitrile by the nickel(0) species , using [Ni(dippe)]. We have found that the initially formed η^2-C,N-nitrile complex must first rearrange to an η^2-C,C-arene complex. This intermediate can be observed as a kinetic product if the reaction is carried out at low temperature. The η^2-arene complex is fluxional, yet it maintains distinct phosphorus environments. The η^2-arene complex then undergoes C-CN cleavage by first making the new Ni-aryl and Ni-CN bonds, and then cleaving the C-CN bond. In the transition state, the C-CN bond is at a 30° angle to the NiP_2 plane, allowing the two carbons to approach the metal closely without steric interference with the phosphines. The energetics have been mapped out completely using DFT, and provide good agreement with experiment.

We have also investigated C–C bond activation selectivities by Pt(dippe) with asymmetric acetylenes. These reactions have been found to be highly dependent on the chelate ligand employed, with bis-phosphine or P-N ligands being active for C-C cleavage. Only Ph-acetylene bonds are cleaved in these studies.

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.

Future Plans

We are now examining other resonance and inductively stabilized R-H bonds to see how their M-C bond strengths vary. We are also examining the effect of substitution of phosphine for CNR in the activity of [Tp'Rh(L)] towards C-H bonds in polyfluoroaromatics to see if the effect is larger than with isocyanide ligands. We are looking at C-CN cleavage in a variety of polycyclic aromatic nitriles.

DOE Publications for 2008-2010:

1. "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*, 1834-1840. (DOE)
2. "Study of the reactivity of 2-methyl-3-butenenitrile with Ni(0)-N-heterocyclic carbene complexes," Alberto Acosta-Ramírez, David Morales-Morales, Juan Manuel Serrano-Becerra, Alma Arévalo, William D. Jones and Juventino J. García, *J. Mol. Catal. A, Chemical*, **2008**, *288*, 14-18. (DOE)
3. "Solvent Effects and Eyring Activation Parameters in the Competitive Cleavage of C-CN and C-H Bonds in 2-Methyl-3-Butenenitrile Using [(dippe)NiH]$_2$," Brett D. Swartz, Nicole M. Reinartz, Juventino J. Garcia and William D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 8548-8554. (DOE)
4. "Experimental and Theoretical Examination of C–CN Bond Activation of Benzonitrile using Zerovalent Nickel," Tülay A. Ateşin, Ting Li, Sébastien Lachaize, Juventino J. García, and William D. Jones, *Organometallics* **2008**, *27*, 3811-3817. (DOE, NSF)
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6. "Synthesis, Characterization, and C–H/C–C Cleavage Reactions of Two Rhodium-Trispyrazolylborate Dihydrides," Douglas D. Wick and William D. Jones, *Inorg. Chim. Acta*, **2009**, *362*, 4416-21. (DOE)
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8. "Energetics of C-H Bond Activation of Fluorinated Aromatic Hydrocarbons Using a [Tp'Rh(CNneopentyl)] Complex," Meagan E. Evans, Catherine L. Burke, Sornanong Yaibuathes, Eric Clot, Odile Eisenstein, and William D. Jones," *J. Am. Chem. Soc.* **2009**, *131*, 13464-13473. (DOE)
9. "Diverse Chemical Applications of N-Heterocyclic Carbenes, *J. Am. Chem. Soc.* **2009**, *131*, 15075-7.
10. "Reactivity Differences of Pt^0 Phosphine Complexes in C–C Bond Activation of Asymmetric Acetylenes," Ahmet Gunay, Christian Müller, Rene J. Lachicotte, William W. Brennessel, William D. Jones, *Organometallics* **2009**, *28*, 6524-6530. (DOE)

DE-FG02-03ER15459 **Christopher W. Jones**

"Developing the Science of Immobilized Molecular Catalysts"

Co-PI's: Weck, M.; Davis, R.; Ludovice, P.; Sherrill, D.;
Postdocs: Venkatasubbaiah, K.; Zhu, X.; Liu, Y; Brunelli, N.; Zheng, X.; Madhavan N.; Norman, A.;
Students: Pinon, V.; Takatani, T.; Key, R.; Long, W.; Sears, J.; Swann, A.; Jain, S.; Gill, C.; Goyal, P.; Richardson, J. M.; Shiels, R. A.; Xi., Y.;
Contact: C. W. Jones, P. J. Ludovice, Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332; cjones@chbe.gatech.edu; pludovice@chbe.gatech.edu
M. Weck, Chemistry, New York University, New York, NY 10003; marcus.weck@nyu.edu
R. J. Davis, Chemical Engineering, University of Virginia, Charlottesville, VA 22904; rjd4f@virginia.edu
C. D. Sherrill, Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332; sherrill@gatech.edu

Goal

Immobilized organometallic catalysts, in principle, can give high rates and selectivities like homogeneous catalysts with the ease of separation enjoyed by heterogeneous catalysts. However, endowing molecular catalysts with easy separation characteristics is often not sufficient to justify the expense of making supported catalysts. In this work, we seek to develop supported catalysts with enhanced catalytic properties, with specific attributes not found in the original homogeneous complexes. A significant focus is placed on developing novel strategies for the synthesis of cooperative catalysts, systems that require the simultaneous or sequential activation of substrates by two distinct catalytic sites. By assembling an interdisciplinary research team that can probe all aspects of immobilized organometallic catalyst design, the entire reacting system can be considered, where the active molecular site, for example a metal complex, the active site-support interface and the properties of the support can all be considered simultaneously from both experimental and theoretical points of view. In particular, researchers at GT, NYU and the UVA are developing design principles for supported metallated salen catalysts that follow a monometallic (Ru- and Al-Salen) or a bimetallic (Co- and Al-Salen) pathway. Using these model systems, the fundamental principles that can be used to understand and design future classes of supported, cooperative catalysts may be elucidated.

DOE Interest

The work performed in this program elucidates fundamental principles important in the design of immobilized catalysts. These catalysts have the potential to be very active and selective while being easy to separate for the reaction media. All of these aspects provide a substantial energy advantage in chemical processing.

Recent Progress (2009-present)

In the last year, significant focus has been placed on developing structure-property relationships for our previously reported oligomeric cyclooctene supported Co-salen catalysts in the hydrolytic kinetic resolution (HKR) of epoxides. In parallel, we have also explored their utility in epoxide ring-opening reactions using other nucleophiles, such as alcohols and phenols.

The Bigger, the Better: Ring-size Effects of Macrocyclic Oligomeric Co-salen Catalysts. We recently reported the ring-expanding olefin metathesis of cyclooctene salen monomers to generate Co-salen complex with pendent Co-salen units tethered on a macrocyclic ring. This system enforces the cooperative bimetallic HKR mechanism and exhibits outstanding catalytic properties. However, due to the uncontrollable features of the cyclization reaction, a mixture of macrocyclic oligomers with different ring sizes was obtained. MALDI-TOF mass spectra revealed compositions ranging from cyclic dimer to cyclic decamer with decreasing population from low molecular species to high molecular species. We hypothesized that the ring size might have a great impact on the selectivity and reactivity of the macrocyclic oligomeric catalysts.

We have developed a purification procedure to separate macrocyclic salen ligands based on ring-size. Pure dimers, trimers, tetramers as well as ‘tetramer to hexamer’ and ‘pentamer to decamer’ mixtures were obtained. We compared the catalytic efficiency of these isolated cyclic Co-salen complexes in the HKR of allyl glycidyl ether. The results showed the different ring-size oligomers exhibited dramatically different catalytic behavior. The dimer had no catalytic activity and an increase of the ring size resulted in accelerated rates, with the largest size oligomers exhibiting superior catalytic efficiencies (Figure 1). The cause of the different catalytic behaviors was investigated by NMR spectroscopy and computational modeling. These studies revealed that the dimer ring is highly strained, preventing efficient interactions between pendent salen moieties, resulting in the poor reactivity in the bimetallic HKR reaction. For higher mass oligomers, the accelerated reaction rate was attributed to the higher flexibility of the pendent Co-salens afforded by the increased ring size.

The standard mixture of oligomeric cyclooctene macrocycles (**1**) was also used in the asymmetric ring-opening of epoxides using alcohols and phenols as nucleophiles. The cyclooctene-based catalyst (**1**) and our bi-salen catalyst (**2**) were found to be more active than

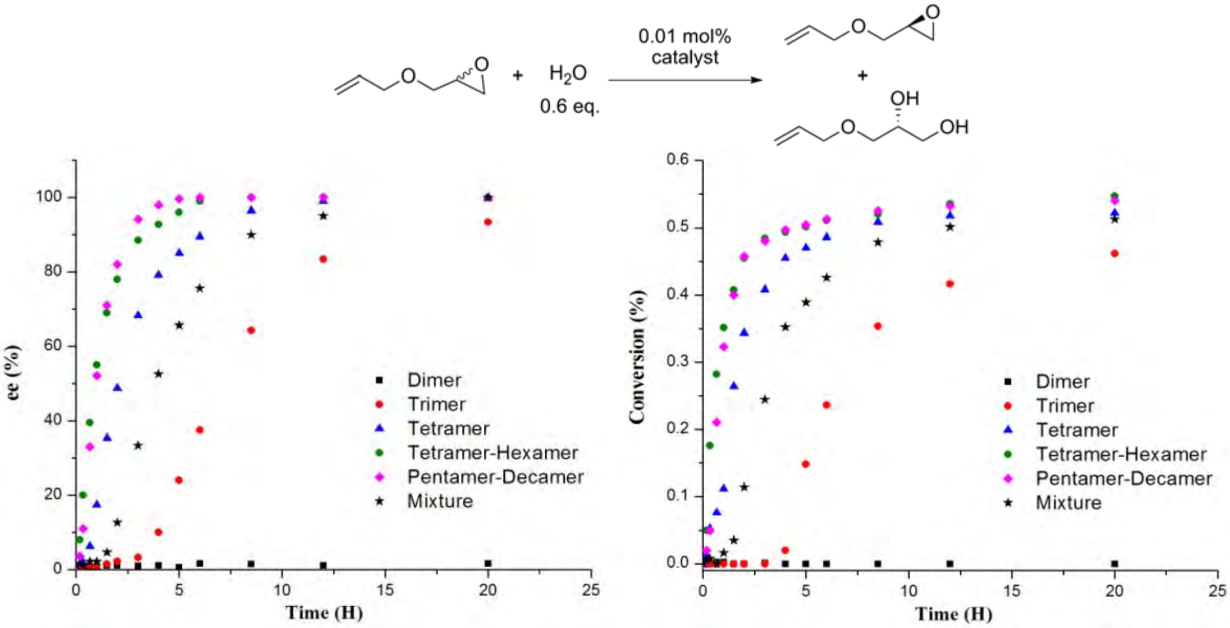

Figure 1. HKR of allyl glycidyl ether catalyzed by macrocyclic Co-salen complexes with different ring sizes. Enantiomeric excess kinetic plot (**A**) and conversion kinetic plot (**B**).

Jacobsen's cyclic oligomeric catalyst in the kinetic resolution of epichlorohydrin using methanol as the nucleophile (Figure 2).

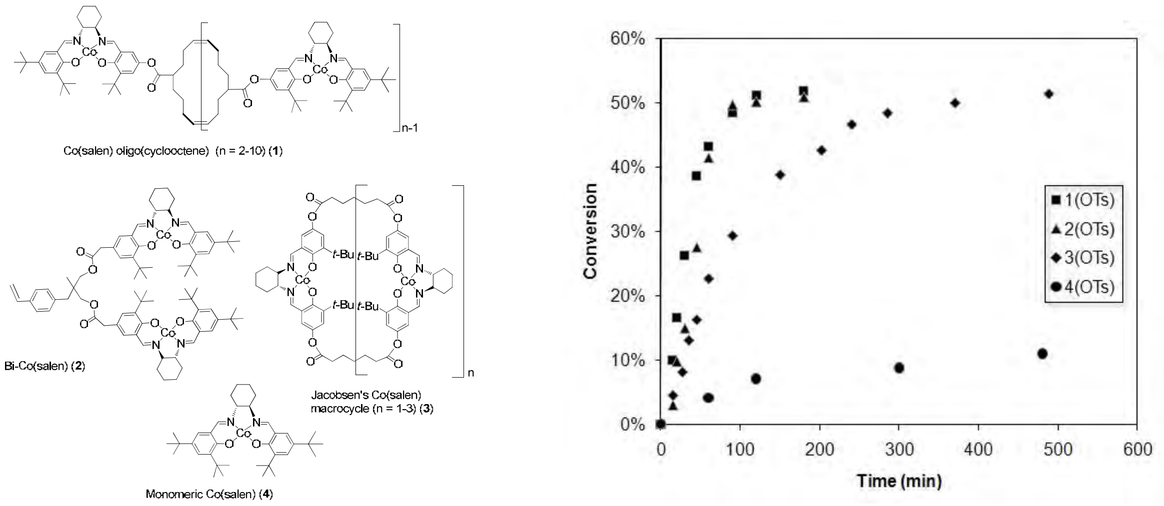

Figure 2. Asymmetric ring-opening of *rac* 1-epoxyhexane with methanol catalyzed by **1**(OTs)**, 2**(OTs)**, 3**(OTs) and **4**(OTs) at 0.1 mol% Co loading**.**

Shell Cross-Linked Micelle (SCM) Based Nanoreactor for HKR of Epoxides. The research team is also developing shell crosslink (SCL) micelle based nanoreactors with catalysts located in the core of the micelle. Our long term goal is to develop SCL micelle nanoreactors containing multiple catalysts for performing catalytic tandem reactions using isolated catalytic sites. Due to physical separation of catalysts (some catalysts located in the core, others on the surface of micelle), even non-compatible catalysts can be used to carry out individual reactions without mutual interference or quenching. We have synthesized SCL micelles containing salen-Co complexes and investigated the catalytic HKR of epoxides with these micelle systems. Through systematic variations of variables such as micelle size, composition, block

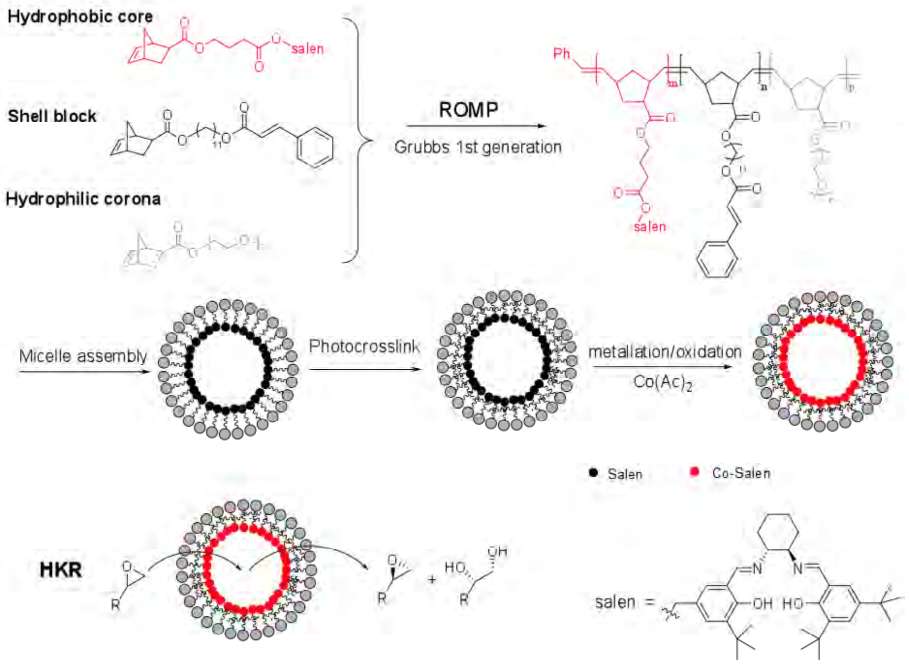

Figure 3. Monomer building blocks for SCL design, micelle formation and HKR.

ratio and crosslink degree, we expect to optimize catalytic efficiency. The initial SCL micelles (Figure 3) are based on three norbornene monomers: norbornene-PEG, norbornene-diester, norbornene-cinnamate - amphiphilic block copolymers were synthesized and the polymerization processes were monitored by ^{1}H NMR spectroscopy and GPC. After optimization of procedures for micelle formation, including micelle photocrosslinking, metallation, oxidation and purification, high quality salen-Co loaded SCL micelles were synthesized reproducibly. The HKR reactions were tested under various conditions and optimized catalysts are under development.

What is the Most Active HKR Catalyst? Over the course of the last several years, we have developed numerous new HKR catalysts. However, the conditions under which these catalysts were evaluated often differed from the procedures used in the literature. Recently, we assembled all of the new HKR catalysts we have developed along with the best cooperative catalyst reported in the literature. The catalysts were compared under rigorously identical conditions, and the relative activities of each catalyst was elucidated. Some of our catalysts are among the most active HKR catalysts reported, with the oligomeric cyclooctene-based catalyst the most active catalyst currently known.

Asymmetric Henry Reaction. Recently, we began extending our studies of enantioselective cooperative catalysis using supported metal complexes (Co-salen, Al-salen) to acid-base bifunctional catalysis. The reaction between a carbonyl compound and a nitroalkane, better known as the Henry (or nitroaldol) reaction, is an important C-C bond formation reaction that produces β-nitroalcohols. The products of the Henry reaction can contain up to two contiguous chiral carbon centers and reduction of the nitro group in β-nitroalcohols can lead to the formation of aminoalcohols, which occur widely as natural and synthetic products as well as chemical intermediates. Homogeneous metal complexes and organocatalysts have been reported to catalyze the Henry reaction with high enantioselectivities. Compared to homogeneous catalysts, there is much less success reported with heterogeneous catalysts, although the advantages of easier separation and recycle of heterogeneous catalysts are significant drivers for research. It has been reported that chiral-ligand-modified nanocrystalline MgO (NAP-MgO) is effective and reusable for catalyzing the Henry reaction with comparable enantiomeric excess (ee) to a homogeneous catalyzed system. However, the nature of the active sites on the nanocrystalline MgO and the synergistic role of the ligand on the catalyst needs further exploration. It is well-known that the surface structures and therefore the catalytic properties of MgO materials depend on their preparation method. Therefore, we are proceeding to synthesize MgO catalysts with different surface structures to elucidate the structure-reactivity relationships for the chiral Henry reaction of benzaldehyde with nitromethane. The first step of this project is to reproduce the literature results that showed high yield and ee's for the reaction of benzaldehyde with nitromethane. It was speculated that a certain arrangement of surface hydroxyl groups, especially those on edges and corners, with the ligand of (S)-(-)-binol were critically important for high ee's. Thus, we plan to explore the effects of base site distribution on MgO as well as the interaction of base sites with the chiral ligand on the MgO catalyst.

Electronic Structure of Metal Salens. The electronic structure of metal-salen systems is intricate because of electronic near degeneracies. Thus, we undertook several detailed, systematic studies of model d_0, d_2, and d_6 metal-salen complexes, utilizing the robust complete-active-space self-consistent field (CASSCF) method to fully account electronic near - degeneracies. These computations were then improved by third-order perturbation theory (CASPT3) to capture the usual, “dynamical” electron correlation effects. From these computations, we obtained the energies for low-lying singlet, triplet, and quintet electronic states, because it is not always clear for a given system which is actually the ground state (this is a serious issue that is routinely ignored in the literature). Our goal is to use these high-quality benchmarks to help select a more efficient computational method for routine, yet reliable computations of these systems. Overall, the popular B3LYP and BP86 density functional theory (DFT) methods performed rather poorly with singlet-triplet, triplet-quintet, and singlet-quintet energy gap mean absolute deviations of up to 40 kcal mol^{-1}. Moreover for the d^6 series, B3LYP results never reproduced the CASPT3 ordering of states, and only correctly identified the ground state for one third of the test cases. Fortunately, DFT and CASSCF optimized geometries agreed to normally within 0.1 Å root mean squared deviation. Clearly, the reliability of DFT methods is still highly debatable for the energetics of metal-salen systems (although geometries appear reliable). Our recent work extends the systematic study to include d^4 metal-salen complexes [the Cr(II)-, Mn(III)-, Fe(IV)-, Mo(II)-, Tc(III)-, and Ru(IV)-metal centers]. We have also investigated the performance of the new M0 family of meta-generalized gradient approximation (meta-GGA) DFT functionals, which are reported to be superior for metal-containing systems. The entire M0 family (M05, M05-2X, M06, M06-2X, M06-HF, and M06-L), B3LYP, and BP86 functionals were tested. It was found that there was no statistical improvement for the energy gaps of any M0 family functional compared to the B3LYP or BP86 functionals. Furthermore, only the B3LYP and M06-2X functionals performed well enough to obtain all but one correct ordering of states. It appears that the metal-salen systems are difficult for even the more advanced DFT functionals. Therefore, the accuracy of any functional should be assessed on a case-to-case basis since over all test cases here, DFT results were unreliable.

Our results suggest that future computational modeling of transition-metal-salen systems needs to be very carefully assessed against experiment and higher-level theory. Fortunately, main-group metals should be free of these difficulties. Hence, we have devoted significant effort to studying the Al(III)-salen complex as a ‘well-behaved’ system. Current work, utilizing the BP86 functional, addresses the cyanide addition to an αβ-unsaturated imide as catalyzed by Al(Cl)-salen, suggesting that at least two steps of the mechanism require the cooperation between two Al-salen complexes. This further supports the conclusion that this Al-salen catalyzed reaction is a cooperative one, as suggested by experiment.

Publications From This Project (2008-present) (40% of papers with multiple PIs)

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2. Sears, J. S.; Sherrill, C. D., Assessing the Performance of Density Functional Theory for the Electronic Structure of Metal-Salens: The d2-Metals. *J. Phys. Chem. A* **2008,** *112*, 6741-6752.
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DE-FG02-05ER15699 **Dorothee Kern**

The choreography of an enzyme's dance – molecular pathways of conformational transitions

Postdocs: Young-Jin Cho, Francesco Pontiggia
Students: Jordan Kerns, Dimitar Pachov
Collaborators: Michael Hagan (Brandeis University)
Contacts: Brandeis University, Dept. of Biochemistry/HHMI, 415 South Street, Waltham, MA 02453, dkern@brandeis.edu

Goal

We want to utilize the unique properties of extremophiles (enzymes that live under extreme conditions) to study protein structure, dynamics and catalysis under a wide range of physical conditions. The goal is to characterize the entire energy landscape of enzymes including the chemical steps and protein conformational rerrangements to identify basic physical principles of enzyme catalysis. Particular attention is devoted to their dynamic character, on of the missing pieces for future rational design of biocatalysts.

DOE Interest

Biocatalysis and biotransformations offer attractive new alternatives to chemical catalysis and transformations. Enzyme catalyzed biomass transformation for the mass production of biofuels has recently become a key focus.

Recent successes in predicting and designing protein structures demonstrate the power of a combined approach between computation and experiment. However for enzyme function **well-defined and efficient changes in structure** are essential. The lack of understanding of this aspect of protein chemistry is most likely the reason for the limited success of designing biocatalysts. Our research is aiming to provide such information. We are particularly taking advantage of nature's evolution of biocatalysts that can work under extreme conditions, so called extremophiles.

Recent Progress

Recent advances in technology development including NMR relaxation[6,7] and novel x-ray crystallography[1] allowed us to characterize the energy basins in an energy landscape, the valleys in the mountains. The concept of pre-existing low populations of conformational substates which are essential for protein function, and the concept of a population shift via selected ligand binding, and not induced fit, is now becoming more widely accepted[1-7]. However, this concept raises the key subsequent question of *how* proteins can convert from one folded structure to another, how they climb over the mountain (the energy barrier) from one valley to another. This new question of the molecular pathways for conformational transitions will be addressed in this talk[1-4].

The energy landscape of extremophilic adenylate kinase (Adk) both during catalysis and in the absence of substrates is being characterized, which allows identification of dynamics that are linked to enzyme catalysis. Ultra-high resolution crystallography on a kinase during catalysis together with new NMR relaxation techniques delivers big surprises into the chemical mechanism of phosphotransfer of kinases (Fig. 1). Second, using a combination of high-pressure NMR experiments and computation on a piezophilic and mesophilic enzyme homolog, the transition pathway of the opening and closing of the enzyme and in particular information about the transition-state can be inferred (Fig. 1).

This example illustrates the power of combining computation with NMR and x-ray to unravel not only the functional essential states that are sampled by the protein but also the pathways of conformational transitions. Of particular value has been our studies of nature's evolution of extremophilic enzymes to be highly active under "nonstandard" conditions. New concepts learned from these enzymes will offer better advances in enzyme optimization and design.

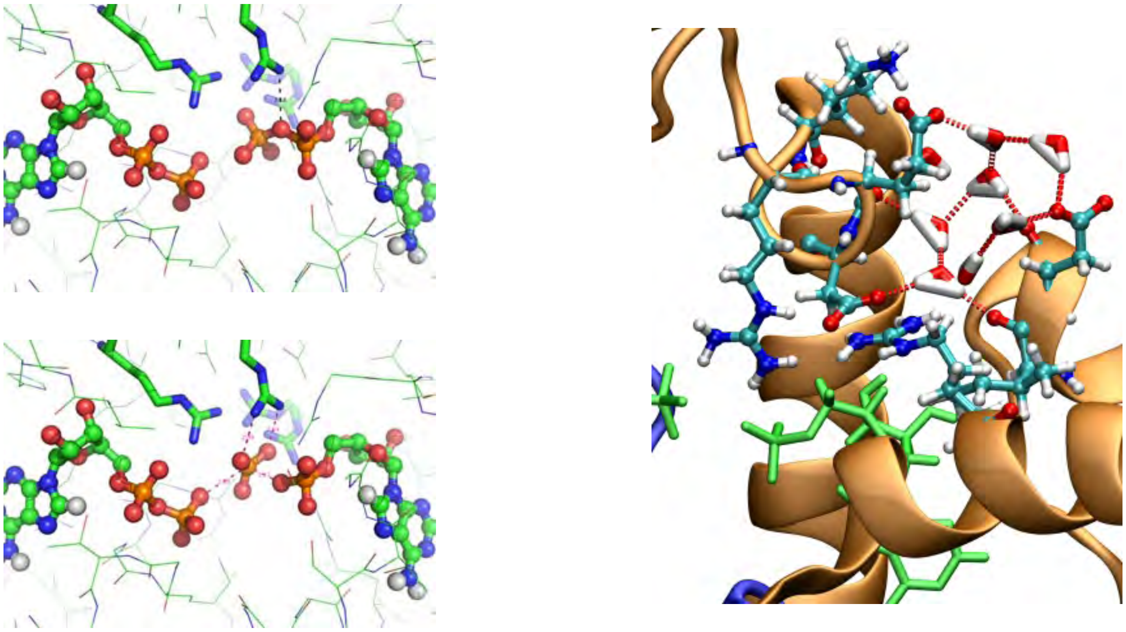

Fig. 1: An enzyme caught in the act. Left: Snapshots of the *chemical step*, the phosphotransfer step, in adenylate kinase (Adk) during turnover. Two ADP molecules in the active site of thermoAdk, determined by x-ray crystallography of the enzyme during turnover. The electron density indicates partial occupancy of the b-phosphate in the AMP site with 70 % ADP/ADP (top) and 30% AMP/ PO3- (bottom) (resolution 1.25 Å). In parallel, the kinetics of phosphotransfer was measured by NMR relaxation (data not shown).
Right: Snapshots of the transition pathways for lid opening (*conformational step*) of piezoAdk (right) calculated by Targeted molecular dynamics and validated by high-pressure NMR experiments. An extended network of hydrogen-bonded water molecules is seen for piezoAdk in the transition state (water molecules are shown in red and white) in very good agreement to our pressure dependence of the opening rate measured by NMR for piezoAdk.

Future Plans
Chemical step: We are currently refining a number of x-ray structures during catalysis, in the presence of substrate analogues, transition state analogues and some active site mutants to piece together the atomistic details of the chemical reaction catalyzed in the active site. Strikingly, we can trace movements of active site Arg that coincide with the changes of the transferable phosphoroyl group by the identification of partial occupancy. These crystallographic data are complemented with NMR dynamics to measure exactly the rates of the reaction.

Large conformational rearrangement (opening and closing of the enzyme): We are working on new computational approaches to simulate the rate-limiting opening/closing events to yield free-energy profiles for the enzyme. The results from the computation is being quantitatively being tested by NMR relaxation experiments (providing dynamic data at atomic resolution), enzymatic assays, and single molecule FRET experiments (enabling the dissection of the contribution of individual ternary complexes to the overall rate enhancement). Our preliminary results are very encouraging that detailed the energetic contribution of atomic interaction in an enzyme can be computed opening the door for rational design of efficient enzymes in the future.

Publications in part supported by DOE (2007-2010)

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Nicolai Lehnert

Development of Biologically Inspired Catalysts for Multielectron Reductions of Substrates Relevant to Energy Applications

Additional PIs: N/A
Postdoc: N/A
Students: Deidra Gerlach, Thomas Chae
Collaborators: Levi Thompson, Dimitri Coucouvanis
Contacts: University of Michigan, 930 N University - CHEM 2807, Ann Arbor, MI 48109; lehnertn@umich.edu

Goal

To develop and optimize biologically inspired catalytic arrays, comprised of a catalytic site and an electron reservoir (which can be an electrode surface), that are capable of multielectron reductions of substrates. The catalytic material requirements must meet these parameters: be cost efficient, energy efficient, water stable, and proficient at reducing a variety of substrates. While developing these materials, insight into the mechanisms and outer shell influences that mediate the rate of reduction in the related enzymes will be investigated.

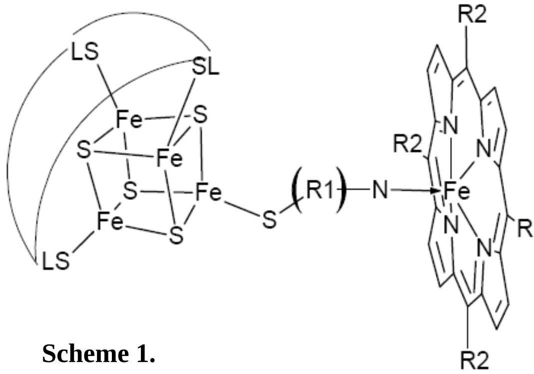
DOE Interest

The global push to move from the total reliance on fossil fuel to an economy based on alternatives to petroleum is upon our shoulders. Hydrogen is the ultimate clean fuel with the highest achievable energy density, and its use as a primary energy source is therefore desirable. About 95% of the current hydrogen production stems from natural gas reforming, and hence, from fossil fuels. Hydrogen could be produced electrochemically from water; however, current catalysts for hydrogen production are either inefficient or based on expensive, unsustainable platinum catalysts. Besides the substantial cost factor, the global platinum production would not be sufficient to support the demand for electrochemical catalysts for a global hydrogen economy. In order to make progress towards the usage of hydrogen as a fuel, catalysts based on inexpensive and abundant metals are needed for the electrochemical production of hydrogen from water, and the utilization of hydrogen via oxidation in fuel cells to power, for example, automobiles.
Ammonia is a major contributor to the agricultural and manufacturing industries with annual production of around 150 million tons. The primary means of producing ammonia is through the Haber-Bosch process requiring significant energy to proceed at high temperatures and pressure to react gaseous hydrogen with nitrogen. New catalysts based on inexpensive and abundant metals are investigated for the electrochemical production of ammonia from either (a) dinitrogen and water, or (b) urea via reductive cleavage of this abundant molecule available from sewage and manure.
By using nature's catalysts as a guide, materials can be produced that harness the energy stored at the atomic level or produce industrial products at a fraction of the cost compared to conventional methods. The enzymes used as an archetype here for catalyst development are assimilatory sulfite/nitrite reductases (aSiR/NiR) and hydrogenases. Both enzymes contain an active site that is directly (covalently) linked to a [4Fe4S] cluster as electron source. SiR/NiRs are capable of achieving up to six-electron reductions of substrates, producing hydrogen sulfide and ammonia from higher oxidized

precursors, while hydrogenases are able to catalyze both the production and utilization of hydrogen. The iron-based clusters found in the active sites of these enzymes therefore serve as a blueprint for the design and development of new catalysts resilient to oxidation from water with strong reductive capabilities for the output of desired product. These catalysts are organometallic analogs of the active sites of the aSiR/NiR and hydrogenases, and hence, are biologically-inspired but not biomimetic.

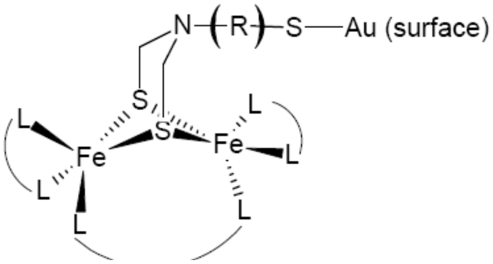
Recent Progress

Electron Transfer. The active site of aSiR/NiR's has been identified as a siroheme covalently bound through a sulfide/cysteine to a [4Fe-4S] cluster. This enzyme has the ability to efficiently catalyze the six-electron reduction of sulfite and nitrite to form the biocompatible products hydrogen sulfide and ammonia that can be assimilated by plants. This active site utilizes the same basic principles as the hydrogenase active site in the sense that in both cases iron centers efficiently catalyze the multi-electron reduction of substrates at low potentials while gaining electrons from a proximal [4Fe-4S] cluster. Our efforts in developing catalytic scaffolds based on the aSiR/NiR active site design have so far led to the synthetic and spectroscopic investigation of macromolecules that consist of synthetic $(Fe_4S_4)^{2+}$ cubane clusters that are coordinatively linked to a heme (or other macrocycle) center. Preliminary results here are primarily synthetic at this point, and in particular, have focused on the development of suitable organic linkers to connect the heme and cluster units of the envisioned catalytic array, shown in Scheme 1. The nature of the bridge that connects the two components is of central importance as it mediates the critical electron transfer across the bridge. The ligands thus tested as bridges are para-thiopyridine varieties where the thiol has a preference to bind to the cubane cluster, allowing the pyridine nitrogen to bind to the axial position of both iron and zinc porphyrins. Thus far, UV-Vis absorption spectroscopy and ^{1}H-NMR proton shifts provide evidence for the linkage occurring between the two metal structures. However, no crystal structure has been obtained yet to further prove this point. Furthermore, steps are being taken to limit the possible sites of the cluster for binding to the heme component, which should aid in the isolation of discrete molecules in crystalline form. With the use of this complex, various ligands can be tested for maximum electron transfer rates between the two desired metal centers.



Scheme 1.

Electron Donating & Geometry Controlling Ligands. A large amount of focus has been put on biomimetic model complexes of hydrogenases as seen in the considerable amount of papers published in this area. Using this well laid foundation, the first generation model complexes featuring carbonyl ligands has been modified with phosphine ligands to give electron density back to the diiron site. An assortment of phosphorus donating ligands has being accumulated in order to optimize the electron density for the complete complex. Likewise, synthetic focus has turned toward designing new functionality into



Scheme 2.

the phosphine ligands to achieve, for example, water solubility of the hydrogenase model complexes. Our approach is to design and synthesize water-soluble complexes for an attachment to electrode surfaces to test these complexes under real application conditions in electrochemical/fuel cells for the generation and utilization of hydrogen. Scheme 2 highlights the design of the synthetic catalysts under development.

Future Plans

Sulfite/Nitrite Reductase Project: Isolation of the complete complex, full characterization of electron transfer capabilities using electrochemical and spectroscopic techniques, followed by catalytic studies for efficiency of reduction of small nitrogen compounds, in particular nitrite and urea.

Hydrogenase Models: The diiron core will be equipped with specifically designed phosphine ligands and a ligand allowing for ample electron transfer through the bridging sulfides of the core of the complex. Through this electron transferring ligand the catalytic core will be tethered to a gold surface where the reductive and oxidative capabilities of the material will be probed. Optimization of the process will be achieved by testing different variants of the complex.

Publications (2008-2010)

N/A

Abstract for the 2010 DOE/BES Catalysis Sciences Meeting

Stable Mononuclear Organometallic Pd(III) Complexes and Their C–C Bond Formation Reactivity

Liviu M. Mirica,* Julia R. Khusnutdinova
Department of Chemistry, Washington University, St. Louis, Missouri 63130-4899
e-mail: mirica@wustl.edu

DOE Interest

The proposed research program addresses the DOE/BES scientific mission of developing novel efficient catalysts for energy-related chemical transformations.

Goal

The goals of this research program are to investigate in detail the chemistry of mononuclear Pd(III) complexes and to develop novel catalysts for C–C, C–N, and C–O bond formation reactions.

Recent Progress

Both dinuclear and mononuclear organometallic Pd(III) complexes have been recently proposed as active intermediates in the oxidative functionalization of C–H bonds and oxidatively induced C–C bond formation reactions, respectively. While a few dinuclear organometallic Pd(III) complexes have been characterized, no mononuclear organometallic Pd(III) complexes have been isolated and characterized to date. We have successfully synthesized a series of Pd(III) complexes supported by a tetradentate, nitrogen-donor ligand. These complexes were isolated and characterized by X-ray diffraction and several spectroscopic techniques that confirm the presence of paramagnetic d^7 Pd(III) centers.[1] Interestingly, these Pd(III) complexes undergo light-induced C–C bond formation reactions to give the corresponding homocoupled products ethane or biphenyl. Particularly remarkable is the observation for the first time of ethane formation from a monomethyl Pd complex.[1] This transformation has direct implications into catalyst development for oxidative oligomerization of methane in particular and oxidatively-induced Pd-catalyzed C–C bond formation reactions in general.

Publications

1. Khusnutdinova J. R.; Rath N. P.; Mirica L. M. *J. Am. Chem. Soc.* **2010**, *submitted*.

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Djamaladdin G. Musaev
Craig L. Hill
Keiji Morokuma

Principles of Selective O_2-Based Oxidation by Optimal (Multinuclear) Catalytic Sites

Postdocs: Yurii Geletti, Zhen Luo, Jorly Joseph

Students: Jie Song, Yu Hou, Kevin O'Halloran

Collaborators: Alex Kaledin (Emerson Center),

Affiliations: Emory University, Department of Chemistry
dmusaev@emory.edu, chill@emory.edu, morokuma@emory.edu
phone: 404-727-2382, 404-727-6611, 404-727-2180

Goals. To develop combined experimental and theoretical approaches enabling molecular-level understanding of the mechanisms of selective (non-radical), reductant-free oxidation of organic substrates by O_2 and H_2O oxidation catalyzed by metal oxide cluster systems (polyoxometalates or "POMs") that have two or more proximal and synergistically interacting metal centers. POMs of particular interest are those with two and more adjacent d-electron transition metals (γ-MM'-Keggin and γ-M_n-Keggin complexes). To design optimally effective catalysts by careful examination of the experimentally and computationally accessible atomistic parameters of the POM systems, including proximal interacting metal centers, central heteroatom(s), bridging ligands, and counterions. To develop innovative computational methodologies for the study of new catalytic reactions involving multi-center transition-metal catalysts and large systems.

DOE Interest. The proposed research addresses the catalytic selective oxidation of organic substrates by O_2 and H_2O oxidation. 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 and more adjacent d-electron-containing metals, 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.

Recent Progress:

Our ongoing program focuses in part on synthesis, characterization, and catalytic activity of oxidatively robust POM complexes in which a catalytic active site interacts with proximal metal centers in a synergistic manner.

Developing a viable water oxidation catalyst (WOC) has proven particularly challenging. An effective WOC must be stable to air, water and heat (oxidative, hydrolytic, and thermal stability) and fast. There are many research groups working on heterogeneous and homogeneous WOCs. Heterogeneous WOCs generally have the advantages of low cost and, critically, oxidative stability, but they are harder to study and thus optimize than homogeneous catalysts and they tend to deactivate by surface poisoning or aggregation. In contrast, homogeneous WOCs are more amenable to spectroscopic, crystallographic, physicochemical, and computational investigation, and thus more readily optimized. In addition, each individual molecule of a homogeneous catalyst is, in principle, capable of doing chemistry. However, nearly all homogeneous catalysts contain organic ligands that are thermodynamically unstable with respect to oxidative degradation. As a result, all homogenous WOCs with organic ligands reported to date are oxidatively deactivated. A general goal is to realize WOCs that have the stability, durability, and accessibility of heterogeneous metal oxide catalysts with the activity, selectivity and tunability of homogeneous catalysts. To this end, the development of a stable and fast homogenous WOC, without organic ligands (i.e. carbon-free) would be of great interest to a substantial and growing community of investigators.

I. Multi-Ru-oxo cluster systems. Recently, we reported the Rb_8K_2 salt of the WOC polyanion $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, **1(0)**. This complex comprises a Ru_4O_4 core stabilized by two multiply ligating oxidatively-resistant polyoxometalate (POM) ligands. Now, we have completed full characterization of this unique prototype WOC (as definitively as it is conceptually and developmentally important). Multiple X-ray crystal structures (see Figure 1) along with FTIR and other spectroscopic methods confirmed its structure in the solid state, while computational, electrochemical, potentiometrical, UV-vis titration, and other techniques established its resting oxidation state (all 4 Ru centers are in 4+ oxidation state) and confirmed that the structure in aqueous solution is identical to that in the solid state. This $[Ru^{IV}Ru^{IV}Ru^{IV}Ru^{IV}]$ compound is denoted as **1(0)**, where the number **n** given in parenthesis indicates the n-electron oxidation (+) or/and reduction (-) states of **1**]. Kinetic studies show that the four electron oxidized state of **1**, **1(+4),** is the most likely reactive intermediate oxidizing water to O_2.

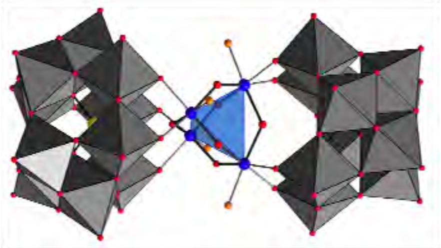


Figure 1. X-ray structure of the polyanion in **1(0)**, highlighting the central $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4]^{6+}$ core (ball-and-stick representation, Ru: blue, μ-O: red, $O(H_2)$: orange, H omitted for clarity) and the slightly distorted Ru_4 tetrahedron (transparent blue). The polytungstate fragments are shown as gray polyhedra; Si as yellow spheres.

The geometries and electronic structures of the catalyst in five different oxidation states: $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, **1(0)**, $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{9-}$, **1(+1)**, $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{8-}$, **1(+2)**, $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{7-}$, **1(+3),** and $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{6-}$, **1(+4)**, were computationally studied using the density functional and COSMO levels of theory. It was found that the several HOMOs and LUMOs of the studied complexes are bonding and anti-bonding orbitals of the $[Ru_4O_4(OH)_2(H_2O)_4]^{6+}$ core, and the first four one-electron oxidations of **1,** leading to formation of **1(+1), 1(+2), 1(+3)** and **1(+4)**, respectively, involve only $\{Ru_4\}$ core orbitals. In other words, catalyst instability due to ligand oxidation in the widely studied Ru-blue dimer, $[(bpy)_2(O)Ru^V\text{-}(\mu\text{-}O)\text{-}Ru^V(O)(bpy)_2]^{4+}$, is not operable for **1**: the latter all-inorganic catalyst is predicted to be stable under water oxidation turnover conditions. The calculated HOMOs and LUMOs of all the studied species are very close in energy and exhibit a "quasi-continuum" or "nanoparticle-type" electronic structure similar to that of nano-sized transition metal clusters. This conclusion closely correlates with the experimentally reported oxidation and reduction features of **1** and explains the unusual linear dependence of oxidation potential versus charges for these compounds. It is predicted that at higher pH compound **1** will, initially, release protons from the $\mu\text{-}O_{Ru}$ oxygen centers.

II. Multi-Co-oxo cluster systems: Co_4-based soluble, stable and fast water oxidation catalyst. The Ru_4O_4-based catalyst **1** is fast, oxidatively and hydrolytically stable, but Ru is neither abundant nor inexpensive and thus very likely prohibitive for use on a realistic scale. Therefore, discovery of a stable and fast carbon-free homogenous WOC, based on earth-abundant elements would be highly useful.

This week, we reported a homogeneous catalyst $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$ (**2**) comprising a Co_4O_4 core stabilized by oxidatively resistant polytungstate ligands (Figure 2). This catalyst is free of carbon-based ligands (thus hydrolytically and oxidatively stable) and it self assembles in water from salts of earth abundant elements (Co, W and P). With $[Ru(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine) as an oxidant, we observe catalytic turnover frequencies for O_2 production $\geq 5\ s^{-1}$ at pH 8.

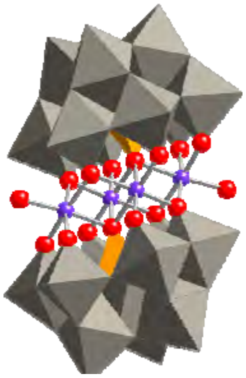


Figure 2. X-ray structure of **Na_{10}-2** in combined polyhedral ($[PW_9O_{34}]$ ligands) and ball-and-stick (the Co_4O_{16} core) notation. Co: purple, O/OH_2(terminal): red; PO_4: orange tetrahedra; WO_6: gray octahedra. Hydrogen atoms, water molecules and the sodium cations are omitted for clarity.

Complex **2** is substantially faster than the other 43 soluble WOCs reported to date. The pH dependence of the rate reflects the pH dependence of the 4-electron H_2O/O_2 couple. Extensive spectroscopic, electrochemical, and inhibition studies firmly indicate that **2** is stable under catalytic turnover conditions: neither hydrated cobalt ions nor cobalt hydroxide/oxide particles form *in situ*. Thus, this catalyst exhibits all the required properties of a viable WOC: fast, selective, and stable to air, water and heat (oxidative, hydrolytic and thermal stability).

Computational studies of the electronic structure of **2** provide additional support for the oxidative stability of the polytungstate ligands. The four top HOMO's of a high-spin ground state **2** are mostly cobalt core orbitals, and there is almost no involvement of tungstate orbitals. These findings indicate that the polytungstate ligands are unlikely to participate in the water oxidation reaction and should be effectively inert under catalytic conditions.

Development of "reactive" force fields to study interaction of the targeted POMs

with water, proton and hydroxo ions in liquid phase. Recently, we have constructed the total potential for water with an excess of H^+ (or OH^-) ions and any number of metal ions (M) as a sum of valence (V_{ij}, V_{ijk}, V_{ijkl}), electrostatic and Lennard-Jones repulsive terms, the latter being added mainly to prevent formation of unwanted bonds and united atoms,

$$U(r) = \sum_{i<j} V_{ij}(r_{ij}) + \frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} + \sum_{i<j<k} V_{ijk}(\theta_{ijk}) + \sum_{i<j<k<l} V_{ijk}(\tau_{ijkl}) \qquad (1)$$

The summations run over the atoms; q_i are atomic charges; e_{ij} and s_{ij} are Lennard-Jones parameters. The valence two-body potential is based on Tersoff's [J. Tersoff, *Phys. Rev. B* **37**, 6991-7000, (1988)] original model for two interacting sites *i* and *j*,

$$V_{ij}(r_{ij}) = f_C(r_{ij})[a_{ij}(\mathbf{r})\, f_R(r_{ij}) + b_{ij}(\mathbf{r})\, f_A(r_{ij})] \qquad (2)$$

where the local repulsive $f_R(r) = A\exp(-\lambda_1 r)$ and attractive $f_A(r) = -B\exp(-\lambda_2 r)$ forces are modulated by non-local geometry dependent functions $a_{ij}(\mathbf{r})$ and $b_{ij}(\mathbf{r})$, respectively, which are required to have symmetry with respect to *i-j* exchange. The three- and four-body potentials, which are simple polynomials of their respective variables, are added specifically for HOH bend and H_3O improper torsion modes.

The potential function is parameterized by 30 variables for all the O-H type interactions and by additional 15 variables for the M-O and M-H interactions. These parameters are optimized by a least-squares procedure that minimizes the r.m.s. between Eq. 1 and an extensive set of *ab initio* data generated by molecular dynamics simulations, normal mode sampling and scanning of the potential energy surface. All electronic structure calculations have so far been carried out at the B3LYP/6-31+G(d,p) level of theory, known to be reasonably accurate for H_2O-H_2O, H_3O^+-H_2O, OH^--H_2O and transition metal complexes involving O and H atoms.

Exploratory calculations have already yielded encouraging results for solvation of the $Cu^{2+}(^2D)$ ion. Both the DFT and RFF calculations predict that the $Cu^{2+}(^2D)$ ion forms four short Cu-O bonds and two long Cu-O bonds. All O-Cu-O angles are either 90 of 180 degrees. Thus, now, molecular dynamics simulations are possible for Cu^{2+} solvation in liquid water and will be performed upon RFF integration into TINKER suite of MD codes.

Table 1. DFT and RFF calculated geometry (in Å) and energy parameters (in kcal/mol) of the solvated Cu^{2+} ion.

	R_S	R_M	R_L	DE_1	DE_2
DFT	2.01	2.09	2.25	23.5	29.6
RFF	2.11	2.11	2.11	26.7	28.2

Future Plans:

Our team in ongoing efforts will to (1) elucidate the mechanism and controlling factors in the oxidations of water and organic complexes catalyzed by our new complexes, including the pioneering WOCs, **1** and **2**, and tune the reactivity of these catalysts by addressing appropriate fundamental properties (such as the POM ligand(s) atoms themselves, counter cations, ionic strength and temperature); (2) prepare and characterize the Co_9- and Mn_4-POM systems, and investigate their activities for O_2 binding and catalytic organic substrate and H_2O oxidations; (3) investigate new POMs with d-electron-metal active sites in sterically protected pockets; and (4) continue our efforts on fitting and testing “reactive” force fields in simple systems such as the $M_6O_{19}^{n-}$ POMs, where M = Mo, W, Nb and Ta, and the γ-M_2-Keggin POMs (where M = Co and Ru); to apply the newly developed “reactive” force fields for $Ru_2W_{10}O_{40}$ to study oxo-transfer from its oxidized form to various substrates.

Publications (2008-2010):

Solely funded by DOE-BES Catalysis:

1. Qiushi Yin, Jeffrey Miles Tan, Claire Besson, Yurii V. Geletii, Djamaladdin G. Musaev, Aleksey E. Kuznetsov, Zhen Luo, Ken I. Hardcastle, Craig L. Hill „A soluble molecular fast organic-structure-free water oxidation catalyst based on abundant metals“ *Science*, **2010**, *in press: ScienceExpress, 2010, 11 March.*
2. David Quinonero, Alexey Kaledin, Aleksey E. Kuznetsov, Yurii, V. Geletii, Claire Besson, Craig L. Hill, Djamaladdin G. Musaev, „Computational studies of the geometry and electronic structure of an all-inorganic and homogeneous tetra-Ru-polyoxometalate catalyst for water oxidation and its four subsequent one-electron oxidized forms“, *J. Phys. Chem. A.*, **2010**, *114* (1), pp 535–542
3. Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. “ The role of the heteroatom (X = Si^{IV}, P^{V} , and S^{VI}) on the Reactivity of $\{\gamma\text{-}[(H_2O)Ru^{III}(\mu\text{-}OH)_2Ru^{III}(H_2O)][X^{n+}W_{10}O_{36}]\}^{(8-n)-}$ with the O_2 Molecule”, *Dalton Trans.*, **2010**, *submitted*
4. Y. V. Geletii, C. Besson, Y. Hou, Q. Yin, D. G. Musaev, D. Quinonero, R. Cao, K. I. Hardcastle, A. Proust, P. Kogerler, C. L. Hill, „Structural, Physicochemical and Reactivity Properties of and All-Inorganic Catalyst for Water Oxidation“, *J. Am. Chem. Soc.* **2009**, *131*, 17360-17370.
5. Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. “On the Mechanism of the Divanadium-substituted Polyoxotungstate $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ Catalyzed Olefin Epoxidation by H_2O_2: A Computational Study.” *Inorg. Chem.*, **2009**, *48*, 1871-1878.
6. Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. “ Dioxygen and Water Activation Processes on Multi-Ru-substituted Polyoxometalates: Comparison with the “Blue Dimer” Water Oxidation Catalyst” *J. Am. Chem. Soc.* **2009**, *131*, *6844-6854.*
7. Prabkahar, R.; Morokuma, K.; Geletii, Y. V.; Hill, C. L.; Musaev, D. G. “Insights into the the Mechanism of H_2O_2-based Olefin Epoxidation Catalyzed by the Lacunary $[\gamma\text{-}(SiO_4)W_{10}O_{32}H_4]^{4-}$ and di-V-substituted-γ-Keggin $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ Polyoxometalates. A Computational Study.” In "Computational Modeling for Homogenous and Enzymatic Catalysis", Morokuma, K.; Musaev, D. G. Eds. Wiley: New York, **2008**, 215-230.

b. Jointly funding by DOE-catalysis and other DOE sources:

8. Yurii V. Geletii, Bogdan Botar, Paul Kogerler, Daniel A. Hillesheim, Djamaladdin G. Musaev, Craig L. Hill, „An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogenous Catalyst for Water Oxidation“, *Angew. Chem. Intern. Ed.* **2008**, *47*, 3896-3899. *Selected as the VIP (“Very Important Article”) by the reviewers and editor.*
9. Yurii V. Geletii, Claire Besson, Zhuangqun Huang, Yu Hou, Qiushi Yin, Djamaladdin G. Musaev, David Quinonero, Alexsey Kuznetsov, Rui Cao, Kenneth I. Hardcastle, Anna Proust, Bogdan Botar, Paul Kögerler, Tianquan Lian and Craig L. Hill, “An All-Inorganic, Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation. Reaction Mechanism”, *International Symposium on Relations between Homogeneous and Heterogeneous Catalysis*, ISHHC XIV, 13-18 September 2009, Stockholm, Sweden
10. Yurii V. Geletii, Claire Besson, Yu Hou, Qiushi Yin, Zhuangqun Huang, Tianquan Lian, Djamaladdin G. Musaev, and Craig L. Hill, “Multinuclear Transition Metal Substituted Polyxometalates: a New Family of All-Inorganic Homogeneous Catalysts for Water Oxidation in Artificial Photosynthesis”, 61st Southeastern Regional Meeting of the ACS (*SERMACS), 2009*, Oct. 21-24, San Juan, Puerto Rico

c. Jointly funded by DOE and other sources:

11. Rui Cao, Jong Woo Han, Traves M. Anderson, Daniel A. Hillesheim, Martin L. Kirk, Djamaladdin G. Musaev, Keijji Morokuma, Yurii V. Geletii, Craig L. Hill, „Late Transition Metal Oxo Compounds and Open Framework Materials that Catalyze Aerobic Oxidations“, *Prog. Inorg. Chem.*, **2008**, *pp.245-272.*

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

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

Postdoc:	Dr. Deborah Smith
Students:	Lihao Tang, Jongwook Choi, Mary Pulling, John Hartung
Collaborators:	Dr. James Franz, Dr. Tudor Spataru
Contact:	Jack Norton, Columbia Chemistry, 3000 Broadway, MC 3102 New York, NY 10027; Phone 212.854.7644 jrn11@columbia.edu

Goal

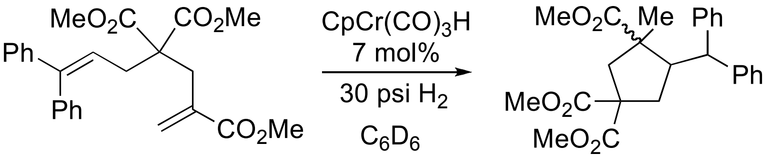
We are developing transition-metal complexes that *catalyze* the generation of radicals from alkenes and H_2. We intend to find catalysts that are practical for radical cyclizations, and to maximize the number of substrates to which these catalysts are applicable.

DOE Interest

Radical cyclizations have many synthetic applications, but are traditionally carried out by the stoichiometric use of Bu_3SnH. The toxicity of that reagent has limited the industrial use of this chemistry. A *catalytic* reaction with H_2 as the only stoichiometric reagent is ideal from the standpoint of atom economy — efficient and green, with no waste.

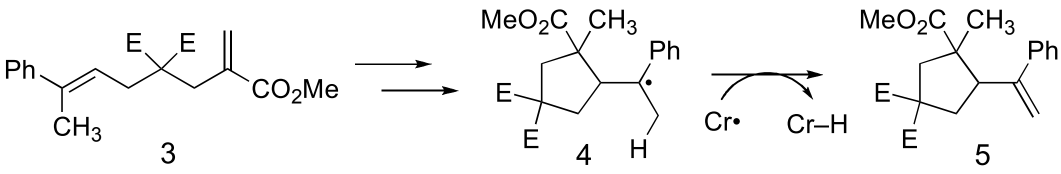
Recent Progress

New Substrates for Tin-Free and Catalytic Radical Cyclizations: We have extended our work on catalyzing the radical cyclization of 1,6 dienes to the diene **1**. The radical arising from H• transfer to **1** should cyclize rapidly as a result of the Thorpe-Ingold effect. Treatment of **1** with H_2 in the presence of $CpCr(CO)_3H$ affords the cyclization product **2** *exclusively* after 1.5 days at 50 °C. The high yield may result from a decrease in the rate of the competing hydrogenation and isomerization reactions as well as from the increase in the rate of cyclization. The rate with **1** is slower than with our original substrate (without the CO_2Me substituents), probably because these substituents decrease the rate of the initial H• transfer.



1 2

Because this reaction is terminated by a second H• transfer it consumes an equiv of H_2. However, replacing one Ph by a methyl allows $CpCr(CO)_3H$ to be regenerated by abstracting H• from the cyclized **4** *without stoichiometric consumption of any reagent!* Thus $CpCr(CO)_3H$ *catalyzes* (41% after two days) the conversion of the diene **3** to its isomer **5**.



Unusually Weak M–H Bonds with Vanadium: Various reports have suggested that V–H bonds are unusually weak. We have thus determined (from their pK_a values and the potentials of the corresponding anions) the strength of those in $HV(CO)_4$(P–P). The results in Table 1 appear to be the first *solution* measurements of V–H bond strengths, and imply that the bonds in **6** are significantly weaker than the M–H bonds in other neutral hydrides — 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 k_H for H• Transfer from **6a–d** to Styrene at 285 K in C_6D_6.

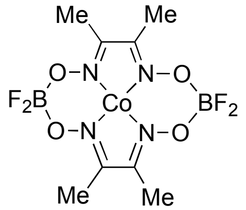
	E^o (V)	pK_a	M–H BDE (kcal/mol)	Relative k_H (styrene)
$HV(CO)_4$(dppm) (**6a**)	–1.18 (1)	18.7(1)	57.9	20.0
$HV(CO)_4$(dppe) (**6b**)	–1.12 (1)	17.4(1)	57.5	10.6
$HV(CO)_4$(dppp) (**6c**)	–1.17 (1)	17.1(1)	56.0	8.2
$HV(CO)_4$(dppb) (**6d**)	–1.19 (1)	16.7(1)	54.9	6.7
$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$			62.2	1

We have determined the rate constants k_H for H• transfer to styrene from the vanadium hydrides **6** by observing the rate at which styrene is hydrogenated by **6**. (We have shown that back transfer is small by treating styrene with **6**-d_1.) The resulting k_H for **6** (Table 1) is 7 to 20 times faster than k_H for $CpCr(CO)_3H$. 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 k_H values *decrease* in the order **6a**>**6b**>**6c**> **6d**, a trend opposite that expected from the bond strengths. The increasing size of the chelate ligands is presumably responsible.

When used in *stoichiometric* amounts the vanadium hydrides **6** effect the radical cyclization of dienes like **1** more rapidly, and under milder conditions, than does $CpCr(CO)_3H$; the hydrides **6** are, however, not *catalytic* for such dienes under H_2. A *stoichiometric* amount of **6c** can effect the conversion of **3** to **5** quantitatively in 4.5 h, and can even slowly (83% yield steadily over 19 days!) *catalyze* that conversion.

Cobalt Catalysts Effective for H• Transfer under H_2: We have found that under H_2 some Co^{II} complexes can provide H•, presumably via Co^{III} hydrides. These complexes promise to be better catalysts than $CpCr(CO)_3H$; generating a reactive hydride *in situ* will keep its concentration low, and should thus minimize hydrogenation as a side reaction. In preliminary experiments **7** under H_2 cyclizes **1** to **2** quantitatively in 24 hours.



Co(dmgBF$_2$)$_2$

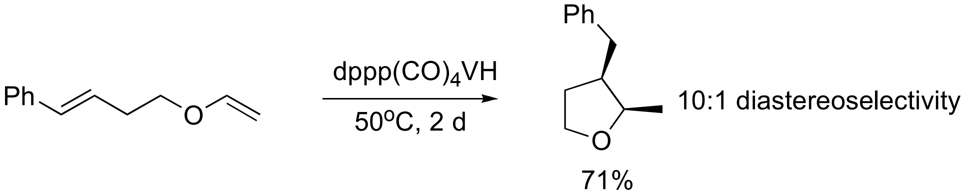
7

Complex **7** under H_2 is also effective as a catalyst for the conversion of **3** to **5**, giving a quantitative yield in less than 7 hours.

Future Plans

Additional Substrates: We will check the compatibility of our reaction with various functional groups, and learn how slow a rate of radical cyclization it can tolerate. We will test alkenes activated by other substituents (e.g., vinyl ethers, unsaturated nitriles, and unsaturated sulfones), and alkynes, as substrates for H• transfer. We will measure the rate constants for H• transfer to appropriate model compounds.

We have prepared the substrate below by treating (E)-4-phenylbut-3-en-1-ol with Pd(OCOCF$_3$)$_2$ in butyl vinyl ether, and have found its cyclization with the vanadium hydride **6c** to be clean if a little slow.



Improved *Catalysts*: As an alternative way of regenerating vanadium hydrides from vanadium radicals we will try reduction of the metalloradicals by one e$^-$ in the presence of a weak acid.

We will screen other Co^{II} complexes (e.g., that of Costa) as catalysts under H_2. We will measure the rates at which they activate hydrogen and transfer H•.

Publications (2007 – 2010)

1. "Kinetics of Hydrogen Atom Transfer from (η^5-C_5H_5)Cr(CO)$_3$H 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.
2. "Tin-Free and Catalytic Radical Cyclizations", D. M. Smith, M. E. Pulling and J. R. Norton*, *J. Am. Chem. Soc.* **2007**, *129*, 770-771.
3. "Unusually Weak Metal–Hydrogen Bonds in HV(CO)$_4$(P–P) and Their Effectiveness as H• Donors", J. W. Choi, M. E. Pulling, D. M. Smith, J. R. Norton*, *J. Am. Chem. Soc.* **2008**, *130*, 4250–4252.

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5. “Chain – Transfer Catalysis by Vanadium Complexes during Methyl Methacrylate Polymerization”, J. W. Choi, J. R. Norton*, *Inorg. Chim. Acta* **2008,** *361,* 3089-3093.
6. “Catalysis Involving the H• Transfer Reactions of First-Row Transition Metals”, J. Hartung and J. R. Norton*, in *Catalysis without Precious Metals*; Bullock, M., Ed., Wiley-VCH: Weinheim, in press.

Supported Molecular Catalysts –the Support as Co-Catalyst

Justin M. Notestein

Northwestern University, Department of Chemical and Biological Engineering, Evanston IL 60208

e-mail: j-notestein@northwestern.edu

Molecular catalysts are often supported to aid in catalyst separation or to allow new reaction conditions. While improving handling, this often comes at the expense of reaction rates or selectivities due to hard-to-control interactions with the surface. Here, two classes of molecular catalyst are supported on oxides, which strongly activate the catalyst as compared to the soluble species. In the first example, Mn triazacyclononane complexes are combined with carboxylic acid-functionalized oxides that are both supports and necessary co-catalysts. In H_2O_2 solutions, a partially reduced active species is formed on the oxide surface, as shown by UV-vis and XAS. In alkene epoxidation / dihydroxylation, their selectivities and productivities are a function of the type and density of surface carboxylic acid and the support properties. At similar co-catalyst loadings, the supported species are >10x more productive than when in solution. This system is being expanded to other oxidation catalysis and to different Mn complexes. In the second example, Lewis acidic calixarene-Ta(V) complexes are explored in epoxidation and hydroamination. In one pot, $TaCl_5$, calixarene ligands, and SiO_2 supports are combined to create the active supported catalyst. As above, the SiO_2 support dramatically increases productivities in epoxidation with H_2O_2, but also does so in alkyne hydroamination, which has not previously been observed. Support properties not easily replicated by soluble catalysts can control the catalyst local environment and suppress side reactions. The supported molecular species are also more active and selective than the analogous oxide heterogeneous catalysts. These catalysts are now being explored for catalytic reductions such as hydrodenitrogenation. Overall, synergistic interactions can arise between supports and molecular species. Solid supports can, in some cases, be considered as drop-in replacements for soluble co-catalysts, with the added benefits of producing a stable, solid material.

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

Catalytic Growth of Molecular-Scale Wiring

Department of Chemistry, Columbia University, New York, NY 10027
email: cn37@columbia.edu

Graduate students and post-docs: Matthew Carnes, Noah Tremblay, Kyle Plunkett, Felix Fishcher, and Haitao Liu, Alon Gorodetsky
Collaborators: Louis Brus (Columbia), Michael Steigerwald (Columbia), Mark Hybertsen (Columbia), Ionyss Kymissis (Columbia), and Shalom Wind (Columbia)

Project Start Date: February 1, 2008

Abstract

Research Goals: The objective of this proposal is to develop catalytic methods to grow molecular wires from active metal-molecule linkages. In particular we are interested in methods to synthesize, pattern, and functionalize nanoscale carbon. We will study two different systems in this context. In one, we will study new molecules that can be polymerized with metal carbene complexes. We will use this as a method to grow wiring from activated systems to create oligomeric, molecular-scale wires that are both structurally and electronically in contact with a metal surface. In the other system, we will develop chemical seeds in the form of a molecular hemisphere that able to encode the catalytic growth of a particular single walled carbon nanotube.

Significant Achievements: We have made significant progress towards our research goals during this funding period. We continue our pioneering studies on the metathesis of cyclooctatetrene derivatives with strained double bonds. We showed in the previous funding period that these monomers made living polymers in some cases. During this funding cycle we have developed the synthetic chemistry to functionalize these monomers so after polymerization they can form graphene ribbons. These studies are nearing fruition and provide the basis for our studies in the coming funding period. In the course of these studies, we found that these strained monomers would react with low valent nickel to form a plethora of new nickel-carbon species. This work was featured in *Angewandte Chemie* and is currently being explored in the context of catalysis. We continue our studies of the synthesis and reactions of nano- carbon. We recently completed a synthesis of molecules that could form the seeds for the growth of single walled carbon nanotubes. We are incorporating these into metal surfaces to create single-walled carbon nanotubes. Through our synthetic efforts we found that these materials form the basis for efficient solar cells. In related work, we have developed photochemical reactions that allow us to pattern graphene. This work was published as a communication in *The Journal of the American Chemical Society* and will be used in the current funding period to develop a method to fabricate molecular scale wiring. In the course of this study we made an unexpected but potentially very useful observation—that carbon nanotubes and other carbon based nanostructures could serve as a catalyst for the etching of silicon oxide. This work was featured on the cover of *The Journal of*

the American Chemical Society and allows patterning of silicon wafers on very small lengthscales without lithographic masks.

Potential Impact in Areas of DOE Interest: The importance to the Department of Energy and its mission is three-fold. First, the science in this proposal 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.

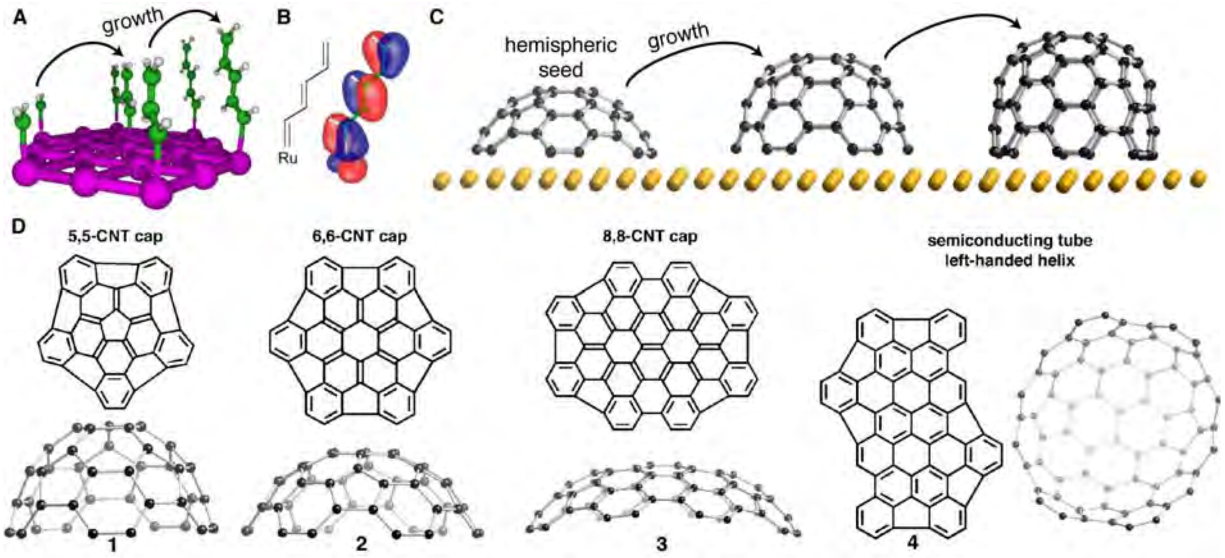


Figure 1. Specific aims of this proposal. (A) For Specific Aim 1: the catalytic growth of wires using metathesis from carbene functionalized surfaces is developed. (B) The conjugation of the wire should extend into the metal through the d-p π-bond. (C) For Specific Aim 2: a hemispheric seed is used as 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.

Latest Publications (2008-2010) Acknowledging this Grant

(1) “Helical Dibenzoc[a,e]cyclooctatetrene: A Spring-Loaded Monomer”, M. Carnes, D. Buccella, M. L. Steigerwald, and C. Nuckolls, *Ang. Chem. Int. Ed.*, **2008**, *47*, 2982-2985.
(2) “Molecular Electronic Devices Based on Single-Walled Carbon Nanotube Electrodes”, A. K. Feldman, M. L. Steigerwald, X. Guo, C. Nuckolls, Acc. Chem. Res., **2008**, *41*, 1731–1741.
(3) “Reactions of Strained Hydrocarbons with Alkene and Alkyne Metathesis Catalysts”, M. Carnes, D. Buccella, T. Siegrist, M.L. Steigerwald, and C. Nuckolls, *J. Am. Chem. Soc.*, **2008**, *130*, 14078-14079.
(4) “A Stable Tetraalkyl Complex of Nickel(IV)”, M. Carnes, D. Buccella, J. Y.-C. Chen, A. P. Ramirez, N.J. Turro, C. Nuckolls, and M. Steigerwald, Ang. Chem. Int. Ed., 2009, 48, 290-294. Highlight in *Ang. Chem. Int. Ed.*, **2009**, *48*, 260-61.

(5) “Expeditious Synthesis of Contorted Hexabenzocoronenes”, K. N. Plunkett, K. Godula, C. Nuckolls, N. Tremblay, A. C. Whalley, and S. Xiao, *Org. Lett.*, **2009**, *11*, 2225-2228.

(6) “Solar Cells from a Solution Processable Pentacene with Improved Air Stability”, A. A. Gorodetsky, M. Cox, N. J. Tremblay, I. Kymissis, C. Nuckolls, **2009**, *Chem. Mat.*, *21,* 4090-4092.

(7) “Electrical Double Layer Catalyzed Wet-Etching of Silicon Dioxide”, H. Liu, M. L. Steigerwald, C. Nuckolls, **2009**, *J. Am. Chem. Soc.*, *131*, 17034-17035. Editors’ Choice in June 26, 2009 *Science Magazine*.

(8) “Photochemical Reactivity of Graphene”, H. Liu, S. Ryu, Z. Chen, M. L. Steigerwald, C.Nuckolls, L. Brus, *J. Am. Chem. Soc.*, **2009**, *131*, 17099-17101.

(9) “Photovoltaic Universal Joints: Ball-and-Socket Interfaces in Molecular Photovoltaic Cells” N. J. Tremblay, A. A. Gorodetsky, M. Cox, T. Schiros, B. Kim, R. Steiner, Z. Bullard, A. Sattler, W-Y. So, Y. Itoh, M. F. Toney, H. Ogasawara, A. P. Ramirez, I. Kymissis, M. L. Steigerwald, C. Nuckolls, *Chem. Phys. Chem.*, **2010**, accepted for publication.

(10) “Bending Hexabenzocoronene into a Bowl”, A. C. Whalley, K. N. Plunkett, C.-Y. Chiu, A. A. Gorodetsky, M. L. Steigerwald, C. Nuckolls, **2010**, *Nature Chem.*, submitted for publication.

DE-FG02-06ER15815 **Oleg V. Ozerov**

Catalysis of C-F activation by highly electrophilic Si compounds

Additonal PI's:	None
Postdocs:	Christos Douvris, Mason Haneline, C. M. Nagaraja
Students:	Weixing Gu, Billy J. McCulloch, Loren Press
Collaborators:	Dmitry G. Gusev (Wilfrid Laurier University)
Contact info:	Texas A&M University, Department of Chemistry, TAMU – 3255, College Station, TX 77842

Goal

Development of a novel approach to activation and catalytic conversion of C-F bonds that utilizes highly electrophilic main group catalysts and understanding of the mechanistic issues of the electrophilic C-F activation.

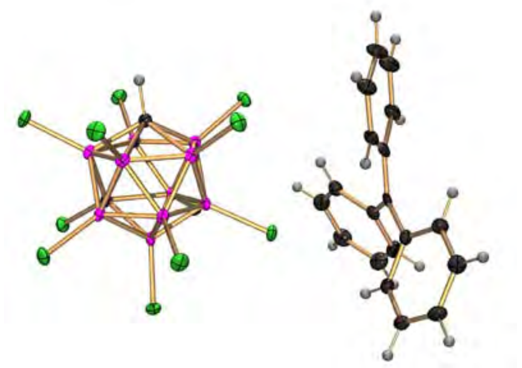
DOE interest

Although fluoroorganics benefit our society in a number of different ways, there is a growing understanding of the effects of fluoroorganic pollutants on the environment. The most publicly known example of fluoroorganics' effect on the environment is undoubtedly the story of CFC refrigerants that are destructive towards the ozone layer. What is less well-known is that CFCs are very potent greenhouse gases. Interestingly, nuclear energy industry is a major contributor to CFC emissions. CFC replacements (HFCs and HCFCs) are ozone-safe but are themselves only somewhat less potent greenhouse gases. Perfluorocarbons (PFCs) are another class of "super-greenhouse gases" (SGHGs). They are an unwanted by-product in aluminum manufacture and are also broadly used in semiconductor industry for etching silicon wafers. Because of the long lifetimes and of the very high global warming potentials (thousands of times that of CO_2) the emissions of SGHGs contribute very significantly to radiative forcing. Reductions in the use of SGHGs and supplanting the need for them with new technologies are ultimately the way to curtail their release into the environment. However, this requires innovation and time for implementation. In the meantime, destruction of the stockpiles and of the generated waste streams is necessary to alleviate the effect. Polyfluoroalkanes are among the least reactive molecules. Development of new, efficient methodologies for SGHG abatement under mild conditions would reduce the impact of many energy-intensive industries on the environment.

Recent Progress

Silylium and alumenium-based catalysis. Implementations of the catalytic C-F activation based on both the silylium cycle and the alumenium cycle have been realized. The silylium-based chemistry displays higher activity and the capacity to attack more resistant substrates, but is limited to the replacement of C-F by C-H. The alumenium chemistry accomplishes replacement of C-F by C-C, as well as C-H. Through the scavenging action of the trialkylaluminum reagents, the alumenium chemistry is insensitive to small amounts of moisture in the solvent or reagent.

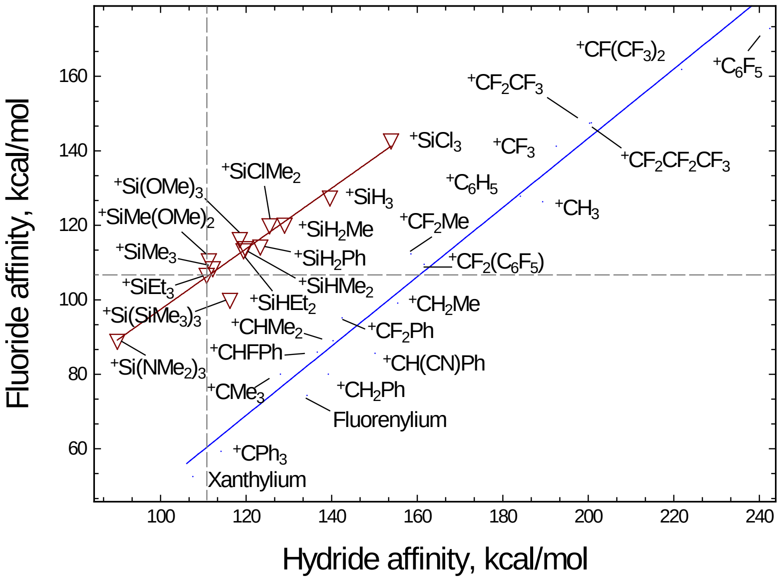
Carborane syntheses. The C-F activation chemistry mediated by silylium and alumenium cations is made possible in solution by the use of halogenated carborane anions, remarkable weakly coordinating anions. We have initially relied on the synthetic procedures from the literature, chiefly from the Reed group. Recently we have developed improved methods for undecahalogenation. Simple reflux of Cs[$HCB_{11}H_{11}$] in SO_2Cl_2 with exclusion of moisture leads to high-yield conversion to Cs[$HCB_{11}Cl_{11}$], and reflux with Br_2/$SbCl_5$ leads to isolation of the [$HCB_{11}Br_{11}$]$^-$ salts.



Representation of the X-ray structure of $Ph_3C[HCB_{11}Br_{11}]$

Representation of the X-ray structure of $Et_3Si[HCB_{11}H_5Cl_6]$

Computational studies. In collaboration with Prof. Dmitry Gusev, we have initiated computational explorations of the C-F activation reactions. At first, we have set out to determine the basic thermodynamics of the elementary reactions in the catalytic cycle. To this end, fluoride and hydride affinities (FA and HA) of various silylium and carbocations have been calculated, in the gas phase, and in the model PhCl solution. The computational findings summarized in a figure to the right provide valuable insight into reactivity and some surprising basic knowledge. For example, the FA and HA of silylium cations are essentially equal. The HA of carbocations are uniformly larger than that of trilalkylsilylium cations we used in catalysis. However, the FA of fluorinated carbocations exceeds the FA of trialkylsilylium cations; by as much as 40-50 kcal/mol for perfluorocarbocations. This allows us to conclude that activation of perfluorocarbons (as of yet unaccomplished) will likely require much more fluorophilic silylium catalysts, e.g., Cl_3Si^+, I order to make the fluoride transfer kinetically feasible.



Plot of the calculated FA *vs*. HA data in chlorobenzene.

Future work

The main focus of future work is on two directions: development of cheaper, more soluble, less coordinating carborane and dodecaborate anions, and approaches to activation of perfluoroalkanes. We will continue to use computational insight to advance the experimental chemistry in this project.

Publications

Gusev, D. G.; Ozerov, O. V. " Hydride and Fluoride Affinities of a Series of Carbenium and Silylium Cations in the Gas Phase and C_6H_5Cl Solution", submitted.

Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. "Hydrodefluorination and Other Hydrodehalogenation of Aliphatic Carbon-Halogen Bonds Using Silylium Catalysis", *J. Am. Chem. Soc*. **2010**, *132*, 4946.

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Gu, W.; Haneline, M. R.; Douvris, C., "Carbon−Carbon Coupling of C(sp^3)−F Bonds Using Alumenium Catalysis", *J. Am. Chem. Soc*., **2009**, *131*, 11203.

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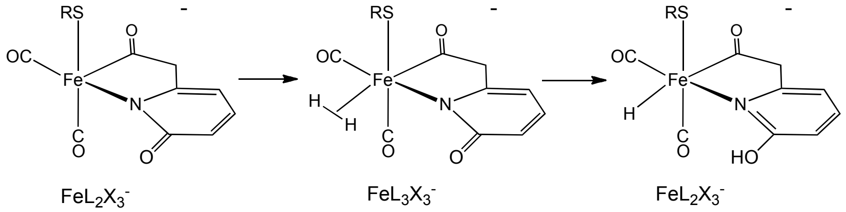
DE-FG02-90ER14146r **Thomas B. Rauchfuss**

Supramolecular Platforms for Small Molecule Activation

Students: James R. Lansing, Brian C. Manor, Mark R. Ringenberg, Aaron M. Royer
Postdoc: Bryan C. K. Chan
Collaborators: Thomas Cundari (University of North Texas), Stephen P. Cramer (LBL), Wolfram Meyer-Klaucke (EMBL-Hamburg), Luca DeGioa (Milan)
Contacts: 600 S. Goodwin, Urbana, IL 61801; rauchfuz@uiuc.edu

Goal

Develop new concepts and platforms for the activation of gaseous substrates relevant to the production of fuels. A major focus is inspired by the active site of the hydrogenase enzyme called Hmd (H_2-forming methylenetetrahydromethanopterin dehydrogenase), the probable relevant states of which are shown below:

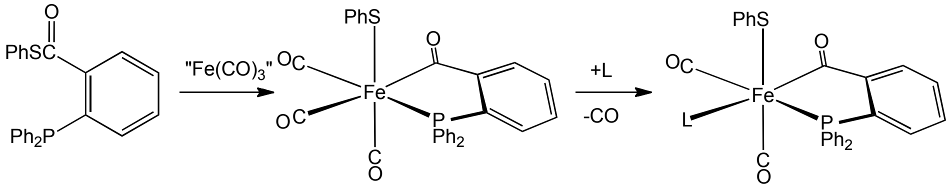


DOE Interest

Understanding and managing small molecules is at the heart of the BES mission because these small molecules are the fuels or products of our nation's most important energy-producing processes.

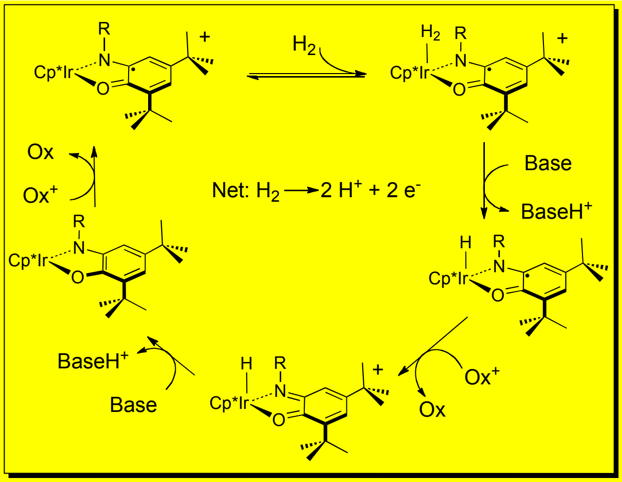
Recent Progress

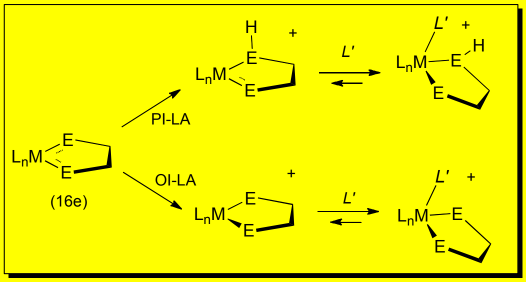
Structural Model for the Hydrogenase Hmd: We have developed an efficient route to a model for the active site of this enzyme via the oxidative addition of phosphine thioesters, e.g. $Ph_2PC_6H_4$-2-C(O)SPh, to $Fe(CO)_3$ sources.



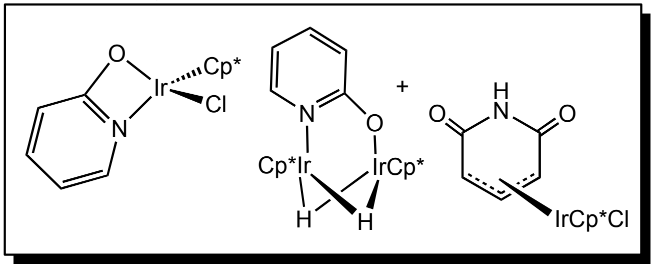
Our preliminary report outlined the synthesis of the active site model, which was spectroscopically characterized. We have since crystallized the tricarbonyl and established its stereoselective reactivity.

Non-innocent Ligands in Hydrogen Oxidation: We demonstrated that redox-switching of non-innocent amido-phenolate ligands induces H_2 activation. The specific case, which exhibits "oxidatively induced Lewis acidity" (OI-LA) is the amidophenolate Cp*Ir(N(R)$OC_6H_2R_2$), which will oxidize H_2 only upon ligand-centered oxidation. The work on non-innocent ligands complements our recent studies on protonation-induced Lewis acidity (PI-LA), which was demonstrated with diamido complexes of Cp*Ir(III). Both oxidation and protonation would diminish the pi-donor interaction between the metal and the amido ligand. We continue to seek such interactions for first-row metals.





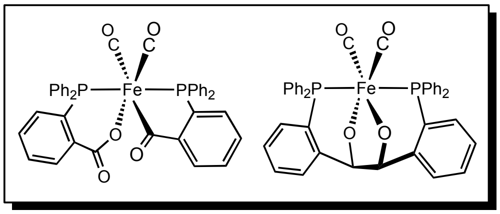
Pyridin-2-oate for Second Coordination Sphere Control: Our interest in pyridin-2-oate (conjugate base of 2-hydroxypyridine) is motivated by the occurrence of a modified pyridin-2-oate as a cofactor in the active site of Hmd. We had unable to generate biomimetic pyridin-2-oate complexes of Fe, in retrospect because the active site structure had been misassigned). In the interim, we investigated Yamaguchi et al.'s report on alcohol dehydrogenation catalyzed by Cp*IrCl(κ^2-2-pyridin-2-oate). We confirmed that this monomer is exceptionally reactive toward alcohols as well as H_2. Under catalytic conditions, the monomer converts to [Cp*$_2$Ir$_2$(μ-*N*,*O*-pyridin-2-oate)(μ-H_2)]$^+$, which is inactive. One spin-off of this work was the discovery a new kind of allyl complex, Cp*IrCl(η^3-pyridin-2,6-dionate).



Future Plans

Hmd Modeling: We are developing second generation models for the active site of Hmd, focusing on the second coordination sphere. Design features of interest are enolizable phenacetyl ligands and proton-relay sites trans to labilizing acyl ligands. The overall goal is to enhance the affinity of centers for small molecules by appending "sensory" components.

New Fe(II) Platforms: Encouraged by the successful oxidative addition of thioesters, we are examining new platforms for Fe^{II}-CO/H derivatives that could be useful for small molecule activation. Some recently complexes are shown below.



New Dimensions in Transfer Hydrogenation: Although not detailed above, we have extensive experience with transfer hydrogenation using the Ikariya-class of Ir diamido catalysts. These species represent one of the simplest systems for H_2 heterolysis, yet they have largely been ignored for any applications aside from asymmetrical catalysis.

Publications (2008-2010)

"Artificial Hydrogenases" Barton, B. E.; Olsen, M. T.; Rauchfuss, T. B. *Current Opinion in Biotechnology*, **2010**, in press.

"Oxidation of Dihydrogen by Iridium Complexes of Redox-active Ligands" Ringenberg, M. R.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics*, **2010**, in press.

"Activation and Deactivation of Cp*Ir(TsDPEN) Hydrogenation Catalysts in Water" Letko, C. S.; Heiden, Z. M.; Rauchfuss, T. B. *Eur. J. Inorg. Chem.* **2009**, 4927-4930.

"Oxidative Addition of Thioesters to Fe(0): Active-Site Models For Hmd, Nature's Third Hydrogenase" Royer, A. M.; Rauchfuss, T. B.; Gray, D. L. *Organometallics* **2009**, *28*, 3618-3620.

"Proton-Assisted Activation of Dihydrogen: Mechanistic Aspects of Proton-Catalyzed Addition of H_2 to Ru and Ir Amido Complexes" Heiden, Z. M.; Rauchfuss, T. B *J. Am Chem. Soc.* **2009**, *131*, 3593-3600.

"π-Complexes of Lignols with Mn(I) and Ru(II)" Morvan, D.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **2009**, *28*, 3161–3166.

"Redox-Activation of Alkene Ligands in Platinum Complexes with Non-innocent Ligands" Boyer, J. L.; Cundari, T. R.; DeYonker, N. J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2009**, *49*, 638–645.

"Supramolecular Architectures Based on Organometallic Half-sandwich Complexes" Rauchfuss, T. B.; Severin, K. in "Molecular Nanostructures" Atwood, J.; Steed, J. eds. Wiley-VCH, 2008; pp. 179-201.

"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.; Wilson, S. R. *Comptes Rendus* **2008**, *11*, 922-925.

"Lewis Base Adducts Derived from Transfer Hydrogenation Catalysts: Scope and Selectivity" Heiden, Z. M.; Gorecki, B. J.; Rauchfuss, T. B. *Organometallics,* **2008**, *27*, 1542-1549.

“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.

Theoretical investigation of Ni(II) complexes for hydrogen oxidation

S. Chen, S. Raugei*, R. Rousseau, and M. Dupuis
Pacific Northwest National Laboratory, Richland, WA 99352
Email: simone.raugei@pnl.gov

Recent advances in Ni-based bio-inspired catalysts [1] obtained in the Center for Molecular Electrocatalysis (EFRC) at PNNL demonstrated the possibility of generating H_2 or cleaving H_2 heterolytically, with an efficiency approaching that of the [Ni-Fe]-hydrogenase enzyme. In these catalysts the transformation between H_2 and protons proceeds via an interplay between proton, hydride and electron transfer steps and involves the interaction of a dihydrogen molecule with both a Ni center and with pendant amine bases incorporated in a six-member ring, which act as proton relays. By using density functional theory-based calculations, we have carried out a detailed characterization of the rate limiting steps of the H_2 oxidation by the complex $[Ni(P_2^{Cy}N_2^{Me})_2]^{2+}$ in acetonitrile, which is one of the most efficient catalysts for H_2 oxidation designed at our EFRC. To efficiently map the very complex free-energy landscape of this catalyst, we made use of harmonic estimates to the free energies along with solvation free energies via a continuum description of solvent. Results (see Figure 1) indicate that the H_2 translational entropy loss upon its coordination to the metal center is a major energetic bottleneck. Once the H_2 molecule enters the coordination sphere of the metal, it immediately reacts ($\Delta G^{\ddagger} \approx 7$ kcal/mol) forming a proton-hydride species, which further evolves ($\Delta G^{\ddagger} \approx 5$ kcal/mol) toward a di-proton intermediate. The calculated reaction barriers and reaction energies are consistent with experimental measurements on the same catalyst. Hydrogen activation is mainly achieved by (1) the interaction between the $\sigma(H_2)$ bond orbital and an empty *d* orbital of nickel and (2) the polarization of the H-H bond induced by the strong electrostatic field due to the N atoms of the pendant amines. Overall our study suggests that this catalyst is already well-designed for H_2 splitting in that all energetic contributions to the barriers already are low (about 5 kcal/mol) and the entropic contribution is high. We are currently analyzing the effect of both P and N substituents on the energetics of the reaction, to determine what modifications can be made to lower the energetic component of the reactivity to enhance the catalytic rate.

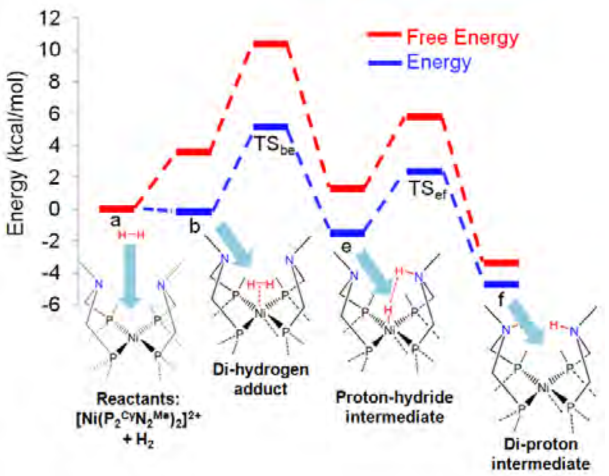


Figure 1. Energy profile for the H_2 oxidation by $Ni(P_2^{Cy}N_2^{Me})_2]^{2+}$ complex.

References

[1] M. Rakowski, DuBois and D. DuBois, *Acc. Chem. Res.* **42**, 1974 (2009).

DE-FG02-09ER16094. **Justine P. Roth**

Isotopic Studies of O–O Bond Formation during Water Oxidation

PI: Justine P. Roth
Postdoctoral: Alfredo M. Angeles-Boza
Students: Daniel C. Ashley, Soraya Simpson
Collaborator: Christopher J. Cramer (University of Minnesota)
Contact: Department of Chemistry, Johns Hopkins University,
3400 N. Charles St. Baltimore, MD 21218
E-mail: jproth@jhu.edu

Goal: To develop new mechanistic probes for understanding water oxidation catalysis.

DOE interest: The photo-catalytic oxidation of water and concomitant production of hydrogen as a fuel is of paramount importance in the basic energy sciences. This approach is without question one of the most formidable challenges in the physical sciences; however, it is also one of the most promising solutions to the world's energy crisis. To develop a light-driven water oxidation catalyst akin to the natural photosystem II, a four photon process must be effected which converts two molecules of H_2O to O_2 and 4 hydrogen atom ($4H^+ + 4e^-$) equivalents. The fundamental mechanistic insight and predictive understanding required to design such catalysts is not yet available. The sponsored research aims to test two generalized mechanisms that define the "difficult" O−O bond forming step in water oxidation catalysis. The first is a radical based mechanism in which two oxygen radical equivalents couple. The second is a nucleophilic attack mechanism involving water or hydroxide attack and the concomitant two-electron reduction of an electrophilic metal oxo species.

Recent Progress: Change in the $^{18}O/^{16}O$ isotopic composition of natural abundance water occurs during its oxidation to molecular oxygen. A competitive oxygen isotope fractionation technique with high precision and a low detection limit, originally used to study oxygen evolution by photosystem II, is now being applied to investigate synthetic inorganic compounds previously reported to oxidize water. These compounds are believed to react with water through dinuclear manganese, iron and ruthenium intermediates under acidic conditions. Fractionation factors determined from the analysis of the oxygen produced reveal ^{18}O enrichment relative to water and, thus, the presence of inverse oxygen kinetic isotope effects (^{18}O KIEs). Possible origins of the inverse ^{18}O KIEs are being examined experimentally and computationally. Density functional theory calculations provide isotopic vibrational frequencies of relevant structures that allow for the computation of ^{18}O KIEs or the inference of boundary conditions which can then be used to evaluate mechanisms of water oxidation.

Future Plans: The start date for the present award was August 2009.

(1) Collaborative computational studies will examine the basic mechanisms of O–O bond formation by ferrate and permanganate. These efforts will inform measurements (in progress) and computational studies of experimentally complex systems.

(2) Regular access to a dual inlet isotope ratio mass spectrometer. A major instrumentation proposal has been submitted to the NSF for a multi-user instrument. A similar instrument has recently been installed in the JHU Dept of Earth and Planetary Sciences. Collaborative measurements with the groups of Ben Passey and Naomi Levin will be initiated.

(3) H_2O fractionation will be developed as a complementary mechanistic probe. Currently the isotopic composition of O_2 is analyzed to determine that of H_2O; however direct determinations should also be possible using a modified set-up as in Levin's labs.

Publications:

(1) D. C. Ashley, D. W. Brinkley, J. P. Roth* *Inorg. Chem. (Forum on Dioxygen Reduction and Activation)* **2010**, 49, 3661-3675. "Oxygen Isotope Effects as Structural and Mechanistic Probes in Inorganic Oxidation Chemistry."

(2) J. P. Roth* "Heavy Atom Isotope Effects as Probes of Small Molecule Activation" in *Physical Inorganic Chemistry Principles, Methods and Models,* A. Bakac Ed. Wiley: Hoboken NJ, **2010**, pp. 425-458.

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

Toward Mechanism-Based Design of Biomimetic Green Oxidation Catalysts

Postdocs: Voltaire Organo, Xianru Sun
Students: Olga Makhlynets, Wanhua Ye, Jeffrey Wikstrom, Taryn Palluccio, Celeo Guifarro.
Collaborators: Lawrence Que, Jr. (University of Minnesota); Daniel Nocera (MIT); Richard S. Staples (Michigan State University); Bruce M. Foxman (Brandeis); Alexander Filatov (SUNY - Albany); John Caradonna (Boston University).
Contact: Department of Chemistry, Tufts University, 62 Talbot Ave, Medford, MA 02155; Elena.rybak-akimova@tufts.edu

Goal

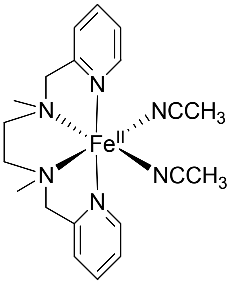
To determine the mechanisms of biomimetic catalytic hydrocarbon oxidations with hydrogen peroxide or dioxygen as terminal oxidants, and to identify iron-containing intermediates that are kinetically competent to carry out selective green oxidations. The long-term goal of the project is to apply mechanistic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

DOE interest

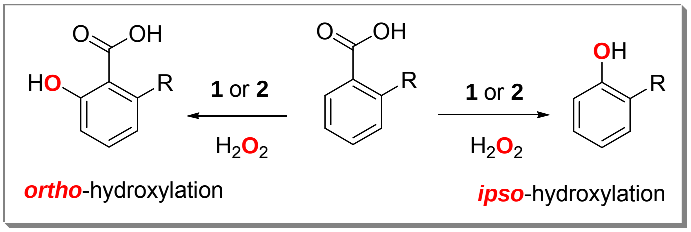
Dioxygen and hydrogen peroxide are ideal oxidants because they are readily available and environmentally clean, producing water as the only byproduct. These reagents allow for the most efficient, atom-economy approach to oxidative functionalization of organic molecules, thus saving energy in chemical 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.

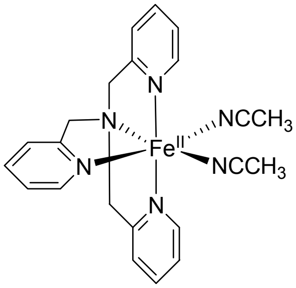
Recent Progress

Substituent-Directed Aromatic Hydroxylation at Non-Heme Iron: Regioselective hydroxylation of aromatic acids with hydrogen peroxide proceeds readily in the presence of iron(II) complexes with tetradentate aminopyridine ligands $[Fe^{II}BPMEN(CH_3CN)_2](ClO_4)_2$ (**1**) and $[Fe^{II}TPA(CH_3CN)_2](OTf)_2$ (**2**) , where BPMEN = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-ethylenediamine, TPA = tris-(2-pyridylmethyl)amine. Two *cis*-sites, which are occupied by labile acetonitrile molecules in **1** and **2**, are available for coordination of H_2O_2 and substituted benzoic acids. The hydroxylation of the aromatic ring occurs exclusively in the vicinity of the anchoring carboxylate functional group: *ortho*-hydroxylation affords salicylates, while *ipso*-hydroxylation with concomitant decarboxylation yields phenolates. The outcome of the substituent-directed hydroxylation depends on the electronic properties and the position of substituents in the molecules of substrates: 3-substituted benzoic acids are preferentially *ortho*-hydroxylated, while 2- and, to a lesser extent, 4-substituted substrates tend to undergo *ipso*-hydroxylation/decarboxylation. These two pathways are not mutually exclusive and likely proceed via a common intermediate. Electron-withdrawing substituents on the aromatic ring of the carboxylic acids disfavor hydroxylation, indicating an electrophilic nature for the active oxidant. Complexes **1** and **2** exhibit similar reactivity patterns, but **1** generates a more powerful oxidant than **2**. Spectroscopic and labeling studies exclude Fe^{III}-peroxoacid and Fe^{IV}=O species as potential reaction intermediates, but strongly indicate the involvement of an Fe^{III}-OOH intermediate that undergoes intramolecular acid-promoted heterolytic O-O bond cleavage, producing transient iron(V) oxidant.



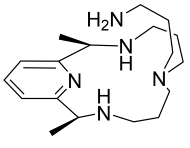
1



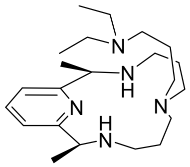


2

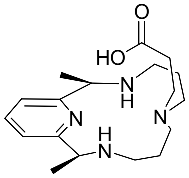
Oxidations with iron(II)and nickel(II) aminopyridine macrocycles. Novel nickel(II) complexes of pyridine-azamacrocycles (PyMACs) with pendant arms have been prepared and characterized. Simple, direct and selective mono-functionalization of PyMACs can be accomplished either by derivatization at the pendant arm of metal complexes or by utilizing Michael addition reaction on free ligands. Nickel(II)-PyMAC complexes with a flexible pendant arm exhibit structural and color changes due to “on-off” arm coordination to the metal center. These changes can be induced by varying the pH of the solution or changing the solvent. Pendant arms with varying hydrogen bonding and proton-donor properties have shown to affect the peroxidase-like activity of Ni(II)-PyMAC complexes in the oxidation of ABTS with hydrogen peroxide. The complex bearing an appended carboxylic acid functionality is the most active catalyst; the corresponding iron complex is an efficient catalyst for olefin epoxidation.



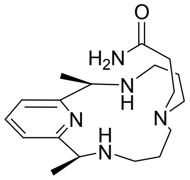
LNH_2



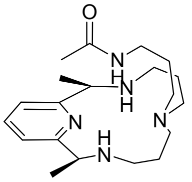
$LNEt_2$



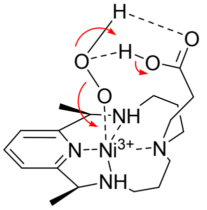
LCOOH



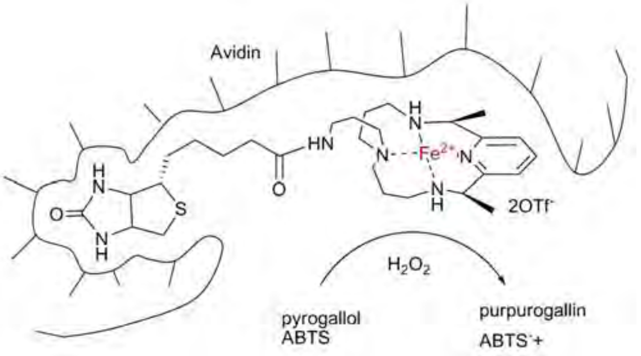
$LCONH_2$



LNHCOMe



Pendant arms were also used to append an anchoring group for embedding redox active catalysts into protein environment. Biotin-avidin molecular recognition motif combined with iron PyMACs afforded artificial non-heme peroxidases.



Mechanistic studies on oxidations catalyzed by Fe-PyMACs focused on generating Fe(IV)=O intermediates and exploring their reactivity. Iodine(V) compounds (e.g. IBX esters) proved to be excellent oxygen atom donors that cleanly yields ferryl(IV) species in solution. Surprisingly, the ability of these $(L)Fe^{IV}=O$ intermediates to transfer an oxygen atom is limited.

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.

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

Transition Metal Mediated Transformations of Small Molecules

PI: Ayus man Sen
Department of Chemistry
The Pennsylvania State University, University Park, PA 16802
Phone: (814) 863-2460; Fax: (814) 863-5319
Email: asen@psu.edu
http://research.chem.psu.edu/axsgroup/

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

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.

An additional project involves the catalytic transformation of biomass. The production of chemicals and liquid fuel directly from biomass is of great current interest, given the diminishing reserves of coal, oil, and natural gas – the predominant current sources of chemicals and fuel. Further, the use of biomass substantially reduces net carbon dioxide emission because the latter is recycled in the biomass regeneration.

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 has been devoted to catalytic systems for the polymerization of functional monomers. Cyclic olefin copolymers are an important class of amorphous, transparent materials. Among them, the ethene/norbornene (E/NB) copolymer is of great commercial importance. Due to its unique characteristics, such as high transparency, excellent barrier property, and high mechanical strength, E/NB copolymer is used in pharmaceutical packaging, disposable diagnostic, moldings for optical lenses, etc. We have synthesized and characterized of several (N~O)-ligated palladium(II) complexes and employed them for ethene homopolymerization, as well as ethene/norbornene and carbon monoxide/norbornene copolymerizations. Most notably, these catalysts show good activity for ethene/non-polar functional norbornene copolymerizations, resulting in nearly alternating copolymers with “living” characteristics. They are also active for ethene/polar functional norbornene copolymerizations. In addition, we have studied the step-wise formation carbon monoxide/norbornene copolymers by ^{13}C NMR spectroscopy.

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.

The effect of Lewis acids ($AlCl_3$ and $Sc(OTf)_3$) on the reactivity ratios for (meth)acrylate/1-hexene and methacrylate/norbornene radical copolymerizations was also investigated. The reactivity ratio r_1 for both methyl acrylate and methyl methacrylate decreases in the presence of Lewis acids; 1-alkene reactivity ratio r_2 is close to zero. The substantial decrease in r_1 values and an increased polymerization rate demonstrate that Lewis acids promote (meth)acrylate cross-propagation significantly more than self-propagation, especially for methyl acrylate. The alkenes do not undergo self-propagation under our conditions. Furthermore, due to (a) enhanced binding of the Lewis acid to the carbonyl group on the monomer compared to those on the polymer and (b) the facile exchange of the Lewis acid between the monomer and the polymer, only a catalytic amount to Lewis acid is required to strongly influence alkene uptake and copolymerization rate.

Existing technologies to produce liquid fuel from biomass are typically energy intensive multi-step processes. We have discovered that hexose from a wide range of biomass-derived carbohydrates, cellulose, and even raw lignocellulose (e.g., corn stover) can be converted to 2,5-dimethyltetrahydrofuran (DMTHF) in one step in good yields under mild conditions in water. Under the same conditions, 2-methyltetrahydrofuran (MTHF) is formed from pentose. The reaction employs a soluble rhodium catalyst, dihydrogen, and HI /HCl + NaI. The catalytic system is robust and can be recycled repeatedly without loss of activity. Carbohydrates, such as mono and polysaccharides and cellulose, typically constitute 50-80% of plant biomass. DMTHF is superior to ethanol and has many of the desirable properties currently found in typical petroleum-derived transportation fuels.

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. In addition, we will continue to work on the catalytic transformation of biomass to chemicals and fuel.

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. 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.

The production of chemicals and liquid fuel directly from biomass is of great current interest, given the diminishing reserves of coal, oil, and natural gas – the predominant current sources of chemicals and fuel. Further, the use of biomass substantially reduces net carbon dioxide emission because the latter is recycled in the biomass regeneration.

Refereed Publications Based on DOE Grant (2007-present)

1. "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.
2. "Perspective on Metal-Mediated Polar Monomer/Alkene Copolymerization," Ayusman Sen and Sachin Borkar, *J. Organomet. Chem.*, **2007**, *692*, 3291.
3. "Selective Heterogeneous Catalytic Hydrogenation by Recyclable Poly(allylamine) Gel-Supported Palladium(0) Nanoparticles," Yiying Hong and Ayusman Sen, *Chem. Mater.*, **2007**, *19*, 961.
4. "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.
5. "Copolymerization of Ethene with Styrene Derivatives, Vinyl Ketone, and Vinylcyclohexane Using a (Phosphine-sulfonate)palladium(II) System: Unusual Functionality and Solvent Tolerance," Sachin Borkar, David K. Newsham, Ayusman Sen, *Organometallics*, **2008**, *27*, 3331.
6. "Effect of Lewis and Bronsted Acids on the Homopolymerization of Acrylates and Their Copolymerization with 1-Alkenes," Rong Luo, Ying Chen, Ayusman Sen, *J. Polym. Sci., A: Polym. Chem.* **2008**, *46*, 5499.
7. "Electron-Transfer-Induced Iron-Based Atom Transfer Radical Polymerization of Styrene Derivatives and Copolymerization of Styrene and Methyl Methacrylate," Rong Luo and Ayusman Sen, *Macromolecules*, **2008**, *41*, 4514.
8. "Effect of Lewis Acids on Reactivity Ratios for (Meth)acrylate/Nonpolar Alkene Copolymerizations," Ying Chen and Ayusman Sen, *Macromolecules*, **2009**, *42*, 3951.
9. "Palladium-Catalyzed Nonalternating Copolymerization of Ethene and Carbon Monoxide: Scope and Mechanism," Rong Luo, David K. Newsham, and Ayusman Sen, *Organometallics*, **2009**, *28*, 6994.
10. "One Step Catalytic Transformation of Carbohydrates and Cellulosic Biomass to 2,5-Dimethyltetrahydrorofuran for Liquid Fuel," Weiran Yang and Ayusman Sen, *ChemSusChem*, **2010**, in press.

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

Platinum Oxo Complex Reactivity and Dioxygen Activation

Students: Malathi Weliange, Alice Raphael, Morgan Moody, Liping Chen

Contact: P. R. Sharp, Department of Chemistry, University of Missouri, Columbia, MO
65211; Phone: 573-882-7715; email: sharpp@missouri.edu

Goals

Understanding of 1) the relationship of late transition metal oxo and hydroxo complexes to oxygen activation and hydrocarbon oxidation and 2) the controlling factors in halogen photo-elimination from organometallic halogen complexes.

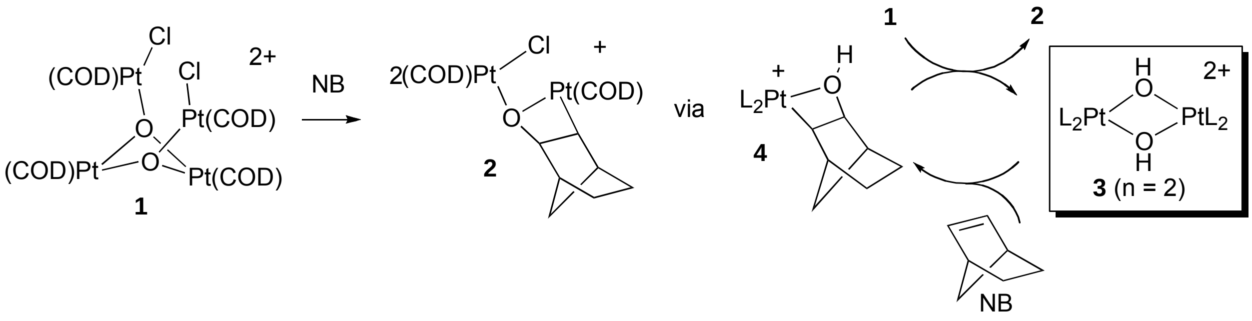
DOE Interest

1) Understanding 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. 2) Halogen photo-elimination is a critical step in possible solar energy conversion and storage cycles. Optimization could lead to practical processes for energy conversion and storage.

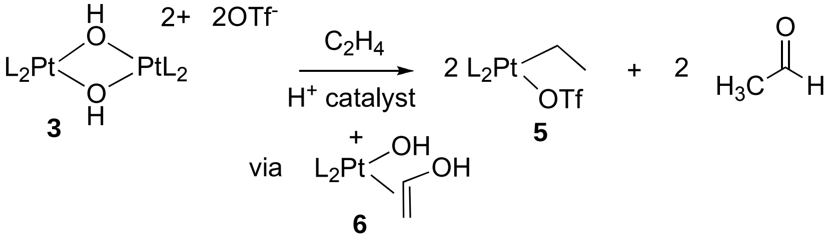
Recent Progress

Alkene oxidation chemistry. Previously, we reported the formation of platinaoxetane **2** from oxo complex **1** and norbornene. We have now shown that the reaction is proton catalyzed and mediated by hydroxo complex **3**. The reaction of **3** norbornene to give **4** is itself proton catalyzed.

Scheme 1. L_2 = COD



Hydroxo complex **3** is involved in ethylene oxidation to acetaldehyde. The reaction approximates the stoichiometry given in eq 1 and is proton catalyzed.

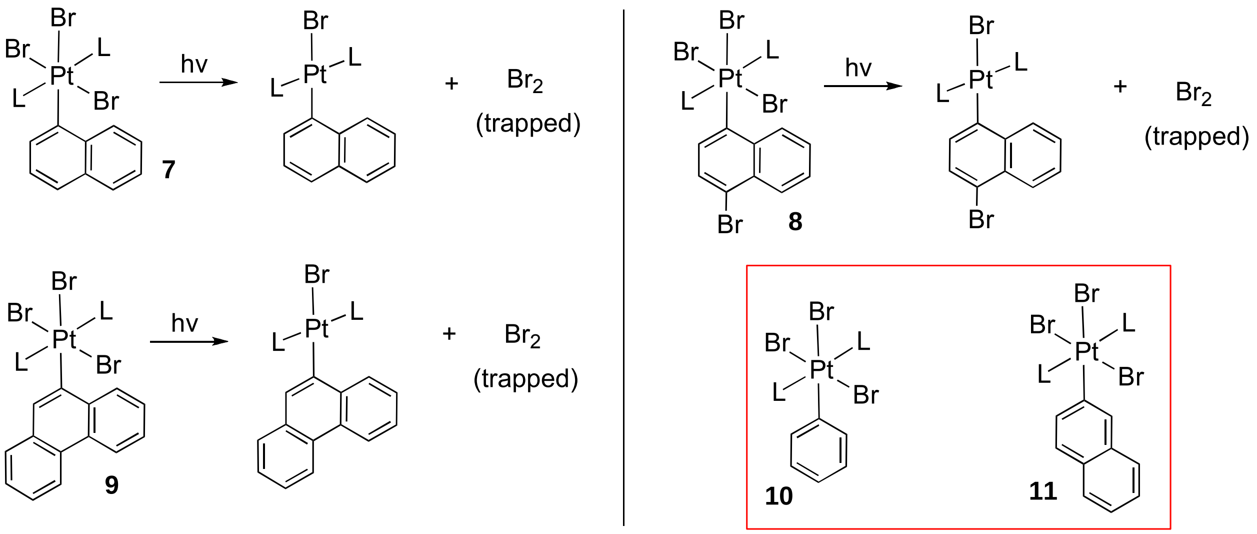


(1)

Intermediate **6**, is detected and its decomposition to acetaldehyde and **5** also appears to be proton catalyzed. Reactions of **3** with propylene and 1-butene appear similar but show an increasing tendency to give allyl complexes.

Bromine photoelimination. Pt(IV) complexes **7**, **8** and **9** (Scheme 2) photoeliminate bromine (ϕ ~ 10% at 313 nm). Complex **10** is photoinactive while **11** is photoactive but with a 20 times lower quantum yield. DFT calculations on the lowest energy triplet states indicate that the *peri*-hydrogen atom in **7**, **8** and **9** is responsible for the high photoactivity. Steric interactions trigger facile bromine loss and prevent recombination (Fig 1).

Scheme 2. L = PEt_3



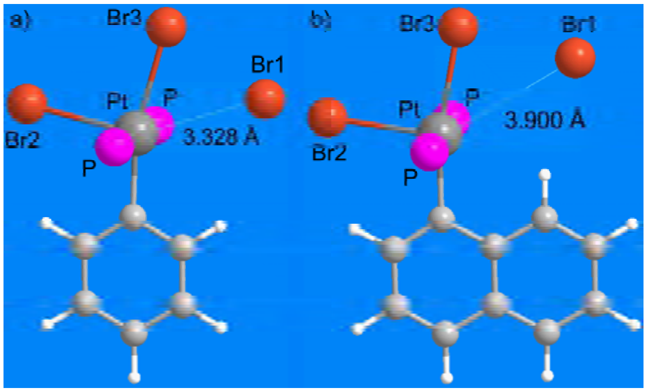


Figure 1. Drawings of the lowest energy triplet structures for a) *trans*-$Pt(PMe_3)_2(Ph)(Br)_3$ (**10'**) and b) *trans*-$Pt(PMe_3)_2(1\text{-naphthyl})(Br)_3$ (**8'**). PMe_3 methyl groups removed for clarity.

Future Plans

1) We will continue our work on the alkene oxidation. In particular we are interested in why changing the alkene from propylene to 1-butene results in greater yields of allyl complexes. 2) The tremendous variability possible in the photoactive Pt(IV) organometallic complexes **7-9** presents an excellent opportunity to explore structural and electronic features in halogen photoeliminations. We will explore the effect of alterations on the quantum yields and use DFT to guide work and understand the results.

Publications (2008-2010)

Singh, A.; Anandhi, U.; Cinellu, M. A.; Sharp, P. R. "Diimine Supported Group 10 Hydroxo, Oxo, Amido, and Imido Complexes" *Dalton Trans*., **2008**, 2314 - 2327. DOI: 10.1039/b715663d

Wu, J.; Sharp, P. R. "Synthesis and Characterization of a Family of Platinaoxetanes" *Organometallics*, **2008**, *27(6)*, 1234–1241. DOI: 10.1021/om7010479

Singh, A.; Sharp, P. R. "Rh And Ir Dibenzo[*a,e*]cyclooctatetraene Complexes: Chloro, Hydroxo, and Mixed Au Oxo Complexes" *Inorg. Chim. Acta*, **2008**, *361(11)*, 3159-3164. DOI: 10.1016/j.ica.2007.12.007. Invited contribution to a special edition in honor of R. Angelici.

Wu, J.; Sharp, P. R. "CO, Isocyanide, Alkene and Alkyne Insertions into Platinaoxetane Pt-O Bonds" *Organometallics*, **2008,** *27(18)*, 4810-4816. DOI: 10.1021/om8005849

Weliange, M.; Szuromi, E.; Sharp, P. R. "Proton-Catalyzed Oxo-Alkene Coupling: 2-Platinaoxetane Formation" *J. Am. Chem. Soc.* **2009**, *131*, 8736-8737. DOI:10.1021/ja902180k

Wu, J.; Sharp, P. R. "Reactivity and Stability of 2-Platinaoxetanes" *Organometallics*, **2009,** *28 (24)*, 6935–6943. DOI: 10.1021/om900828k

Weliange, M.; Sharp, P. R. "Alkene oxidation by $[(COD)Pt(OH)]_n^{n+}$: Mechanistic studies." 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, (2010)

Weliange, M.; Szuromi, Endre; Sharp, P. R. "Platinaoxetane formation." 238th ACS National Meeting, Washington, DC, United States, August 16-20, (2009).

DE-SC0002217 **Lawrence R. Sita**

Investigation of Energy-Efficient Dinitrogen Activation and N-atom Transfer Processes

Postdoc: TBD
Students: Brendan Yonke
Collaborators: Andrei Vedernikov (University of Maryland), Masakazu Hirotsu (Osaka City University, Japan)
Contacts: University of Maryland, Rm 0300, Bldg 091, College Park, MD 20742
lsita@umd.edu

Goals

The central hypothesis of the research program is that the unique steric and electronic features of the monocyclopentadienyl (η^5-C_5R_5), amidinate {η^2-[N(R^1)C(X)N(R^2)]} (CpAm) and guanidinate {η^2-[N(R^1)C(X)N(R^2)]} (CpGu) ligand environments are ideally suited for experimentally and computationally investigating groups 4, 5, and 6 early transition metal-mediated N_2 activation, N≡N bong cleavage, and N-atom functionalization within several isostructural series of CpAm- and CpGu-based dinuclear $[L_nM]_2(\mu\text{-}N_2)$ complexes in which the nature of the metal center can be varied as a function of group and row position, formal oxidation state and d^n electron count.

The specific aims of the project are to pursue a combined experimental and theoretical approach to: (1) establish energy profiles for all pathways leading to N_2 multiple bond activation and cleavage – including the molecular and electronic structures of ground-state precursors, intermediates and products, as well as those of interconnecting transition states, (2) determine relative energies and barrier heights for all structures and processes as a function of metal group and row position, formal metal oxidation state, d^n electron count, and (3) elucidate possible roles played by one- and two-electron reduced or oxidized species in facilitating N_2 activation, N≡N bond cleavage, N-atom functionalization, and N-atom transfer processes.

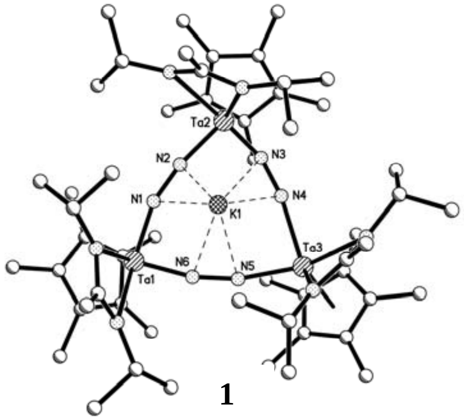
DOE Interest

The current energy and environmental costs for existing nitrogen-based fertilizer production employing the Haber-Bosch (HB) process, which converts dinitrogen to ammonia through direct hydrogenation over iron-based catalysts at high temperature and pressure are quite high, but presently unavoidable. Accordingly, the development of well-defined transition-metal-based homogeneous catalysts that can mediate the direct conversion of dinitrogen to ammonia, and other N-atom functionalization and N-atom transfer processes at, or near, ambient temperatures, still presents important experimental and theoretical challenges with enormous potential societal benefits.

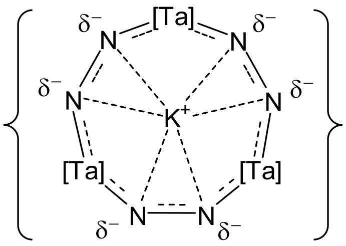
Recent Progress

A. New Dinuclear and Multinuclear μ-N_2 Complexes. Synthetic and mechanistic investigations have served to expand the range of CpAm and GuAm di- and multinuclear metal complexes of the groups 4, 5 and 6 transition metals. In addition to second- and third-row group 6 dinuclear $[ML_n]_2(\mu\text{-}\eta^1, \eta^1\text{-}N_2)$ complexes (*vide infra*), the group 5 trinuclear compound **1** shown in Scheme 1 was isolated and structurally characterized. Compound **1** represents the first example of a new fundamental form for multinuclear dinitrogen complexes and isolation of this cyclic structure provides potential clues regarding the mechanistic pathway by which these dinitrogen complexes are formed.

Scheme 1



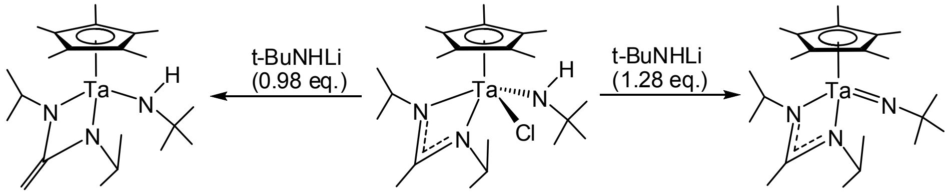
1



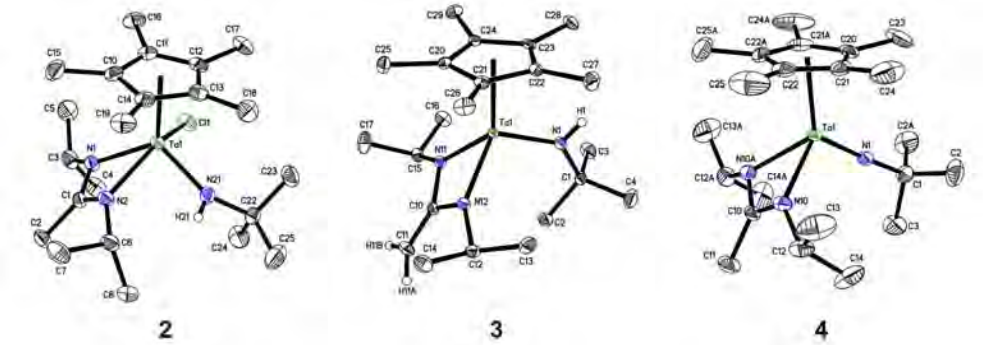
3 [Ta(V)]	+9
1 $[N_2]^{4-}$	- 4
1 $[N_2]^{3-}$	- 3
1 $[N_2]^{2-}$	- 2
1 e	- 1
charge	- 1

B. Investigation of Coupled Proton – Electron Transfer for N-Atom Functionalization. Progress has been made with the synthesis of stable, isostructural series of mononuclear groups 4, 5 and 6 M(IV) imido complexes, which represent the first known examples of this class of compounds. Of particular interest has been the ability to prepare tautomeric forms, **3** and **4**, that do not interconvert (see Scheme 2).

Scheme 2



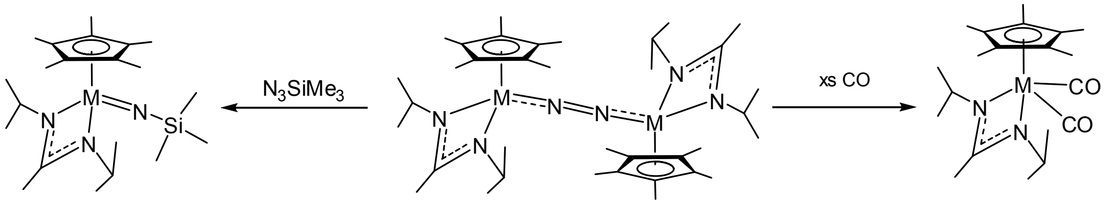
3 **2** **4**



2 **3** **4**

C. Investigation of Group 6 $[ML_n]_2(\mu\text{-}\eta^1, \eta^1\text{-}N_2)$ Chemistry. Facile synthetic accessibility of the CpAm-based group 6 dinuclear dinitrogen complexes **5** and **6** is serving to rapidly establish a wealth of new fundamental synthetic transformations that are being explored for N-atom transfer processes. Scheme 3 presents two of these synthetic transformations.

Scheme 3



5: M = Mo
6: M = W

Publications (2009-2010)

(1) Fontaine, P. P.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. "Dinitrogen Complexation and Activation within Mid-Valent Group 6 [M(IV, d^2), M(IV, d^2)] 'End-On-Bridged' Dinuclear Complexes, $\{(\eta^5\text{-}C_5Me_5)M[N(i\text{-}Pr)C(X)N(i\text{-}Pr)]\}_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2)$ (M = Mo and W; X = Me or NMe_2)", **2010**, submitted and under revision.

(2) Yonke, B. L.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. "Non-interconverting Tautomers of a Monocyclopentadienyl, Monoamidinate Ta(IV) Imido," in preparation

DE-FG02-08ER15996 **Jeremy M. Smith**

Mechanisms of N-H Bond Formation Relevant to Nitrogen Fixation

Contact Information: Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces NM 88003. Tel: (575) 646-3346. E-mail: jesmith@nmsu.edu

Student Names: Jeremiah J. Scepaniak, Salvador Muñoz, Keith A. Jones

Collaborators: Haobin Wang (New Mexico State), Ranko P. Bontchev (Cabot Micropowders), Martin L. Kirk (New Mexico), Joshua Telser (Roosevelt), Karsten Meyer (Erlangen), Jeremy N. Harvey (Bristol).

Goal: Understanding the mechanisms of N-H bond formation/cleavage relevant to the formation of ammonia from iron nitrido and related complexes. To provide further insight into the chemistry of the iron nitrido unit, the reactivity of the iron nitrido complexes in two-electron nitrogen atom transfer reactions is also under investigation.

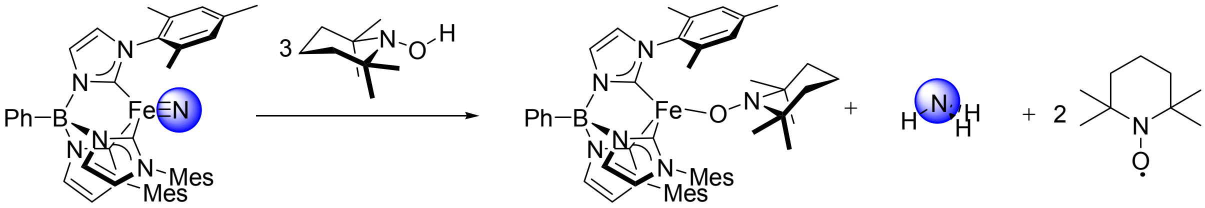
Interest to DOE: The production of ammonia from atmospheric nitrogen is very energy intensive, primarily due to the production of H_2 from fossil fuels. The development of alternative methods for N-H bond formation may lead to more energy efficient methods for ammonia synthesis that do not require H_2.

Recent Progress

1. Hydrogen atom transfer to a metal nitrido complex.

Reaction of the iron(IV) nitrido complex PhB(MesIm)$_3$Fe≡N with 3 equivalents of TEMPO-H leads to high yields of ammonia, along with quantitative formation of the iron(II) complex PhB(MesIm)$_3$Fe(TEMPO), and the TEMPO radical (Scheme 1). Thermodynamic and kinetic investigations into the first step of the reaction mechanism are most consistent with a concerted process involving initial hydrogen atom transfer (HAT) from TEMPO-H:

$$[Fe^{IV}]\equiv N + \text{TEMPO-H} \rightarrow [Fe^{III}]\equiv N\text{-}H + \text{TEMPO}\cdot$$

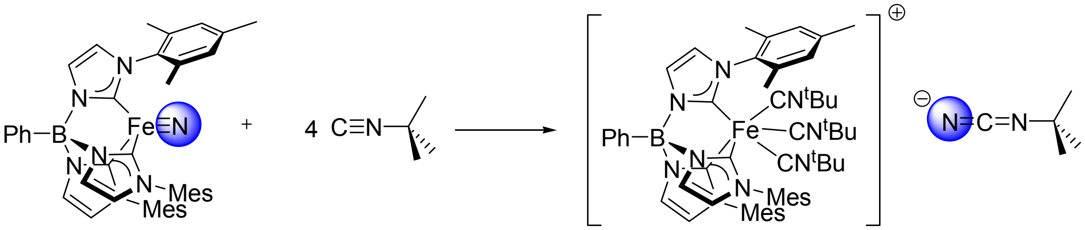


Scheme 1

Consistent with this proposal, the nitrido complex also reacts with an organic radical to provide an iron(III) imido complex.

2. Nitrogen atom transfer from iron(IV) nitrido complexes

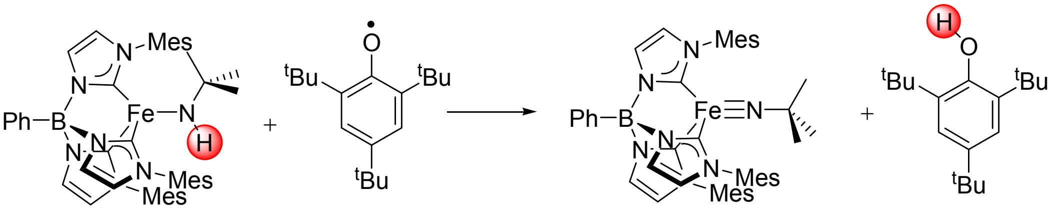
Two-electron reduction of iron(IV) nitrido complexes is effected by a range of nucleophiles, with cleavage of the Fe-N bond occurring for some substrates (Scheme 2). Mechanistic investigations of the reaction with triarylphosphines, supported by electronic structure calculations, suggest a dual nature transition state for nitrogen atom transfer. Consistent with this proposal, the nitrido complexes also react with electrophiles.



Scheme 2

3. Iron(II) amido oxidation

The reaction of the iron(II) amido complex PhB(MesIm)$_3$Fe-N(H)^{t}Bu with the stable 2,4,6-tri(*tert*-butyl)phenoxy radical is solvent dependant. In benzene, HAT to form the iron(III) imido complex PhB(MesIm)$_3$Fe≡N^{t}Bu is observed (Scheme 3), similarly to related cobalt complexes. In THF, electron transfer is competitive with HAT, leading to the spectroscopically characterized complex PhB(MesIm)$_3$Fe-N(H)^{t}Bu$^+$. Computational methods have been used to provide insight into the solvent dependence of reaction mechanism.



Scheme 3

Future plans

1. Mechanism of NH$_3$ formation from iron(IV) nitrido complexes

Synthetic efforts will be directed towards the synthesis of the key intermediate, PhB(MesIm)$_3$Fe≡N-H. This complex will be used to mechanistically probe the subsequent steps of the ammonia forming reaction between PhB(MesIm)$_3$Fe≡N and TEMPO-H. Computational investigations will be used to complement these mechanistic investigations**.**

2. Towards N-N cleavage coupled to hydrogen atom transfer

New iron(II) hydrazido complexes have been prepared in which the spin state of the complex depends on the nature of the tris(carbene)borate ligand. We will investigate the reactivity of these complexes towards hydrogen atom donors (e.g. TEMPO-H) and hydrogen atom acceptors (e.g. 2,4,6-$^{t}Bu_3C_6H_2O\cdot$), specifically for reactions that involve N-H bond formation and/or N-N bond cleavage.

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3. Scepaniak, J.J.; Young, J.A; Bontchev, R.P.; Smith, J.M. "Formation of Ammonia from an Iron Nitrido Complex" *Angew. Chem. Int. Ed.* **2009**, *48*, 3158-3160.

Redox-Active Ligands Facilitate 2e$^-$ Oxo-Transfer Reactions via Biomimetic 1e$^-$ Steps

Jake D. Soper and Cameron A. Lippert
School of Chemistry and Biochemistry, Georgia Institute of Technology
Atlanta, GA 30332-0400
jake.soper@chemistry.gatech.edu

The ability to effect reductive cleavage or oxidative assembly of O_2 has importance in applications ranging from the design of new aerobic oxidation catalysts to the production of clean chemical fuels. Although many synthetic systems mediate these reactions, the chemical features that engender redox selectivity in O_2 activation or production are often not well understood or easily transferrable to other classes of redox catalysts. We speculated that the propensity of some high-valent 4d and 5d metals to avoid odd-electron intermediates might introduce a kinetic barrier to symmetric bimetallic O_2 homolysis by inhibiting access to superoxo $[O_2\bullet]^-$ and peroxo $[O_2]^{2-}$ complex intermediates. To this end, we prepared a series of coordinatively unsaturated oxorhenium(V) complex anions and found that complexes with redox-active catecholate and amidophenolate ligands effect clean bimetallic cleavage of O_2 to give dioxorhenium(VII) products.[i] A structural homolog with redox-inert oxalate ligands is stable in O_2. Experimental and computational data suggest that redox-active ligands lower the kinetic barrier to bimetallic O_2 homolysis at five-coordinate oxorhenium(V) by facilitating formation and stabilization of intermediate species containing partially reduced O_2 ligands.[i] The redox-active ligand gives access to a lower energy reaction pathway for the 1e$^-$ Re–O bond forming reaction because the metal fragment can be oxidized without a change in formal rhenium oxidation state. It is also likely that redox-active ligands facilitate O_2 homolysis by lowering the barrier to the formally spin-forbidden reactions of triplet dioxygen with the closed shell oxorhenium(V) anions. By orthogonalizing 1e$^-$ and 2e$^-$ redox at oxorhenium(V), the redox-active ligand allows high-valent rhenium to utilize a mechanism for O_2 activation that is atypical of oxorhenium(V), but more typical for oxygenase enzymes and models based on 3d transition metal ions: O_2 cleavage occurs by a net 2e$^-$ process through a series of 1e$^-$ steps. Importantly, introduction of a 1e$^-$ redox capacity does not perturb the ability of the metal ion to facilitate 2e$^-$ oxo transfer. This result has implications for design of new multielectron catalysts for oxygenase-type O_2 activation, as well as the microscopic reverse reaction, O–O bond formation from coupling of two M=O fragments for catalytic water oxidation. Further details of this chemistry, and of the effects of ligand-centered 1e$^-$ redox in other 2e$^-$ oxo transfer reactions at high-valent oxorhenium centers,[ii] will be presented.

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

Mechanisms of Organometallic Copper Oxidase Reactions

Students: Amanda E. King, Lauren M. Huffman, Alicia Casitas, Lujuan Yang
Collaborators: Thomas C. Brunold (UW-Madison), Xavi Ribas and Miquel Costas (Universitat de Girona, Spain), Teodor Parella (Universitat Autònoma de Barcelona, Spain)
Contact: 1101 University Avenue
Madison, WI 53706
(608) 265-6288; stahl@chem.wisc.edu

Goals

In our recent work, we have pursued three complementary goals:

1. to elucidate the catalytic mechanism of Cu-catalyzed aerobic oxidation reactions that proceed via organometallic intermediates
2. to probe the organometallic chemistry of copper(III) complexes that have relevance to catalytic processes
3. to develop new aerobic oxidative coupling reactions.

DOE Interest

This project is addressing fundamental questions and practical goals related to chemical catalysis, particularly those associated with the use of molecular oxygen as a stoichiometric oxidant in selective oxidation reactions. Successful development of selective aerobic oxidation reactions has important implications for the development of less-energy-demanding routes for the synthesis of basic chemical feedstocks and value-added chemicals. Moreover, our fundamental studies of copper-catalyzed aerobic oxidation reactions should reveal conceptual links between copper-containing metalloenzymes, model systems and non-biomimetic copper catalyst systems for synthetically useful aerobic oxidation reactions.

Recent Progress

Our recent work has addressed three specific objectives:

(1) to establish a mechanistic framework for copper-catalyzed C–O bond-forming reactions through a study of the oxidative methoxylation of *p*-tolylboronic dimethyl ester.

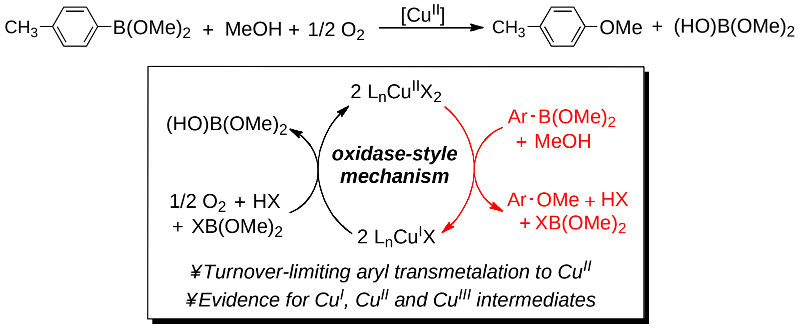
(2) to demonstrate and provide insights into the potential role of arylcopper(III) intermediates in Cu-catalyzed C–N cross-coupling reaction (Ullmann-Goldberg reactions) and in Cu-catalyzed aerobic oxidative coupling reactions involving functionalization of aromatic C–H bonds.

(3) to develop a Cu-catalyzed methods for aerobic oxidative halogenation of arenes.

Each of these objectives is elaborated in more detail below.

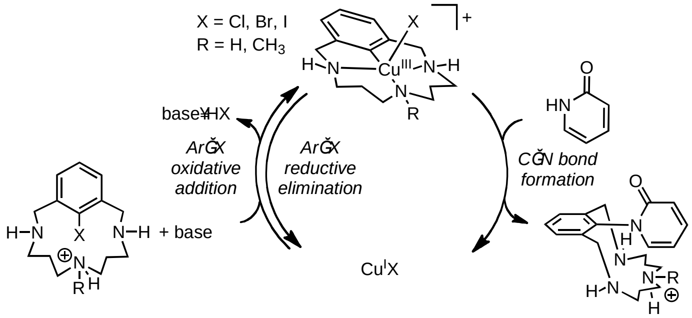
Specific Objective 1. To establish a mechanistic framework for copper-catalyzed C–O bond-forming reactions through a study of the oxidative methoxylation of *p*-tolylboronic dimethyl ester.

Copper-catalyzed aerobic oxidative coupling of arylboronic acid derivatives and heteroatom nucleophiles is a highly useful method for the formation of aryl-heteroatom bonds. Mechanistic studies revealed that this reaction proceeds via an "oxidase"-style mechanism. Kinetic and spectroscopic studies established that transmetalation of the aryl group from boron to Cu^{II} is the turnover-limiting step, and reoxidation of the reduced catalyst by O_2 is rapid. Further mechanistic analysis implicates the involvement of an aryl-copper(III) intermediate that undergoes facile C–O bond formation.

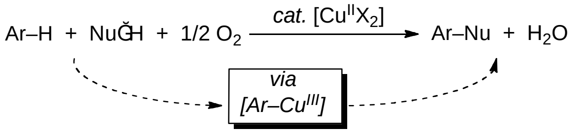


Specific Objective 2. To demonstrate and provide insights into the potential role of aryl-copper(III) intermediates in Cu-catalyzed C–N cross-coupling reaction (Ullmann-Goldberg reactions) and in Cu-catalyzed aerobic oxidative coupling reactions involving functionalization of aromatic C–H bonds.

Copper-catalyzed cross-coupling methods for carbon-carbon and carbon-heteroatom bond formation, known as "Ullmann-Goldberg coupling" reactions, were discovered more than 100 years ago. These classic reactions have returned to the forefront of the field of chemistry in recent years because of their widespread utility in synthesis of pharmaceuticals and novel materials, and because copper represents a lower-cost and less-toxic catalyst alternative to palladium. In collaboration with Prof. X. Ribas (Girona), we prepared and full characterized a series of aryl-copper(III)-halide complexes, elusive species that are frequently invoked in catalytic mechanisms but have not been observed previously. These complexes enabled the first direct observation of aryl halide reductive elimination from Cu^{III} and oxidative addition to Cu^{I} centers. In-situ spectroscopic studies (^1H NMR, UV-visible) of a Cu-catalyzed C-N coupling reaction provides definitive evidence for the involvement of an aryl-copper(III)-halide intermediate in the catalytic mechanism. These observations represent a fundamental breakthrough in the mechanistic understanding of these copper-catalyzed reactions.

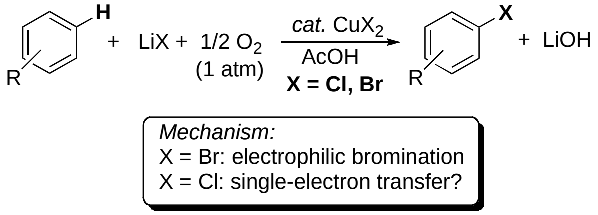


Recent studies by us and other have drawn attention to Cu^{II}-catalyzed methods for aerobic oxidative functionalization of C–H bonds, but very little is known about the mechanisms of these reactions. By employing a macrocyclic arene substrate analogous to that used in our fundamental studies of Ullmann-type coupling reactions, we have identified a Cu-catalyzed method for aerobic methoxylation and amidation of an arene C–H bond. In this work, we provide the first direct spectroscopic evidence for the intermediacy of an aryl-Cu^{III} intermediate during catalysis. These results highlight a mechanistic unity that exists between Cu^{I}-catalyzed cross-coupling reactions and Cu^{II}-catalyzed oxidative coupling reactions.



Specific Objective 3: To develop a Cu-catalyzed methods for aerobic oxidative halogenation of arenes.

Electron-rich aromatic C–H bonds undergo regioselective chlorination and bromination in the presence of CuX_2, LiX (X = Cl, Br) and molecular oxygen. Preliminary mechanistic insights suggest that the bromination proceeds via in-situ generation of molecular bromine, followed by electrophilic bromination of the aromatic ring. The chlorination reactions proceed by different, less-well-defined pathway, probably initiated by single electron tranfer from the arene to Cu^{II}.



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.

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

Institute for Catalysis in Energy Processes

Additonal PIs: ANL: Larry Curtiss, Nada Dimitrijevic, Jeff Elam, Chris Marshall, Jeff Miller, Peter Zapol
NU: Michael Bedzyk, Linda Broadbelt, Donald Ellis, Kimberly Gray, Mark Hersam, Franz Geiger, Joseph Hupp, Harold Kung, Laurence Marks, Tobin Marks, SonBinh Nguyen, Kenneth Poeppelmeier, Randall Snurr, Richard Van Duyne, Eric Weitz
Postdocs: Xufeng Lin, Gordana Ostojic, Baiju Vijayan, S. Yin
Graduate Students: Avram Buchbinder, Alon Danon, Christopher Downing, James Enterkin, Zhenxing Feng, Ivan Konstantinov, Kathryn Kosuda, Tony Liang, Neema Mashayekhi, Martin McBriarty, Brian Quezada, Federico Rabuffetti, Patrick Ryan, Abraham Shultz, Staci Wegener.

Contacts: P. Stair, Dept. of Chemistry, Northwestern University, Evanston, IL 60208; pstair@northwestern.edu

Goal

The Institute for Catalysis in Energy Processes (ICEP) is a joint venture of the Northwestern University Center for Catalysis and Surface Science (NU) and Argonne National Laboratory (ANL). It is organized into three (3) highly integrated efforts. Two of these comprise the **Scientific Themes**: *Chemical Catalysis: Selective Oxidation of Light Alkanes to Fuels* and *Photocatalysis: Reduction of Carbon Oxides*. Research activities of ICEP are in synthesis of catalytic materials, in measurements that reveal catalyst properties and chemistry, and in theory and modeling to understand properties, measurements, and chemistry. In many cases ICEP researchers are the inventors or developers of the methods that can be brought to bear on catalytic systems. The third effort is a natural outgrowth of these strengths. It provides the **Research Expertise** for advancing the scientific themes through the application and development of both experimental methods and theory.

Understanding the elementary catalytic steps in selective oxidation of light alkanes to oxygenates, with an ultimate goal to achieve the ability to design and manipulate selective catalytic sites is the major objective of the *Chemical Catalysis* theme. Understanding the elementary steps in the photocatalytic reduction of CO_2 on oxide surfaces is the major objective of the *Photocatalysis* theme. An important aspect of the ongoing ICEP research is the continued advancement and development of both synthesis and characterization methods. Significant progress has bee achieved in each of these areas as outlined in the extended description of results.

DOE Interest

As emphasized in both the DOE-BES “Catalysis for Energy” and “Directing Matter and Energy: Five Challenges for Science and the Imagination,” reports, catalytic technology is essential for economic prosperity, energy security and environmental preservation in the 21st Century. Due to the abundance of light alkanes in natural gas there is a strong incentive to convert them into higher boiling liquids usable for transportation. Likewise, the development of solar fuels technology from the photocatalytic reduction of carbon dioxide would have a major effect on the nation's reliance on foreign sources of energy and the reduction of green house gases. These are difficult chemistries. Therefore, an improved understanding of the relevant catalytic materials and chemistry combined with the development of advanced catalyst synthesis techniques required to achieve practical technologies are relevant to the interests of DOE.

Recent Progress

Chemical Catalysis

Grafting of well defined organo-vanadium complexes of differing nuclearity all lead to tetrahedrally coordinated V, but both UV-Vis and Raman spectroscopies indicate that the electronic and structural properties of these are different. The changes correlate with differences in reactivity. The role of Ti-oxo nuclearity and separation distance of Au from Ti centers for selective oxidation of alkanes by O_2 is under investigation by preparation of precisely controlled catalyst functions. By control of the siloxane architecture small Au clusters with narrow size distribution and controlled distance from Au to Ti should be possible. Vibrational sum frequency generation results suggest that the orientation of adsorbate molecules on the catalyst surface play a role in the reactivity and selectivity. The orientation of olefins is different from that of alkanes suggesting that the double bond affects surface orientation. DFT modeling of Cu and Co ions in molecular organic frameworks (MOFs) reveals that tetrahedral Co in MOF's are not active due to steric constraints preventing access to the active metal site. In the larger cluster Cu MOF, significant progress has been made in understanding the spin crossing point of the triplet to quintet for breaking of the O-O bond state in the decomposition of hydroperoxide intermediate.

Photocatalysis

Work on the photochemical reduction (PCR) of CO_2 has centered on the synthesis, characterization, and evaluation of new materials for CO_2 PCR along with effort directed toward the elucidation of the details of the mechanism for CO_2 PCR. TiO_2-nanocarbon composites appear to be one promising platform for performing photocatalytic chemistry. Another is titania nanotubes (TiNT), prepared by hydrothermal synthesis. A third is titanyl species grafted onto mesoporous silica. The hypothesis that mixed phase TiO_2 nanomaterials with high interfacial densities can be extremely active photocatalysts has been investigated by synthesis and testing of mixed phase TiO_2 films by direct current (DC) magnetron sputtering. Films sputtered at a low deposition angle showed the highest methane yield. EPR reveals that CO_2 is preferentially adsorbed at under-coordinated Ti sites. Supported titanyls have been characterized by Raman spectroscopy.

Research Expertise

In studies of $SrTiO_3$ surface structure the bonding at the surface was comparable to bulk oxide bonding. We have been able to conclude that many principles that are well known for bulk oxides, such as homologous series with intergrowths and bond valance sums, can be applied equally well to surface structures. Atomic-scale structure determination of WO_X grown on α-Fe_2O_3 (0001) found a reversible redox reaction that not only caused the oxidation state of W to change, but that also caused a dramatic rearrangement in the W cation occupation of Fe A-sites and B-sites on the hematite surface.

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DE-FG02-04ER15514 **Andrzej Sygula**

Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

Postdoc: Dr. Shui Cai
Research associate: Renata Sygula
Graduate Students: Michael Yanney and Athauda Karunarathna
Collaborators: Svein Saebo (MSU), William P. Henry (MSU), Frank R. Fronczek (LSU), Stefan Grimme (Münster, Germany), Tomasz Janowski (Arkansas)
Contact Information: Andrzej Sygula,
Department of Chemistry, Mississippi State University, Mail Stop 9573
Mississippi State, MS 39762
Ph. 662.325.7612
asygula@chemistry.msstate.edu

Goal

Design, synthesis and structural studies of large molecular architectures with curved-surface subunits capable of acting as molecular receptors and forming strong supramolecular inclusion complexes with guest molecules. Development of practical, solution-based synthetic methods for curved-surface polycyclic aromatic hydrocarbons.

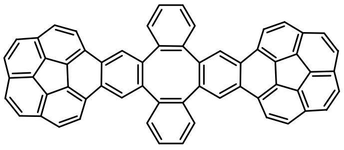
DOE Interest

We have shown recently that using the synthetic methods developed in our laboratory under DOE support, we can construct large molecular assemblies with corannulene subunits acting as molecular receptors for fullerenes. Such molecular tweezers may be able to distinguish between fullerenes of different sizes and shapes, thus allow them to be separated. Also, if attached to a surface, these receptors may extract fullerene molecules from solution or to position them at precise locations on solid supports. This opens some possibilities of applications of buckybowls in separation sciences, nanotechnology and material sciences.

Curved surface polynuclear aromatic hydrocarbons represent a novel class of PAHs that have, until recently, received little study. However, such materials can be formed in fullerene production, and they also represent the end-caps of closed carbon nanotubes; this raises the potential for these PAHs to become more common and perhaps even find their way into the environment. Since so little is known about the chemistry and properties of these systems, basic research is warranted.

Recent Progress

Molecular clips and tweezers with corannulene pincers. Application of the synthetic methodology developed in our laboratory yielded several new molecular clips and tweezers with corannulene pincer(s) and cyclooctadiene (COD) or cyclooctatetraene (COT) tethers. These highly nonplanar systems exhibit clefts of various sizes and shapes with potential to bind guest molecules with geometric selectivity. In addition, conformational flexibility of their tethers allows for an adoption of conformations unavailable for the more rigid tetrabenzocyclooctatetraene tether of the previously synthesized buckycatcher $C_{60}H_{28}$ (**1**).



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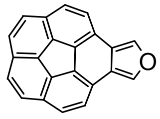

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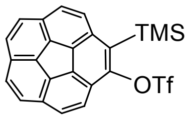
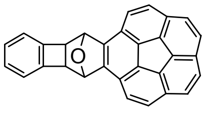


3

Diels-Alder cycloaddition methodology was employed for the preparation of the molecular clips utilizing two synthons recently introduced by us, i.e. isocorannulenofuran (diene) (**2**) or 2-trimethylsilylcorannulenyl trifluoromethanesulfonate (**3**, a precursor for 1,2-didehydrocorannulene, a reactive dienophile). Some of the recently synthesized systems are shown below.



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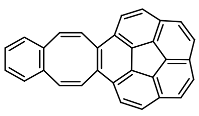

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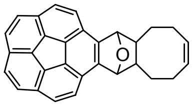

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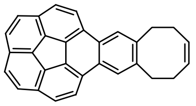

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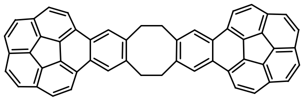
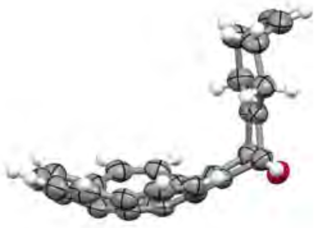


8

X-ray crystal structure determination and/or molecular modeling reveal interesting molecular structures of these systems. For example *endo*-**4** exhibits a "closed-clam" arrangement with the benzene ring of the benzocyclobutane moiety located over the convex side of the corannulene unit. Not surprisingly, a significant shielding of the four hydrogen atoms of the AA'BB' system of the benzene ring is observed with their chemical shifts appearing in the ^{1}H NMR spectrum as broad multiplets centered at 5.4 and 5.9 ppm, significantly upfield from the usual chemical shift of aromatic protons. While **5** has not been characterized by x-ray, it is expected to adopt an "open-clam" conformation of a clip with corannulene and benzene pincers located on the tub-shaped COT tether. Similarly, **6** adopts an "open-clam" conformation with an interesting and rather unusual arrangement of the cyclooctadiene ring with six carbon atoms being almost coplanar and lying in a plane approximately perpendicular to the average plane of the corannulene subunit.

endo-**4** (x-ray)

5 (MM2)

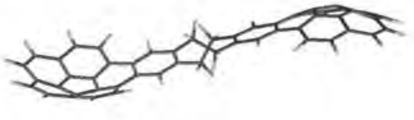


6 (x-ray)

$C_{52}H_{28}$ hydrocarbon **8** represents a more flexible version of buckycatcher **1** with COD tether and two benzocorannulene pincers. Three conformers of **8** located at the B97-D/TZVP computational level. Interestingly, in contrast to the thoroughly studied case of a simpler analog, dibenzo[*a,e*]cyclooctene, twist-boat conformer **8-TB** is calculated to be very strongly favored over the remaining chair (**8-C**) and twist (**8-T**) conformers by over 8 kcal/mol. The unusual preference for **8-TB** results from the intramolecular π-π stacking of the corannulene pincers.

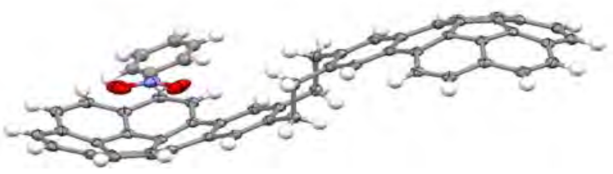
8-TB

8-C



8-T

Somewhat unexpectedly, X-ray crystal structure determination of a 1:1 solvate of **8** with nitrobenzene reveled that the chair conformation **8-C** prevails in the solid state of the solvate clearly demonstrating the importance of solvation effects. The solvating nitrobenzene molecule is encapsulated by two neighboring molecules of **8** and is in van der Waals contacts with the concave sides of the benzocorannulene pincers.



8*$PhNO_2$ (x-ray)

Computational Studies of π-π Stacking of Curved Conjugated Carbon Networks. The energetics of dispersion interactions of a model system of exo-endo corannulene dimer was revisited. The benchmark calculations for the system were performed at QCISD(T) level of theory with aug-cc-pVDZ basis set and the complete basis set correction was estimated at the MP2 level. The benchmark results were compared to the results of DFT calculations with the dispersion-corrected B97-D and ωB97X-D functional as well as M06-2X functional with cc-pVQZ basis set.

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

Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer

Students:	D. T. Shay, F. Jove, E. Sirianni
Postdoc:	A. Gunay
Collaborators:	G. P. A. Yap (U o Delaware), O. Dmitrenko (U o Delaware)
Contact:	Department of Chemistry and Biochemistry,Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19711; theopold@udel.edu

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 terminal oxidant (i. e. the original motivation for this project, and one that will continue to be a focus)
- reduction of O_2 to water close to the thermodynamic potential – in other words, the cathode of any fuel cell based on reactions (of H_2, CH_4, CH_3OH etc.) with O_2
- fixation of nitrogen at modest temperatures and pressures
- transfer of reduced nitrogen species to organic substrates (e. g. aziridination, amination).

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

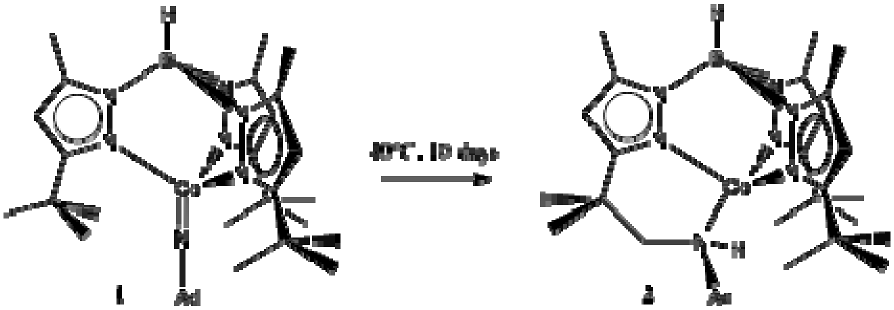
Recent Progress

Cobalt Imido Complexes. Stable terminal imido complexes of the late transition metals (group 9 and beyond) are rare, presumably due to a lack of empty d-orbitals available for π-donation from the NR^{2-} ligand. Such complexes are of interest – inter alia - as intermediates in catalytic NR-group transfer reactions and aminations of hydrocarbons. Our particular interest in the chemistry of cobalt imido complexes of the type $Tp^{R,R'}Co{=}NR$ stems from their isoelectronic relationship to the elusive $Tp^{tBu,Me}Co{=}O$. We have postulated the formation of the latter as a reactive intermediate in the activation of O_2 and N_2O by various $Tp^{tBu,Me}Co$ complexes. To our knowledge no terminal cobalt oxo complex has ever been isolated.

Addition of one equivalent of alkyl azide (RN_3, R = Me, Et, ^{t}Bu, Ad) to a THF solutions of $Tp^{tBu,Me}Co(N_2)$ at room temperature afforded a series of imido complexes $Tp^{tBu,Me}Co{=}NR$, which have all been structurally characterized; magnetic measurements on the representative $Tp^{tBu,Me}Co{=}NAd$ (**1**) have shown it to be an unusual spin-crossover molecule. The energy gap between its diamagnetic ground state (S = 0) and the paramagnetic excited state (according to DFT calculations a triplet, S = 1) was determined both by solid state magnetic susceptibility measurements (ΔH = 9.6(20 kcal/mol) and by variable temperature ^{1}H NMR in solution (ΔH = 6.4(5) kcal/mol).

The thermally accessible open shell configuration of the d^6 ion in this Co^{III} complex distinguishes it from the few other known cobalt(III) imido complexes, all of which are diamagnetic low spin molecules. We wondered whether the difference in the electronic structure might affect the reactivity of **1**. Most interesting is its thermal decomposition (see Scheme 1), as it revealed a pattern related to that of the postulated reactive intermediates ‘$Tp^{tBu,Me}Co{=}NSiMe_3$’ and ‘$Tp^{tBu,Me}Co{=}O$’.

Scheme 1



There are several possible mechanisms for the transformation of **1** into **2**, but based on various related observations, we favor PCET, followed by collapse of the resulting alkyl radical onto the amido ligand (Co^{II}-N(H)Ad) thus generated. In view of our experience with other H transfer reactions (see e. g. Co chemistry referred to above and Cr chemistry described below), we wondered about a possible tunneling contribution to this reaction. Consequently we have measured the activation parameters and kinetic isotope effect (KIE) of the reaction using **1-d$_0$** and **1-d$_{27}$** (containing perdeuteriated *tert*-butyl groups (see Figure 1).

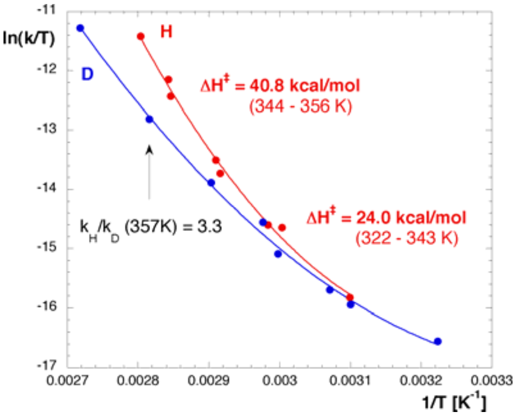


Figure 1. Eyring plots for the reaction of Scheme 1, using **1-d$_0$** and **1-d$_{27}$**.

To our surprise, the Eyring plots for the H- and D-transfers were markedly curved! At low temperatures there was no isotope effect discernable, whereas at elevated temperatures it reached the normal but unremarkable value of $k_H/k_D = 3.3$. These observations are consistent with a two-step mechanism and a change in the rate-determining step with temperature. DFT calculations lend support to this hypothesis. In any event, these data do <u>not</u> represent prima facie evidence for H-atom tunneling (see below for contrast).

If nothing else, these results show that our understanding of this class of reactions (whether it be named PCET, H-atom transfer, or C-H activation) is far from complete. We wish to examine additional cases of PCET to metal bound oxo- and/or imido groups to identify both differences and commonalities.

Iron Imido Compexes: In analogy to cobalt chemistry, Tp^{tBu,Me}Fe(N_2) reacts with alkyl and aryl azides to generate stable imido complexes. We have isolated and structurally characterized both Tp^{tBu,Me}Fe=NAd (see Figure 2) and Tp^{tBu,Me}Fe=N(3,5-Me_2Ph). It remains to be seen whether these complexes will exhibit reactivity similar to cobalt chemistry (i. e., intramolecular PCET), or whether they will engage in intermolecular C-H bond activation.

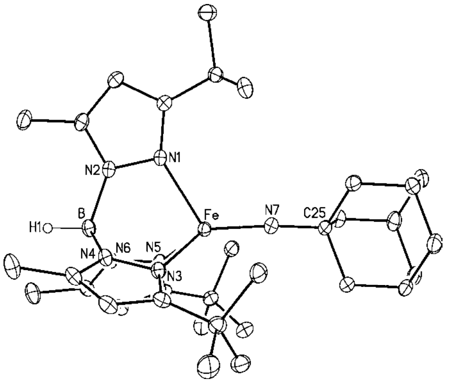


Figure 2. The molecular structure of Tp$^{tBu.Me}$Fe=NAd.

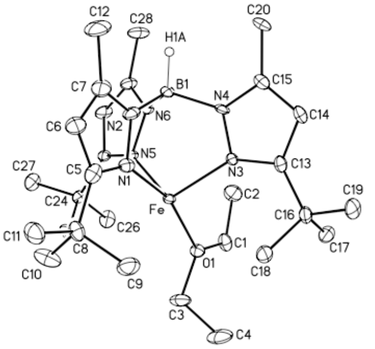


Figure 3. The molecular structure of [Tp$^{tBu.Me}$Fe(OEt_2)]BARF. The BARF anion has been omitted for clarity.

Figure 5 (above) depicts the molecular structure of [Tp$^{tBu.Me}$Fe(OEt_2)]BARF – prepared in high yield by oxidation of Tp$^{tBu.Me}$FeEt with [Cp_2Fe]BARF. This compound readily suffers substitution of the Et_2O ligand and is thus a facile precursor for Fe(II) chemistry.

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. Our fist target is the triply ferrocenylated ligand Tp^{Fc,Me}.

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DE-FG02-07ER15885 **David A. Vicic**

Development of Catalytic Alkylation and Fluoroalkylation Methods

Postdocs: Galyna Dubinina, Iris Kieltsch, Jorge Torres, Eduardo Gomez
Students: Kristen McReynolds, Laura Ackerman, Robbie Lewis
Collaborators: Hideki Furutachi (Kanazawa, Japan), George Stanley (LSU), Yulia Budnikova (Kazan, Russia)
Contacts: Department of Chemistry, University of Hawaii, 2545 McCarthy Mall, Honolulu, HI, 96822; vicic@hawaii.edu

Goal

To develop new methods for alkyl and fluoroalkyl bond forming reactions based on a mechanistic understanding of the organometallic chemistry involved therein.

DOE Interest

Improving our ability to control metal-mediated alkylations and fluoroalkylations will lead to more efficient ways to prepare new high-value commodity and specialty chemicals and new materials. For instance, controlling additions and eliminations of fluoroalkyls may lead to new "greener" ways to prepare high-performance fluoroalkyl polymers and coatings that do not rely on the chemistry of fluoroalkene precursors, which have limited stabilities and storage issues. Fluorocarbon polymers are of high value because they are chemically inert and stable at extreme temperatures, and better ways to prepare more sophisticated fluoropolymers is desirable. Fluoroalkyls are also 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.

Transition-metal alkyls can be directly prepared by many reactions of interest to the Department of Energy, including C-H bond activation of alkanes, olefin insertion, oxidative coupling, transmetalation, etc. While the mild *generation* of metal alkyls from readily available feedstocks is challenging in its own right, the ability to *selectively* and *efficiently* convert the metal-bound alkyl group to useful products remains another challenging endeavor. With regard to coupling chemistry, perhaps the biggest obstacle hampering selectivity is the fact that once a metal-alkyl containing β-hydrogens is generated, competitive β-hydride elimination reactions to form olefins instead of cross-coupled products can occur. This is an important problem as the cross-coupling reaction between an organometallic reagent and an organic electrophile is anticipated to be the most versatile, energy efficient method for forming a new $C(sp^3)$-containing bond. Developing selective methods to cross-couple alkyl groups has ongoing value as $C(sp^3)$ linkages are expected to be pervasive in many newly designed organic molecules and materials.

Recent Progress

Two of our recent objectives were to (1) to develop new perfluoroalkylating reagents using copper and nickel. (2) to investigate the redox properties of nickel-alkyl and nickel-fluoroalkyl complexes to determine the accessibility of different oxidation states and which ligands are best apt to mediate cross-couplings;

Some highlights related to these efforts include:

1) We have prepared and for the first time structurally characterized stable copper^{I}–trifluoromethyl complexes.

2) We have also shown that these copper complexes can trifluoromethylate aryl iodides and bromides in high yields.

3) We have observed an equilibrium between [(SIMes)Cu-CF_3] (**1**, SIMes = 1,3-dimesitylimidazolin-2-ylidene) and the cuprate salt [$(SIMes)_2Cu$][$(CF_3)_2Cu$] (**2**) was observed. Synthetic methods to prepare and isolate **2** were reported. Kinetic data was obtained to suggest that the cuprate form does not play a significant role in trifluoromethylations using *N*-heterocyclic carbene complexes of copper.

4) A variety of nickel and copper complexes bearing the trifluoromethyl ligand have been prepared in order to quantify by electrochemical methods the redox potentials relative to their chloro and methyl counterparts. The effects of coordination number and geometry, as well as the oxidation state of the metal, on the relative ease with which trifluoromethyl complexes can be oxidized have for the first time been identified. In the d^{10} system [(NHC)Cu(X)] (NHC=N-heterocyclic carbene, X=methyl or trifluoromethyl), a single substitution of methyl for trifluoromethyl raised the oxidation potential of the organometallic complex by approximately +0.6 V versus the ferrocene/ferrocenium (Fc/Fc^+) couple, a testament to the extreme electron-withdrawing properties of the trifluoromethyl ligand. The ΔE_{ox} (methyl vs trifluoromethyl) for d^8 nickel complexes were of similar magnitude; however the absolute oxidation potentials were dramatically dependent on the ligand (dippe=1,2-bis(diisopropylphosphino) ethane vs BOXAM=bis(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)amine).

5) Electrochemical analyses of nickel-mediated fluoroalkylations of olefins were performed in order to gain insight into the mechanism of the reaction, which we believe proceeds catalytically through a nickel(I) species.

Future Plans

Fluoroalkyl Cross-Couplings: Prepare high-valent nickel complexes more apt to reductively eliminate aryl-CF_3. Mesh our perfluoroalkylation chemistry with known metathesis and condensation chemistry to achieve greener routes to fluorocarbon polymers.

Alkyl-Alkyl Cross-Couplings: We showed for the first time that nickel complexes bearing redox active ligands can promote alkyl-alkyl cross-coupling reactions. This may be critical feature in catalysis, as the reduction of a ligand *en lieu* of the metal center keeps the nickel in the more stable +2 oxidation state. The utility of redox active ligands with nickel is evident, as one can essentially perform four one-electron redox events to Ni^{IV} without ever having to access Ni^{I} or Ni^{0}. Since our initial report which showed that the proper electronic description of our terpyridine-based catalyst is $[(tpy^{-1})Ni^{II}Me]$, Cardenas has demonstrated by DFT methods that the highly active Fu catalyst is also most likely one in which there is substantial reduction of the pybox ligand. This similarity immediately encourages us to explore other redox-active ligands to see how general and how critical ligand reductions are for cross-couplings with nickel.

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Copper-Catalyzed C-H Amination with Unactivated Amines

Timothy H. Warren
Georgetown University, Department of Chemistry, Washington, DC 20057-1227

Catalytic C-H amination is an attractive strategy to prepare new C-N bonds without the need for a pre-functionalized site. This approach offers substantial opportunities to streamline chemical syntheses by decreasing the number of functional group manipulations such as "hydroxyl to amine". An appealing feature of C-H amination is that protection steps may not be required for this transformation – the relative inertness of the C-H bond insulates it from many traditional functional group modifications. The ability to directly affect the C-H to C-N transformation without the need to isolate, purify, and transform corresponding oxidized precursors promises reduced cost, energy consumption, and environmental impact.

We describe a new catalytic system for C-H amination which employs unactivated amines as substrates along with an inexpensive, simple oxidant. In contrast to most contemporary C-H amination systems which require powerful electron-withdrawing nitrogen substituents (usually discarded in a late synthetic steps), a wide range of aliphatic and aromatic primary and secondary amines may be employed. This new catalytic system was conceived through the observation of a series of stoichiometric reactions involving well defined, reactive copper intermediates, later linked together to form a functioning catalytic cycle. We will discuss mechanistic details along with the inter - and intramolecular substrate scope and selectivity profile for this new C-H amination system. The wide amine substrate scope may lead to the direct use of ammonia in catalytic C-H functionalization offering new pathways to employ this most versatile and inexpensive source of nitrogen atoms for synthesis.

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DE-FG02-09ER16000 **Bradford B. Wayland**

Catalytic Hydrogenation of Carbon Monoxide and Olefin Oxidation

Postdoc: Fernando Jové
Students: Sounak Sarkar , Salome Bhagan
Contacts: Department of Chemistry, Temple University
1901 N 13th Street, Philadelphia, PA 19122;
wayland@temple.edu

Goal

Development of new mechanistic strategies, catalyst materials, and reaction media for the activation and catalytic conversion of carbon monoxide, alkanes, and alkenes to organic oxygenates provide a unifying set of objectives encompassed by this program. Design and synthesis of new classes of materials that manifest reactivity patterns associated with pathways for the hydrogenation of carbon monoxide is the central core objective. Thermodynamic, kinetic - mechanistic and computational studies guide the search for routes to transform CO to 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 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

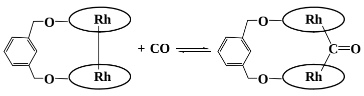
Organo-metal reactivity and thermodynamic studies in water: Application of organometallic transformations in water as a means to circumvent the use of organic solvents is a prominent current theme of environmental and energy related catalysis research. The exceptionally broad range of H_2, CO, and hydrocarbon 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

$M\text{-}CH_2CH_3$ 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 related transformations.

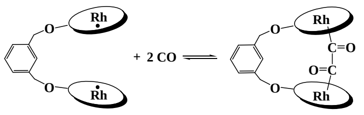
A major objective of this study was advanced by obtaining equilibrium thermodynamic values for reactions of tetra(*p*-sulfonatophenyl)porphyrin rhodium hydride ((TSPP)Rh-H) with carbon monoxide, formaldehyde, and ethene as a bench mark for late transition metal hydride addition reactions with unsaturated 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 set of processes in both organic and aqueous media provide quantitative criteria for the comparison and prediction of substrate reactivity patterns, and aid in identifying the origins of the factors contributing to medium effects.

Tethered bis-metalloporphyrin complexes for reactions where two metal sites occur in the transition state: The general strategy is to utilize the tethering of two or more metal complexes together so as to provide pre-organization for transition states that involve several metal centers. Dramatic rate enhancements for reactions of methane and other saturated hydrocarbons with dirhodium (II) derivatives illustrate the effectiveness of this strategy which is being extended to CO reactions. 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. The *m*-xylyl tethered tetraphenylporphyrin derivative ((TPP)Rh^{II}(*m*-xylyl)Rh^{II}(TPP)) has a weak Rh^{II}-Rh^{II} bond and reacts readily with CO at low pressures 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 formation of both the Rh^{II}-Rh^{II} bond and the dimetal ketone, which directs the reaction with CO to produce a 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.

(TPP)Rh^{II}(*m*-xylyl)Rh^{II}(TPP)



(TMP)Rh^{II}(*m*-xylyl)Rh^{II}(TMP)



Regioselectivity and Equilibrium Thermodynamics for Addition of M-Rh-OH(M=Co,Rh,Ir) to Olefins in Water and Alcohols: Addition of the M-OH unit in (TSPP)M -OH complexes with olefins to form β-hydroxyalkyl complexes is a new class of substrate reactions that was recently developed for oxidation utilizing dioxygen. 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 highpriority future objective. Tuning of substrate reactivity by medium effects will be extended to ionic liquids which are weak donors but support ionic reaction pathways. Substrate reactivity and thermodynamic studies will be expanded to water and alcohol O-H bond reactions with cobalt, rhodium, and iridium macrocyclic complexes. Amphiphilic block copolymers with appended metal complexes that self-assemble into micelles in fluid media and nano-structured arrays on surfaces are being designed for applications in fuel cell and other small molecule catalytic transformations.

Publications (2008-2010)[1-6]

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The Center for Molecular Electrocatalysis **Jenny Y. Yang**

The Role of Proton Relays in Molecular Electrocatalysts for Hydrogen Oxidation

Lead PI: Morris Bullock and Dan DuBois
Contact: Pacific Northwest National Laboratory, Richland, WA 99354; jenny.yang@pnl.gov

Catalysts capable of efficient interconversion of electrical energy and fuels will be important for a flexible and sustainable energy supply in the future. Such catalysts require careful design of both the first and second coordination spheres to achieve high activities. We have reported that nickel complexes containing diphosphine ligands with pendant nitrogen bases incorporated into the second coordination sphere can be efficient and fast catalysts for hydrogen oxidation and production. Current studies are focused on the role of the pendant amines in enhancing the rate of turnover and lowering the overpotential for these catalytic processes. Mechanistic insights from previous studies have led to the design and synthesis of hydrogen oxidation catalysts that turn over at higher frequencies than any previously reported. Details on the kinetic properties, intermediates, and thermochemical quantities in the catalytic cycle will be presented.

DE-SC0002142 **Yan Zhao**

Biomimetic Catalysts Responsive to Specific Chemical Signals

Lead PI: Yan Zhao
Co-PIs: L. Keith Woo, Andrew C. Hillier, Robert J. Angelici
Postdoc: Shiyong Zhang
Student: Gina M. Roberts
Contact: Department of Chemistry, Iowa State University, Ames, IA 50011-3111;
zhaoy@iastate.edu

Conformational control is frequently used by nature to regulate the functions (e.g., binding, transport, and catalysis) of biomolecules. We have prepared amphiphilic foldamers using an amino-functionalized cholic acid as the monomer.[1] The oligocholates can fold into helices with nanometer-sized internal cavities. Cavities of this size are typically observed only in the tertiary and quaternary structures of proteins but are formed in our foldamers prepared in just a few steps from the monomer. The folded conformer resembles a unimolecular reversed-micelle with a hydrophobic exterior and a hydrophilic interior. In addition, the conformational change may be triggered by specific metal ions and small molecules. Our current research focuses on designing organometallic catalysts having ligands with well-controlled conformations.[2] As the ligand responds to changes in solvent composition or the presence of specific metal ions/molecules, the catalyst displays predictable changes in catalytic activity and selectivity.

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Abstracts from Other Investigators Funded in the Area of This Meeting

Trinuclear Copper Complexes for Dioxygen Activation

Theodor Agapie, Emily Y. Tsui, Jacob Kanady, Michael W. Day
California Institute of Technology, Department of Chemistry
Pasadena, CA 91125
agapie@caltech.edu

The active sites of oxidases (laccase, ascorbate oxidase) and oxygenases (particulate methane monooxygenase – pMMO) are known or proposed to contain multicopper centers. Trinucleating ligands based upon a 1,3,5-triphenylbenzene core were envisioned to constrain three copper centers in close proximity. In addition to three bidentate dipyridyl copper binding sites, the ligand variant discussed here (**H_3L**) contains three hydroxyl moieties that may serve as shuttles for the protons necessary for oxygen reduction to water. The prepared tricopper(I) species (**1•3OTf**) was found to react with dioxygen to lead to a tricopper(II) complex (**2•3OTf**). A phosphate analog of **2•3OTf** has been characterized by single crystal X-ray diffraction and shows a tricopper core linked by bridging alkoxides. Reaction of **2•3OTf** with benzoin in the presence of O_2 and base leads to a tricopper benzoate complex. Trinuclear complexes of cobalt and nickel have been prepared as well. Synthetic and reactivity studies of these trimetallic complexes will be discussed.

DE-FG02-06ER15762 **Frances H. Arnold**

Structural and Kinetic Studies of Novel Cytochrome P450 Small-Alkane Hydroxylases

Additional PIs: None
Postdocs: Eric Brustad, Jared Lewis
Students: Michael Chen, Russell Komor, Pedro Coelho
Collaborators: None
Contacts: Chemical Engineering 201-41, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125; frances@cheme.caltech.edu

Goal

The goal of this project is to investigate the structures, biophysical properties, and kinetics of members of two families of cytochrome P450s that have been evolved in the laboratory to catalyze the hydroxylation of gaseous alkanes.

DOE Interest

The entire 'fossil record'—sequences and biochemical properties of all mutants in the lineage, the selection pressure, and even the mutational process—is knowable for laboratory evolution experiments. We have the collection of all the intermediate species along the lineage to P450PMO, a highly efficient and fully-coupled propane monooxygenase. In addition we have obtained mutants of CYP153A6 that are more active on propane and butane and, for the first time, support growth of a strain of P. putida on butane. We are attempting to determine the x-ray crystal structures of these novel small-alkane hydroxylating enzymes and characterize their redox properties, kinetics, and product specificities, in order to observe how these new activities emerged and were refined. We are also investigating methane oxidation catalyzed by CYP153A6, a terminal alkane hydroxylase.

The laboratory-evolved P450s provide an unprecedented opportunity to investigate in detail the acquisition of an important new biological activity. This basic understanding will aid further evolution or design of a possible methane-hydroxylating cytochrome P450 and P450 catalysts for selective alkane oxidation. It will also provide inspiration for future design of new biomimetic catalysts for these key conversions, including the conversion of methane to methanol.

Recent Progress

Structure determination efforts: Heme domains of the intermediates of the lineage to P450PMO were expressed in *E. coli* and purified using immobilized metal affinity chromatography, anion exchange chromatography, and gel filtration to yield a final purity of >99%. Initial crystallization experiments were conducted in high-throughput at the Molecular Observatory Macromolecular Crystallization Laboratory on campus. Conditions for four intermediates were identified and fine-tuned using scaled-up bench-top experiments. This yielded large, single crystals for intermediate J; however, these crystals did not diffract when sent to the Stanford Synchrotron Radiation Laboratory.

Conditions for intermediates ETS8 and PMO gave clusters of crystals that were unharvestable. Dropping the protein concentrations and modifying the crystallization conditions with additives gave single crystals that did diffract. However, the crystals were of a flat, plate-like morphology that diffracted anisotropically and thus did not yield diffraction data suitable for structure determination. Optimization of conditions for intermediate AB2R6 was unable to yield harvestable crystals due to clustering, even when lowering the protein concentration. Optimization of conditions for intermediate 7-7 is currently underway.

Efforts to crystallize CYP153A6 are also currently ongoing. We have completed the initial screening of crystallography conditions available for high throughput crystallization screening offered by the Molecular Observatory for Structural Molecular Biology at Caltech. Five 96-well plates of commercial screening conditions, as well as two 96-well plates of custom conditions, for cytochrome P450 crystallization were screened using the hanging drop vapor diffusion method. Unlike the successes we have obtained with BM3 variant, none of these conditions yielded crystals for A6 over the observation period. We plan to repeat this high-throughput screening at varied protein concentrations, in addition to expanding our screening condition search to other screening kits.

P450-catalyzed methane oxidation: In our effort to study the potential for methane hydroxylation activity of both CYP102A1 (BM3) and CYP153A6 (A6) and their variants derived through directed evolution experiments, we have departed from our usual characterization of these enzymes. Previously, the activity of each enzyme was evaluated in the presence of a cytochrome P450 reductase either as purified enzymes or in whole cells. Now, we have generated the active radical of the cytochrome P450 reaction, Compound I (CMP I), directly in solution with the addition of a terminal oxidant. We have used a variety of terminal oxidants including iodosylbenzene, 3-chloroperbenzoic acid, and hydrogen peroxide to generate CMP I with the purified heme domain of BM3, A6, and their derived variants. Reacting these radicals with methane allows us to probe the ability of each enzyme to break the methane C-H bond directly. In addition to the reactions with methane, other gaseous alkanes were also tested to determine the substrate specificity of each enzyme.

The reaction of CMP I with various alkanes using iodosylbenzene as the terminal oxidant afforded the highest product yield. We found A6 and its derived variants to be active for all gaseous alkanes tested, including methane. This is the first evidence of a cytochrome P450 breaking the methane C-H bond. In contrast to A6, the CMP I of BM3 and $BM3_{PMO}$ appear to have activity only for propane and not methane.

While considerable success has been achieved in altering the substrate specificity and reactivity of cytochrome P450 enzymes by directed evolution, the range of chemistry available to this protein family is still limited by the iron-containing heme center. The ability to swap the iron-heme with porphyrin scaffolds containing other transition metals may significantly expand the chemistry that can be explored using directed evolution. We have exploited a naturally occurring bacterial outer-membrane porin, ChuA, which is selective for the transport of metalloporphyrins into *E. coli*. Overexpression of ChuA and P450-BM3 in iron deficient minimal media supplemented with various metalloporphyrins has allowed us to produce P450-BM3 variants containing cobalt, manganese, zinc or copper porphyrins.

Future Plans

We will continue efforts to obtain crystal structures of CYP153A6 and P450PMO and its evolutionary precursors. Untested intermediates will be screened in a similar manner to those listed above. Further work on the intermediates for which we were unable to identify crystals suitable for structure determination will involve exploration of additional dimensions in crystallization conditions. These additional dimensions will include temperature, crystallization method (hanging vs sitting drop), and serial seeding. Seeding has high potential as we have had some success with single rounds of seeding to improve crystal morphology for highly clustered or poorly formed crystals.

We have established that the reactive radical of CYP153A6 is able to break a methane C-H bond. Efforts are underway to reconstitute this activity for A6 with its reductase under normal turnover conditions, i.e. utilizing NADH and molecular oxygen. We are also testing the non-iron metalloporphyrin-containing P450s for gas alkane oxidation activity.

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3. J. C. Lewis and F. H. Arnold, "Catalysts on Demand: Selective Oxidations by Laboratory-Evolved Cytochrome P450 BM3," *CHIMIA* **63** (2009) 309-312.
4. J. D. Bloom and F. H. Arnold, "In the Light of Directed Evolution: Pathways of Adaptive Protein Evolution" *Proceedings of the National Academy of Sciences* **106** (2009) 9995-10000
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Patents and Inventions (2008-2010)

1. D. J. Koch, "Application of *in vivo* Directed Evolution to Obtain Enzymes with Altered Hydroxylase Activity," DOE Invention Number T-103841 (2008).

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

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

Additional PIs: None
Postdocs: Ashley Berman, Hitoshi Harada, John Curley
Students: Jared Lewis, Denise Colby, Michael Gribble, Rebecca Wilson, Reema Thalji, Sirilata Yotphan, Erika A. Cobar, Mitchelle R. Anstey, Andy Tsai, Rhia Martin, Jason Ji, Vivian Lin
Collaborators: Jonathan A. Ellman (UC Berkeley), Martin Head-Gordon (UC Berkeley),
Contacts: Chemical Sciences Division, Lawrence Berkeley National Laboratory, and Department of Chemistry, Univ. of California, Berkeley, Latimer Hall #1460, Berkeley, CA 94720-1460; rbergman@berkeley.edu

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 convert 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. Substantial indirect evidence has been obtained implicating alkane complex intermediates (species in which alkanes are weakly coordinated to the metal center before C-H bond activation occurs) as intermediates in transformations in which metals insert into carbon-hydrogen bonds. 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. One facet of this research involves 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). In collaboration with several investigators in the UK, we have detected and studied the properties of mononuclear rhenium-alkane complexes at both room temperature (using flash kinetics techniques) and low temperature using NMR methods (Fig. 1). In addition, computational results indicate that with appropriately designed analogous trinuclear rhenium systems, and with appropriate alkanes such as 1,3,5-trimethylcyclohexane, metal-alkane interaction energies can approach 30 kcal/mol, which would make them stable at room temperature. Significant progress has been made toward the synthesis of such trinuclear complexes.

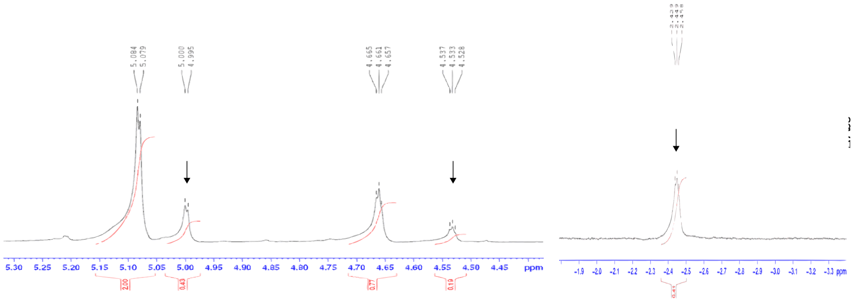
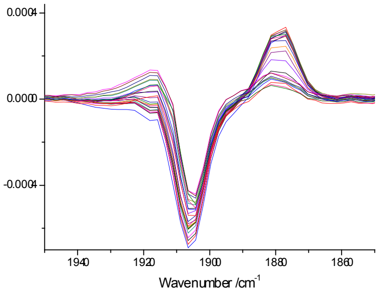


Figure 1. NMR experiment at -78 ^{o}C: new peaks (see arrows) are due to formation of the metal-cyclopentane complex ((tBu)$_2$Cp)Re(CO)$_2$(C$_5$H$_{10}$)



Infra-red flash kinetics at room temperature: band at 1878 cm-1 assigned to alkane complex.

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 have developed new metal-catalyzed C-H activation reactions that couple aryl groups to heterocyclic rings, promote the cyclization of aromatic vinyl ethers, and allow tandem coupling of terminal alkynes to unsaturated oximes followed by pericyclic reactions that provide highly substituted pyridine derivatives.

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) search for general enantioselective C-H bond activation reactions; (d) develop additional metal-catalyzed C-H activation initiated arylation reactions; (e) develop 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, and (f) investigate the mechanisms of our new arylation, alkynylation and cyclization reactions through the use of both experimental studies (e.g., kinetics, isotope labeling) and computational studies.

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DE-AC02-05CH11231 **Robert G. Bergman, Kenneth N. Raymond**

Selective Stoichiometric and Catalytic Reactions in Water-Soluble Host-Guest Supramolecular Systems

Additional PI's: None
Postdocs: Jeffrey Mugridge
Students: Dennis Leung, Michael Pluth, Courtney Hastings, Casey Brown, Dorothea Fiedler
Contacts: Chemical Sciences Division, Lawrence Berkeley National Laboratory, and
Department of Chemistry, Univ. of California, Berkeley, Latimer Hall #1460,
Berkeley, CA 94720-1460; rbergman@berkeley.edu

Goal

Our approach uses supramolecular encapsulation to control the reactivity of bound guest molecules, with the goal of developing useful catalytic processes. The reaction mechanisms by which these processes operate are studied in detail in order to develop fundamental design principles for supramolecular catalysis.

DOE Interest

Homogeneous catalysis is of major economic importance to the energy and chemical industries. Thus, addressing the problems that exist with many of today's catalysts has spurred much research. These problems frequently include low substrate selectivity, rapid catalyst decomposition, and the need to use toxic organic solvents for the catalytic transformations. In a relatively new project that was funded in 2002, we proposed a novel supramolecular approach to these problems. Rather than using cocatalysts, tailoring existing catalysts or using solid-supports for the catalyst, we seek to examine the activity of existing catalysts within supramolecular water-soluble nanovessels, and at the same time explore the potential catalytic activity of the nanovessels themselves.

Recent Progress

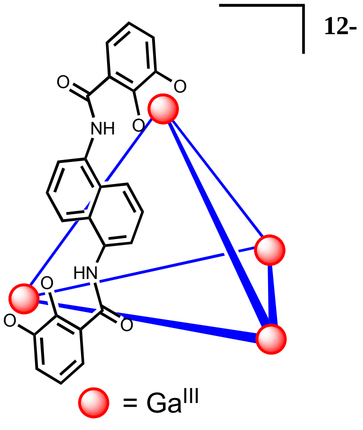

Figure 1. Cavity-containing metal-ligand cluster, or "nanovessel."

Several cationic organic and organometallic compounds have been shown to bind into the cavities of water-soluble chiral clusters or "nanovessels" (constructed earlier by the 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 proceed in the nanovessel cavities; small quantities of the nanovessels have been found to catalyze these reactions with accelerations above 800-fold. We have recently demonstrated that the enantiopure nanovessel furnishes the product of this reaction with enantiomeric enrichment of up to 78% (Figure 2). This represents the highest degree of enantiocontrol achieved in supramolecular catalysis to date. Nanovessels have also been found to perturb the acidities of organic bases, and the pK_a-shift properties of the nanovessels has provided a way of carrying out acid-catalyzed hydrolyses in strongly basic aqueous solution. For example, the nanovessels catalyze the aqueous hydrolyses of orthoformates and acetals at high pH with even larger accelerations (>3000-fold) than those seen for the aza-Cope rearrangement. Recently, we discovered that the nanovessels catalyze the Nazarov cyclization, an acid-catalyzed reaction that forms a new carbon-carbon bond (Figure 3). The rate accelerations for this reaction are on the order of 10^6, the largest so far measured for supramolecular catalysis by orders of magnitude.

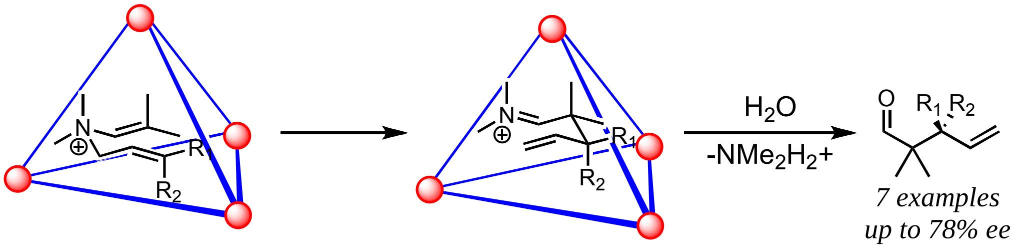

Figure 2. Asymmetric catalysis of the aza Cope rearrangement, producing enantioenriched chiral aldehydes.

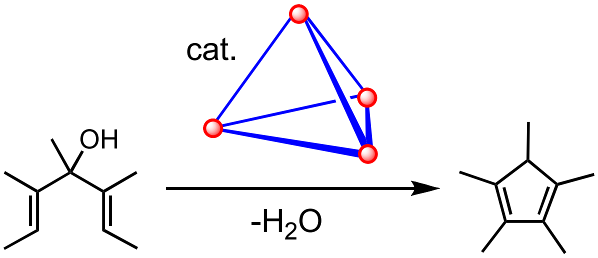

Figure 3. Nanovessel catalysis of the Nazarov reaction.

Future Plans

The mechanism of the nanovessel-catalyzed Nazarov cyclization will be investigated. We are particularly interested in determining the origin of the extremely large rate enhancements that we observe. We will also investigate the catalysis of other acid-catalyzed cyclization reactions by nanovessel encapsulation to determine whether this class of reactions exhibit uniquely large rate enhancements. The reactivity of encapsulated organometallic compounds has been extensively studied in the smallest naphthalene-based cluster, and we plan to extend these studies to larger assemblies based on pyrene and binaphthalene. We expect that these larger nanovessels will be able to accommodate a wider range of organometallic catalysts, and that the resulting host-guest complexes will exhibit larger substrate scope when compared to the reactions mediated by organometallic guests encapsulated in the naphthalene assembly. In conducting future studies, special attention will be paid to the enantioselective generation of chiral products in hopes of developing useful asymmetric reactions.

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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

Postdocs: Ruaraidh McIntosh
Li Yang
Students: Chandrani Chatterjee
Tamara Beilke
Alexandre Bernard
Kittisak Choojun
Pasco Wambua
Contacts: The Ohio State University, Chemistry Department, 100 West 18th Avenue, Columbus, OH 43210; Chisholm@chemistry.ohio-state.edu

Goal

Through the development of a mechanistic understanding of the fundamental reactions involved in the copolymerization of epoxides and carbon dioxide and in the ring-opening polymerizations of cyclic esters we will develop well-defined single-site coordination metal catalysts for the formation of polycarbonates and polyesters from bio based renewable resources as an alternative to current procedures involving fossil fuel derived monomers.

DOE Interest

Studies of the reactions involving porphyrin complexes of the M(III) ions, where M = Al, Cr and Co, and alkene oxides reveal some fascinating influences of the nature of porphyrin 5,10,15,20-tetraphenylporphyrin, TPP, 5,10,15,20-tetra(pentafluorophenyl)porphyrin, TFPP, and 2,3,7,8,12,13,17,18-octaethylporphyrin, OEP, as well as the metal. Under ambient conditions propylene oxide, PO, undergoes ring-opening polymerization, ROP, to give polypropyleneoxide in the order M = Cr > Al >> Co which is effectively inactive. The rate of polymerization is accelerated in the prescence of 0.5 to 1.0 equiv. of a Lewis base such as 4-dimethylaminopyridine, DMAP, or $[Ph_3P=N=PPh_3]^+X^-$ where $X = N_3^-$ or Cl^-. The effectiveness of the promoter follows the order $X = N_3 > Cl$ which in turn is more active than DMAP. For porphyrinaluminum initiators, porphyrinAlX where X = Cl or OEt, the rates of ROP followed the order OEP > TPP > TFPP and while both OEP and TPP gave regioregular PPO with repeating head-tail units the TFPP gave low molecular weight regioirregular PPO. However, upon the addition of the additive/promoter DMAP or PPN^+Cl^- this order is reversed and only regioregular PPO is formed: TFPP > TPP > OEP which is now effectively inative.

Recent Progress

PorphyrinAlOEt complexes react reversibly with CO_2 to give the alkylcarbonate prophyrinAlO_2COEt with the equilibrium favoring the alkylcarbonate in the order OEP > TPP > TFPP. However, upon the addition of the promoter (PPN^+Cl^- or DMAP) this order is reversed.

In studies of the rates of ring-opening of PO porphyrinAlX initiators we find $X = O_2CR > O_2COR > OR$. Thus the TFPPAlX initiator in the presence of the promoters (DMAP or PPN^+Cl^-

) copolymerizes PO and CO_2 to give polypropylenecarbonate, PPC, is the most active and >95% incorporation of CO_2 can be obtained even at low pressures of CO_2 (5-10 Bar).

TPPCoCl which is inactive in the ROP of PO will react with PO and CO_2 to yield propylenecarbonate, PC under ambient conditions.

Styreneoxide, SO, which is much more challenging toward ROP and the formation of polystereneoxide, PSO, will react with TPPCrCl at 60 ºC to give regioirregular PSO. In all the ROP reactions of alkeneoxides with porphyrinMX (M = Al or Cr and X = OR or Cl) the polyalkeneoxides have end groups that are either Cl or OR. When the initiator is an alkoxide and the promoter is PPN^+Cl^-, the end group is an alkoxide: no Cl end group is detected by either MALDI-TOF mass spectroscopy or elemental analysis. This clearly indicates the presence of only one growing chain.

Styreneoxide, SO and CO_2 react (60-80 ºC, 50 Bar) in the presence of TPPCrCl to give styrenecarbonate, SC. *R*-SO and CO_2 give a mixture of *R*-SC (70%) and *S*-SC (30%) indicating that the ring-opening event occurs with significant loss of stereochemistry.

TPPMCl (M = Al or Cr) serve as catalysts for the copolymerization of succinic anhydride, SA and SO to give polystyrene succinate, PSS, as a regiorandom polymer at 60 ºC with turnover frequencies TOF ~100 h^{-1}. Under milder conditions (25 ºC), PO and SA give regioregular polypropylene succinate, PPS, and with phenylsuccinate regioregular polypropylene phenylsuccinate.

Future Plans

We will continue to investigate the ring-opening copolymerization of cyclic anhydrides such as succinic anhydride (a bio based molecule) with epoxides and epoxides and oxitanes in the formation of polyesters. Similarly, studies of the copolymerization of epoxies and carbon dioxide to give polycarbonates will be extended to include a variety of M(3+) cations supported by porphyrins and other planar tetradentate (2-) ligands. Reactions involving trispyrazolylborate ligands with hemilable ether and amine substituents bound to Mg(2+) and Ca(2+) will be explored for the ring-opening polymerization of cyclic esters such as lactide and clycolide and trimethylene will be studied as potential single-site active catalysts that are kinetically persistent in the presence of trace amounts of water.

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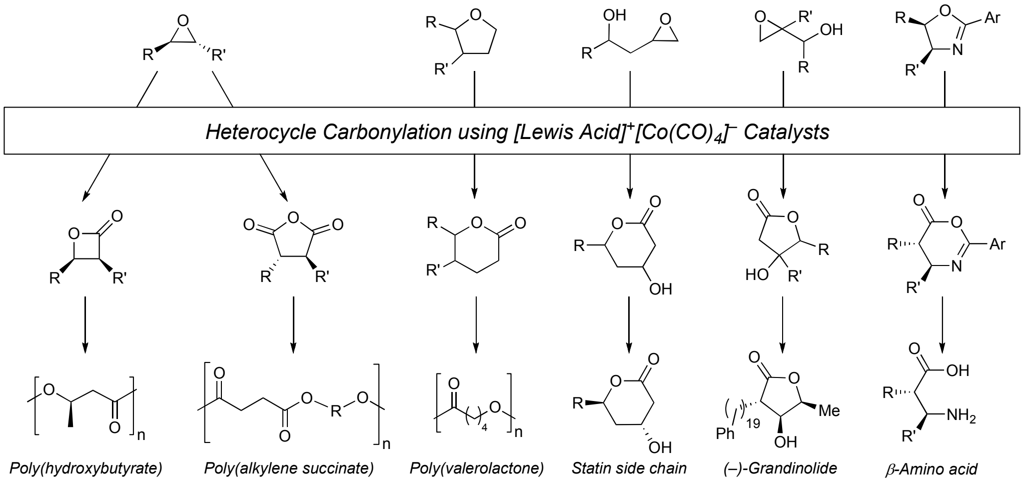
DE-FG02-05ER15687 **Geoffrey W. Coates**

Development and Application of New Catalysts for Heterocycle Carbonylation

Additional PIs: None
Postdoc: David Laitar
Students: John Rowley, John Kramer, Bryan Whiting, Michael Mulzer
Contacts: Cornell University, Department of Chemistry, Baker Laboratory,
Ithaca, NY 14853, gc39@cornell.edu

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.



Applications: Biodegradable Polymers, Fine Chemicals, and Pharmaceutical Buiding Blocks

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, as well as other heterocycles in ring-expansive reactions. 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. In addition, the application of these catalysts for the carbonylation of other heterocycles was developed. Major findings have occurred during the current project period, including:

- Development of a new route to alternated polyesters via enantiopure beta-lactones
- Development of a route to beta-amidoaldehydes via oxazoline hydroformylation
- Development of a low-pressure process for epoxide carbonylation
- Catalytic synthesis of highly fluorinated β-lactones and their corresponding poly(3-hydroxybutyrate)s
- Development of a new catalyst for oxazoline carbonylation
- Development of a multicomponent synthesis of 1,3-oxazinane-2,4-diones from epoxides, isocyanates, and CO;
- Development of a new catalyst for epoxide double carbonylation to succinic anhydrides
- Development of a new catalyst for the synthesis of substituted 3-hydroxy-δ-lactones

Future Work

Future work will focus on the development of a new set of catalysts that address 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-FG02-84ER13297 **Robert H Crabtree**

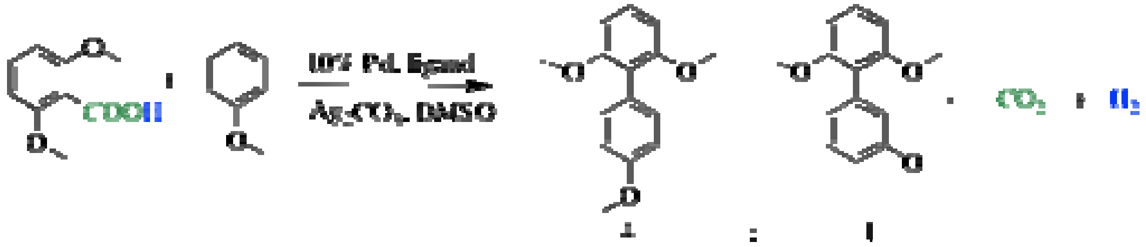
Novel Ir, Ru, Pd and Metal-Free Catalysis of Green Transformations

Students: Graham Dobereiner, Nathan Schley
Collaborators: Odile Eisenstein (CNRS, Montpellier); David Balcells (Barcelona); Roy Periana (Scripps, FL).
Contacts: Yale University Chemistry Dept, New Haven, CT, 06520-8107.
robert.crabtree@yale.edu

Goal: To develop new catalysts for alcohol activation and to follow up additional catalytic reactivity behavior picked up in catalytic screening.

DOE Interest: Alcohol activation provides a green route to sec. amines, sec. alcohols and to amides. The reaction is currently being adapted by the pharmaceutical industry for production. The azaarene hydrogenation discovered as a spin-off of the present work is of interest synthetically and in relation to hydrogen storage.

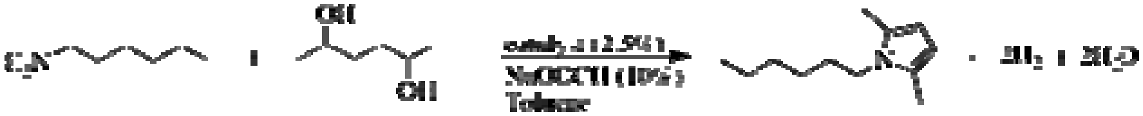
Recent Progress: Numerous results have emerged from this year's work. *Decarboxylative coupling*. Pd coupling reactions are of intense current interest but require boronic acids, stannanes or other activated precursors that are either toxic or readily form waste or have to be synthesized in a separate step. We now find that with Pd catalysis, simple ArCOOH can be a precursor to decarboxylation products ArH or Ar-Ar, particularly under microwave conditions. Isotope labeling showed that D_2O is the source of the D in ArD. With arenes Ar'H, the mixed Ar-Ar' could also be obtained, albeit in modest yields (15-50%) unless the coupling was intramolecular. Our computational collaborators have suggested a mechanism involving b-elimination of CO_2 from a three-coordinate Pd(II) carboxylate intermediate. A communication [1] gave the initial data but we now have much more information. A paper has also appeared on ArCOOH + Ar'H => ArCOOAr' coupling, also seen under some conditions. [2]



Beta alkylation. Previously known with Ru catalysis, we have now found conditions where metal-free bases can be used. The most successful is NaOH, which gives 100% conversion and 81% yield of a 4:1 mixture of alcohol and ketone. Under other conditions, a 75% yield of the a 99:1 mixture of alcohol and ketone can be obtained. Initial oxidation by air is thought to give a trace of ketone. A Meerwein-Ponndorf-Verley mechanism is then proposed to dehydrogenate the alcohols. An aldol reaction gives the coupled enone, which further dehydrogenates the reactant alcohols while itself being reduced to the coupled ketone and alcohol. The secondary alcohol must be benzylic but a wide variation is possible in the primary alcohol, including alkyl cases. A paper is in the final stages of preparation. An interesting feature is that the final exothermic hydrogenation drives the initial endothermic dehydrogenation.

Alcohol Activation. A review was written with Graham Dobereiner. [3]

Pyrrole Synthesis. A remarkable side-product, pyrrole, was seen in some of the amine-alcohol couplings reported in a previous period. By optimization we have been able to obtain 55% yield of the reaction shown, one in which two moles of hydrogen and two moles of water are lost. Backbone functionalization should be easy since the substituted diols are easily obtained from the unsaturated diols. Another novel feature of this reaction is the use of mild sodium formate as base. The reason it works is that the HCOOH formed after proton transfer is irreversibly decomposed to CO_2 and H_2 by the catalyst, [$RuCl_2$(dppf)(2-aminomethylpyridine)].



The same catalyst cyclizes amino-alcohols of the type $HO(CH_2)_nNH_2$ to the lactam where n = 3,4. This is another unusual reaction in which H_2 and H_2O are lost. Diols are converted to the lactone.

I

Arene and Imine Hydrogenation: A substituted benzimidazole-based NHC, mediocre in alcohol activation, is very effective in the hydrogenation of azarenes and imines. For example quinoline is fully reduced in the heterocyclic ring while leaving the carbocyclic ring unaffected. This represents an example of our screening potential catalysts for reactions other than the one aimed at.

Miscellaneous: In work with Periana's group, we identified a 1,3-Shift of an NH Proton to Iridium in Protic N-Heterocyclic Carbenes. [3]

Future Plans: The decarboxylation work is now complete but we have yet to write the full paper integrating the experimental and computational work. The beta alkylation is in the final stages and a paper is to be submitted this summer. The scope and limitations of the pyrrole, lactone and lactam synthesis need to be identified. The arene and imine hydrogenation look interesting and the best catalyst having a bis carboxylate at the remote site shown, implies that attachment to an oxide nanoparticle NP may be possible for improving the lifetime – the catalyst deactivates in a bimolecular way so attachment to a may prevent this. We also plan to see if an IrL_3^+ catalyst series related to the one shown above might have value for arene hydrogenation where an η^2-arene is the likely binding mode in the active species, because free rotation about the Ir-arene bond may be required to permit C=N insertion into Ir-H.

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

Modeling of Catalytic Processes for More Efficient Utilization of Hydrocarbon Resources

Postdoc & Grad Students: Hector Gonzalez, Glenn Morello, Aaron Pierpont, Dr. Nate DeYonker
Undergraduates: Adam Imel, Chuancey Garrett
Collaborators: Brent Gunnoe (UVa), Greg Hillhouse (U. Chicago), Pat Holland (U. Rochester), Paul Marshall (UNT), Angela Wilson (UNT), Pete Wolczanski (Cornell)
Contacts: University of North Texas, Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCaM), Denton, TX 76203; t@unt.edu

Goal

Work in 2009 focused on three key research areas - catalytic arene functionalization by scorpionate and non-scorpionate ligands, catalytic reactions of multiple bonded complexes of the late *3d* transition metals, and computational transition metal thermochemistry.

DOE Interest

Aromatic hydrocarbons are an important feedstock for synthesis of industrial and commodity scale chemicals. Given the prevalence of aromatics in biomass, the importance of their catalysis will only grow. Also, there is interest in the DOE-BES catalysis community to find base metal replacements for precious metal catalysts. Finally, integration of theory and experiment, and development and refinement of computational strategies for transition metal chemistry remains an important benefit that we can bring to our fellow BES-DOE contractors (and the DOE mission).

Recent Progress and Future Plans

1. Catalytic Olefin Hydroarylation

In conjunction with fellow DOE-BES contractor Prof. Brent Gunnoe (UVa), the Cundari group investigated a family of promising TpRu catalysts (Tp = *tris*(pyrazolyl)borate) supporting ligation. More importantly for the near future, we leveraged the results of this dynamic theory-experiment collaboration to identify new and profitable research directions in our hydroarylation catalysis research. Exciting preliminary results are summarized below.

Current and future research in our group seeks to capitalize on the following insights. Ongoing research in our group for 2010 focuses on (a) TpPt, TpNi, and TpCo hydroarylation catalysts (calculations done by Cundari Group PhD student, Hector Gonzalez; results being analyzed); (b) enhancing cationic MpRu catalysts (calculations completed by PhD student, Glenn Morello; experiments ongoing in Gunnoe group); and (c) preliminary work on square planar Pt(II) hydroarylation catalysts (Mr. Gonzalez). Projects (b) is the most mature and discussed below.

Our group has performed preliminary modeling studies of $[Pt(bpy)(THF)(Ph)]^+$, a first-generation Pt(II) olefin hydroarylation catalysts reported by Gunnoe and coworkers.

The research by Mr. Gonzalez is one of the most complicated and intricate catalytic cycles that our group has ever delineated; not only delineation of the main catalytic cycle, but identification of the catalyst resting state, double-alkylation side reactions (ortho-, meta-, and para-), vinylic C-H activation, double insertion (leading to butyl-benzene), and styrene formation .

Several points are worthy of mention. First, the catalyst resting state proposed by our simulations $[Pt(bpy)(C_2H_4)CH_2CH_2Ph)]^+$ is supported by subsequent experiments by the Gunnoe group under non-catalytic (and lower temperature) conditions confirm this prediction. The structure of the resting state also helps to explain why double insertion to form butyl-benzene is not seen as a side reaction for this catalyst: the C=C insertion TS (not shown) requires the olefin substrate to impinge the bpy ligand. Hence, we expect that next-generation diimine catalysts with a similar structure to likewise not be affected by this side reaction.

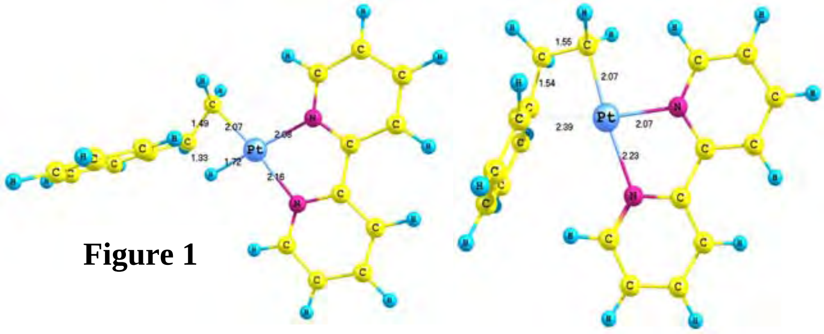

Figure 1

Second, experiments by Gunnoe *et al.* indicate no styrene formation for this Pt-bpy catalyst (in the absence of O_2). Our calculations suggest a possible reason for this: there are two conformers for the initial C=C insertion product, Figure 1, $[Pt(bpy)(CH_2CH_2Ph)]^+$. While a highly agostic structure (β-C-H bond of the phenethyl group) is a stable minimum, there is a lower (by *ca.* 5 kcal/mol) conformer in which the arene ring π-coordinates to the acidic cationic Pt(II) center. The structure of the two isomers suggests that careful manipulation of the ortho C-H bonds of bpy is critical in determining the energetic balance for the agostic isomer, which could favor styrene formation.

Third, vinylic C-H activation of ethylene (a problem for TpRu catalysts) is calculated to be more than 16 kcal/mol higher than the isomeric C=C insertion TS. Hence, one can assume there is substantial "play" with respect to catalyst design before these two reactions become competitive.

Fourth, our work shows that for the cationic Pt-bpy catalyst, double alkylation to make the three isomers of diethylbenzene is competitive with the original alkylation to make ethylbenzene, thermodynamically (both reactions are exothermic by ~10 kcal/mol) and kinetically (both reactions barriers are ~10 kcal/mol). Our next step in this research is to identify experimentally plausible steric and electronic modification to the 1st generation Pt-bpy catalysts that favor alkylation and retard poly-alkylation while maintaining high catalyst activity.

2. Hydrocarbon Functionalization by Late Transition Metals

a. Multiply Bonded Complexes: Our calculations support experimental deductions as to the mechanism of 1,3-dipolar additions of Ni-element multiple bonds to group transfer reagents, *e.g.*, nitrous oxides (N_2O) and organic azides (RN_3). This work shows a good bit of correspondence of the Hillhouse organometallic systems to a classical Huisgen-type mechanism for organic 1,3-addition. Moreover, this study confirmed past predictions made in DOE supported research on the chemistry of such species, as well as informed current work in our group (*vide infra*).

We sought, and continue to seek, to exploit this research in several new research thrusts within our DOE-BES research program: (1) a study of the mechanism of iron-catalyzed azide decomposition for amination (next section), (2) quantifying the role of metal and ligand modification for hydrocarbon functionalization catalysts (section c), and (3) elucidation of full catalytic cycles for N_2O (hydroxylation – this work is underway in our lab by Aaron Pierpont and will be described in due course) and RN_3 (amination) catalysis (next two sections).

b. Iron Catalyzed Amination of Hydrocarbons: In collaboration with Prof. Pat Holland (U. Rochester), we studied what appeared to be a simple Fe-mediated decomposition of organic azides (RN_3, R = aryl or alkyl). Our detailed understanding of this system was only possible through close integration of cutting-edge theory and experiment. Cundari Group post-doctoral associate, Dr. Nathan DeYonker (now on staff at U. of Memphis) doggedly pursued deconvoluting the role of solvent, bi-metallic intermediates, side reactions to hexazene and tetrazene complexes, spin state and coordination number, *etc.* Among the aforementioned factors, solvent was crucial in partitioning the reaction of the Fe-catalyst with the RN_3 reagent to the desired imido complex, the active species for hydrocarbon amination. Solvent plays a crucial role in controlling the preferred linkage isomer of the coordinated azide, but also the spin state of the coordinated azide intermediate (both of these impact the kinetics of N_2 loss) and the spin state of the eventual imido active species (which controls its C-H activating ability).

c. Late Transition Metal Hydrocarbon Functionalization

While our initial intention was to concentrate solely on iron catalysis, other *3d* catalysts emerged as very promising targets. Results by Cundari Group PhD student, Aaron Pierpont, combined with the new collaborations we forged, motivated us to expand the scope of our proposed work to include cobalt and, especially, nickel catalysis. Methane functionalization via $L_nM=E$ active species (L_n = β-diketiminate, dihydrophosphinoethane; M = Fe - Ni, E = NCF_3, NCH_3, O) through a hydrogen atom abstraction (HAA)/radical rebound (RR) mechanism is calculated to be thermodynamically and kinetically feasible. The enthalpies of each reaction decrease in the order Fe > Co > Ni and with the proximity of CF_3 supporting ligand substituents ("fluorination") to the metal center. The HAA kinetics further implicate fluorinated (β-diket)Ni=O as the most promising methane functionalization complexes. Promising Ni-oxides are being studied utilizing N_2O as the transfer reagent. We are expanding this work to surface-bound models and =NX versions that mimic =O due to obvious concerns with regard to dimerization of a highly active Ni-oxo species.

2009 – 2010 Publications Acknowledging DOE Support

178 - "Six-, Five- and Four-Coordinate Ruthenium(II) Hydride Complexes Supported by NNHC Ligands: Synthesis, Characterization, Fundamental Reactivity and Catalytic Hydrogenation of Olefins, Aldehydes and Ketones J. P. Lee, Z. Ke, M. A. Ramírez, T. B. Gunnoe, T. R. Cundari, P. D. Boyle, J. L. Petersen Organometallics **2009**, 28, 1758-1775.

180 - "Unusual Electronic Features and Reactivity of the Dipyridylazaallyl Ligand: Characterization of $(smif)_2M$ (M = Fe, Co, Co^+, Ni; smif = $\{(2\text{-py})CH\}_2N$) and $[(TMS)_2NFe]_2(smif)_2$;" B. A. Frazier, P. T. Wolczanski, E. B. Lobkovsky, T. R. Cundari J. Am. Chem. Soc. **2009**, 131, 3428-3429. (communication).

182 - "Ru(II) Catalysts Supported by Hydrido-tris(pyrazolyl)borate for the Hydroarylation of Olefins: Reaction Scope, Mechanistic Studies and Guides for the Development of Improved Catalysts;" N. A. Foley, J. P. Lee, Z. Ke, T. B. Gunnoe, T. R. Cundari Acc. Chem. Res. **2009**, 42, 585-597 (invited).

183 - "Enthalpy of Formation of Cyclohexadienyl Radical and C-H Bond Enthalpy of 1,4-Cyclohexadiene: Experimental and Computational Re-evaluation;" P. Marshall, C. Garrett, N. J. DeYonker, A. K. Wilson, T. R. Cundari J. Phys. Chem. A **2009**, 113, 6955 – 6963.

185 - "Towards the Intrinsic Error of the correlation consistent Composite Approach (ccCA)", N. J. DeYonker, B. R. Wilson, T. G. Williams, A. W. Pierpont, T. R. Cundari, A. K. Wilson Mol. Phys. **2009**, 107, 1107 – 1121 (Schaefer special issue).

186 - "Accurate Thermochemistry for Transition Metal Complexes from First-Principles Calculations;" N. J. DeYonker, T. G. Williams, A. E. Imel, T. R. Cundari, A. K. Wilson J. Chem. Phys. **2009**, 131, 024106.

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189 - "A Computational Study of Metal-Mediated Decomposition of Nitrene Transfer Reagents;" T. R. Cundari, G. R. Morello J. Org. Chem. **2009**, 74, 5711 – 5714.

191 - "Group-Transfer Reactions of Nickel-Carbene and -Nitrene Complexes with Organoazides and Nitrous Oxide that Form New C=N, C=O, and N=N Bonds;" N. D. Harrold, R. Waterman, G. L. Hillhouse, T. R. Cundari J. Am. Chem. Soc. **2009**, 131, 12872-12873.

194 - "DFT Study of Methane C-H Activation with First-Row Late TM (M: Fe, Co, Ni) $L_nM=E$ Catalysts;" T. R. Cundari, A. W. Pierpont Inorg. Chem. 49, 2038 – 2046 (cover article).

Generation of Efficient Supported (Heterogeneous) Olefin Metathesis Catalysts

California Institute of Technology, Chem. and Chem. Eng. Div., Pasadena, CA 91125

Email: rhg@mit.edu

Post Doctoral Fellow: Daryl Allen

Graduate Student: Matthew Van Wingerden

Abstract

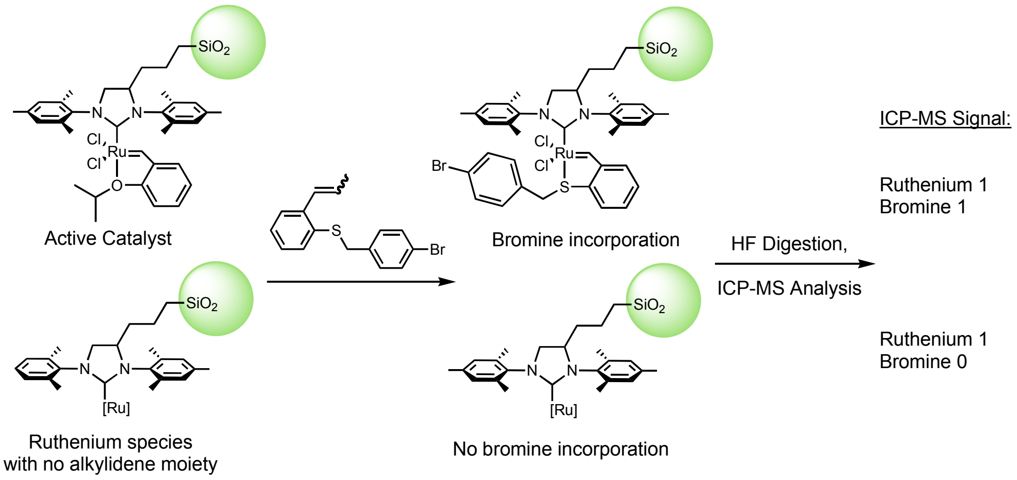
During the 2009 year significant progress has been made on a number of parts of the project. The catalysts that were prepared during the first year of the project were studied in detail, both in the Caltech laboratory and in the laboratories of Materia, Inc., the start up that is commercializing the ruthenium chemistry. These materials are being tested for the conversion of seed oils into chemical products that normally result from the refining of petroleum A spin off of Materia, Elevance just was awarded a DOE grant to fund the test biorefinery that is built on this and related chemistry. A second part of the project was to develop methods for the recovery and regeneration of spent ruthenium based metathesis catalysts. During this period, we have found that the residue of spent catalyst can be converted into an easily recoverable salt that can be converted to active catalyst in moderate yields. During the upcoming grant period, emphasis will be placed on developing methods for the determination of the amount of active catalyst on the support, the development of methods for increasing the lifetimes of the catalyst and developing methods for the conversion of the recovered ruthenium salts to high yields. Further work is being carried out at Materia to test the commercial applications of these catalysts.

Relevance to DOE

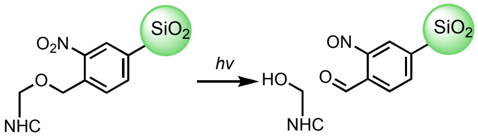
As demonstrated by the funding of the test biorefinery by the DOE (http://www.elevance.com/press/20091204_doe_grant.htm), this research has a direct bearing on the mission of the DOE.

Progress of the Project in 2009

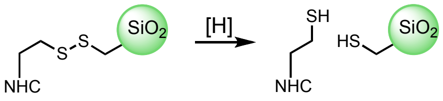
Major advances were made during the past year in the testing of the supported catalysts that have been prepared earlier. The heterogenized ruthenium metathesis catalysts show good life times and utility. During the last reporting period, new complexes had been prepared that were N-heterocyclic carbene complexes in which the backbone of the carbene ligand was substituted. It has now been amply demonstrated that this substitution pattern can lead to higher activities and lifetimes with some substrates. The amount of active catalyst will be determined by using labeled styrenes. These compounds will react with the supported active carbene complex, to attach a labeled complex. We will use bromine to allow for the analysis by ICP-MS. The ratio of the ruthenium to bromine will show the percentage of the ruthenium complex on the support that is still an active metathesis catalyst. Only active catalyst will react with the thio-styrene to yield a labeled alkylidene ligand. Only the active catalyst will give a bromine labeled compound. After digestion the ratio will provide an accurate number for the active catalyst. The alkylidene exchange shown in the follow scheme has been demonstrated and is quantitative.



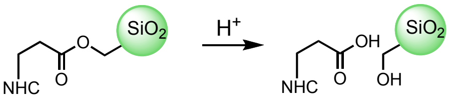
In many cases it is difficult to determine the exact structure of the complex that is attached to the support. Since the exact chemistry is not known at this stage, and the techniques developed will be usable for other studies, a family of cleavable groups are being explored. These are orthogonal types of groups. The cleavage chemistry involves either photochemistry, redox or acid base reactions. Examples are shown below.



Photolabile *o*-nitrobenzyl ether

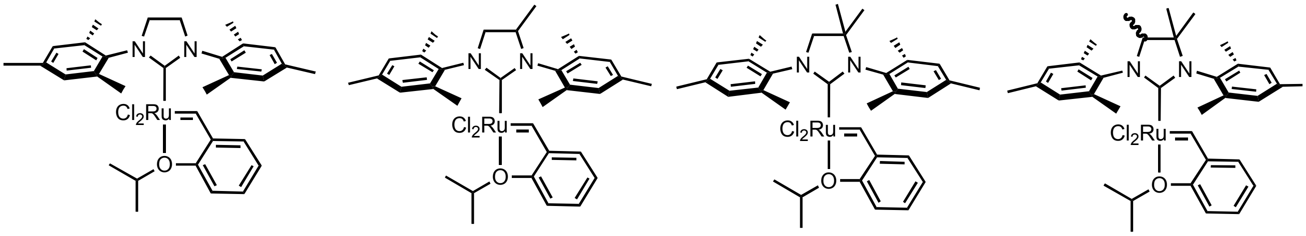


Reductively labile disulfide linkage

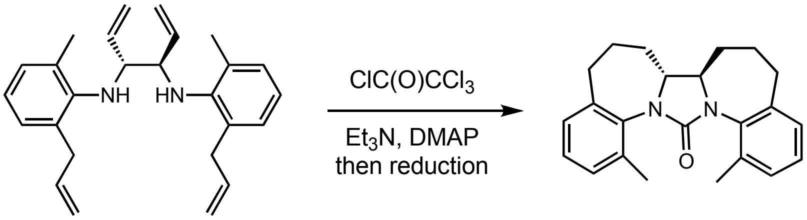


Acid labile ester linkage

More Stable Catalysts: A part of the present project is the synthesis of catalysts with higher turnovers. We have demonstrated in the past that the substitution of the back bone of the catalyst with blocking groups will stabilize the complex.



We are now preparing ligands that link the backbone to the supporting aromatic groups.



In catalysts prepared from these ligands, the interaction of the aromatic groups with the metal center will be controlled by the length of the connecting group. It is interesting that these will be made by a ring closing metathesis reaction.

Most Recent Publications Acknowledging this Grant (2009)

1. "Well-defined Silica-supported Olefin Metathesis Catalysts." D. P. Allen, M. M. Van Wingerden, and R. H. Grubbs, *Org. Lett.* **2009**, *11*, 1261-1264.
2. "The Effects of NHC-Backbone Substitution on Efficiency in Ruthenium-based Olefin Metathesis." K. M. Kuhn, J-B. Bourg. C. K. Chung, S. C. Virgil, R. H. Grubbs, *J. Amer. Chem. Soc.* **2009** *131,* 5313-5320 (Partially supported by NIHMS105170).

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

DE-FG02-86ER13511 Tobin J. Marks

Postdoc: Maximilliano Delferro
Graduate students: Brandon Rodriguez, Linda Williams, Staci Wegener, Michael Weberski
Collaborators: Peter Nickias (Dow Chemical Co.), Ignazio Fragala (U. Catania), Alceo Macchioni (U. Perugia), Jeffery Miller, Neng Guo, Chris Marshall (Argonne National Laboratory), Michael Lanagan (Penn. State U.).

Contact information: Department of Chemistry and the Center for Catalysis and Surface Science, Northwestern University, Evanston IL 60208-3113
t-marks@northwestern.edu http://chemgroups.northwestern.edu/marks/

Date of execution/start: November 15, 2008

Research Goals and Specific Objectives

Model, elaborate, understand, and exploit pathways by which organometallic molecules of varying nuclearity undergo chemisorptive activation and catalytic activity enhancement on solid surfaces. Such processes closely connect to real-world, large-scale industrial processes and to manufacturing cleaner, greener, more environmentally acceptable products, including those from renewal resources. Research combines catalyst synthesis, surface chemistry, homogeneous analogue catalysis, and computation, and involves collaboration with national laboratories and industry. Objectives in the past year were: 1) Investigate binuclear organometallic molecule chemisorption on "super Brønsted acid" oxides, 2) Synthesize and characterize mononuclear and polynuclear catalyst precursors for chemisorption and homogeneous catalysis, 3) Use this information to produce new types of efficient energy storage materials, 4) Computationally model both the catalysis and the resulting materials.

DOE Interest

The catalyst synthesis and characterization activities of this project relate directly to the efficiency, selectivity, and "greenness" of real-world industrial catalytic processes that are currently practiced on a huge scale, and to the ability of these processes to produce cleaner, more environmentally acceptable products. This includes processes using renewable, bio-feedstocks such as polyethylene production from sugar cane, and those which produce high-capacity energy storage materials.

Recent Progress

Nuclearity Effects on Catalyst Activity and Selectivity. The synthesis and characterization of bimetallic 2,7-di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalene-diolato group 10 polymerization catalysts $\{[Ni(CH_3)]_2[1,8\text{-}(O)_2C_{10}H_4\text{-}2,7\text{-}[CH{=}N(2,6\text{-}{}^{i}Pr_2C_6H_3)](PMe_3)_2\}$ and $\{[Ni(1\text{-}naphthyl)]_2[1,8\text{-}(O)_2C_{10}H_4\text{-}2,7\text{-}[CH{=}N(2,6\text{-}{}^{i}Pr_2C_6H_3)]\text{-}(PPh_3)_2\}$ [$\mathbf{FI^2\text{-}Ni_2(PR_3)_2}$] were realized, along with mononuclear analogues $\{Ni(CH_3)[3\text{-}{}^{t}Bu\text{-}2\text{-}(O)C_6H_3CH{=}N(2,6\text{-}{}^{i}Pr_2C_6H_3)](PMe)_3\}$ and $\{Ni(1\text{-}naphthyl)[3\text{-}{}^{t}Bu\text{-}2\text{-}(O)C_6H_3CH{=}N(2,6\text{-}{}^{i}Pr_2C_6H_3)](PPh)_3\}$ [$\mathbf{FI\text{-}Ni\ (PR_3)}$]. Monometallic Ni catalysts were also prepared by functionalizing one side of the $\mathbf{FI^2}$ ligand with a Me_3Si- group, yielding [$\mathbf{TMS\text{-}FI^2\text{-}Ni(PMe_3)}$]. $\mathbf{FI^2\text{-}Ni_2}$ catalysts exhibit large increases in ethylene polymerization activity vs. monometallic analogues, and increased branching and methyl branch selectivity. Higher ethylene concentrations suppress branching. $\mathbf{FI^2\text{-}Ni_2}$-mediated copolymerizations with ethylene + polar norbornenes exhibit a 4x increase in comonomer incorporation versus **FI-Ni**, yielding copolymers with 10% norbornene. $\mathbf{FI^2\text{-}Ni_2}$-catalyzed ethylene + methylacrylate or methyl methacrylate copolymerizations incorporate a remarkable 11% acrylate, while the mononuclear catalysts incorporate negligible amounts. $\mathbf{FI^2\text{-}Ni_2}$ catalysts also exhibit impressive polar solvent tolerance, even in the presence of ethyl ether, acetone, and water. The mechanism of the marked cooperative effects was elucidated. In related work it was shown that heterobimetallic Ni + Pd **FI^2** catalysts uniquely couple Ziegler and free radical polymerization processes.

Heterogeneous Catalytic Synthesis of Energy Storage Materials. Inexpensive materials combining the processability and mechanical properties of inexpensive polymers with the high dielectric constants of ferroelectric oxides are highly desirable for energy storage applications as in large-scale capacitors. To this end, a series of 0-3 metal oxide-polyolefin nanocomposites were synthesized via in-situ olefin polymerization using the single-site catalysts: C_2-symmetric dichloro[*rac*-ethylenebisindenyl]zirconium (IV), $Me_2Si(^tBuN)(\eta^5\text{-}C_5Me_4)TiCl_2$, and $(\eta^5\text{-}C_5Me_5)TiCl_3$ immobilized on methylaluminoxane (MAO)-treated $BaTiO_3$, ZrO_2, 3 mol% yttria-stabilized zirconia, 8 mol% yttria-stabilized zirconia, *sphere*-shaped TiO_2 nanoparticles, and *rod*-shaped TiO_2 nanoparticles. The resulting composites were structurally characterized by X-ray diffraction, SEM, TEM, ^{13}C NMR, and DSC. TEM shows that the nanoparticles are well-dispersed in the polymer matrix, with each individual nanoparticle surrounded by polymer. Electrical measurements reveal that most of these nanocomposites have leakage current densities ~ 10^{-6}-10^{-8} A/cm^2; relative permittivities increase as the nanoparticle volume fraction increases, with measured values as high as 6.1. At the same volume fraction, *rod*-shaped TiO_2 nanoparticle-isotactic-polypropylene nanocomposites exhibit significantly greater permittivities than the corresponding *sphere*-shaped TiO_2 nanoparticle-isotactic-polypropylene nanocomposites. The energy storage densities of these nanocomposites are as high as 9.4 J/cm^3.

Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces. Electrophilic Zr surface alkyls are created in high coverages by chemisorptive protonolysis of group 4 alkyls, and these species exhibit extreme activity for arene and olefin hydrogenation as well as for olefin polymerization. Benzene hydrogenation rates exceed that of any catalyst yet discovered. The kinetics and mechanism were characterized, 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 mononuclear and binuclear precursors. Thus, mono- and binuclear "constrained-geometry catalyst" (CGC) alkyls $Me_2Si(Me_5C_5)(^tBuN)ZrMe_2$ [$CGCZrMe_2$, **1**], 1-Me_2Si(3-ethylindenyl)(^{t}BuN)-$ZrMe_2$ [$EICGCZrMe_2$; **Zr_1**, **2**], (μ-CH_2CH_2-3,3')\{(η^5-indenyl)[1-Me_2Si-(^{t}BuN)]($ZrMe_2$)\}$_2$ [EBICGC$(ZrMe_2)_2$, **Zr_2**, **3**], and (μ-CH_2CH_2-3,3')\{(η^5-indenyl)[1-Me_2Si-(^{t}BuN)]($TiMe_2$)\}$_2$ [EBICGC$(TiMe_2)_2$, **Ti_2**, **4**] undergo rapid chemisorption on highly Brønsted acidic sulfated alumina (AlS) surfaces. ^{13}C CPMAS NMR of the chemisorbed complexes EICGCZr^{13}Me$_2$/AlS (**2***/AlS) and EBICGC(Zr^{13}Me$_2$)$_2$/AlS (**3***/AlS) reveals that chemisorption involves, M-C σ-bond protonolysis at surface Brønsted sites, as well as heterolytic M-C scission with methide transfer to surface Lewis acid sites, forming similar "cation-like" electrophiles, e.g., EICGCM^{13}Me$^+$. Relative rates of ethylene polymerization mediated by these catalysts on AlS are: **4**/AlS > **2**/AlS > **3**/AlS > **1**/AlS, for ethylene polymerization. Ethylene/1-hexene copolymerizations mediated by the same set of catalysts display relative polymerization rates: **4**/AlS > **3**/AlS > **2**/AlS > **1**/AlS. EXAFS studies with Drs. N. Guo and J. Miller at Argonne National Laboratory indicate, for Cp*$ZrMe_3$/AlS where ~ 95% of the Zr sites are catalytically active, that the Cp*$ZrMe_2^+$ cation essentially "floats" above the AlS$^-$ surface with *very weak* ion pairing.

Theoretical Studies. To better understand the above chemisorption/catalytic chemistry, $Cp_2Zr(CH_3)_2$ chemisorption on dehydroxylated γ-alumina (Al_2O_3) was analyzed via DFT. The interactions of catalytically-active $Cp_2ZrCH_3^+$ adsorbates were scrutinized on two possible Al_2O_3 (*110*) surface sites, namely μ_2-O and μ_3-O, representing the principal reactive species on the alumina surface. We find that $Cp_2ZrCH_3^+$ coordination occurs via two different geometries: dioxo-bridged and oxo-bridged, at both μ_3-O and μ_2-O surface sites. This process is compared to that forming $Cp_2ZrCH_3^+H_3CB(C_6F_5)_3^-$ in solution. It is found that interaction of the $Cp_2ZrCH_3^+$ adsorbate species with μ_2-O sites is far stronger than with μ_3-O sites due to the greater unsaturation of the former. Furthermore, the interaction with the μ_3-O sites is weaker than in the parent homogeneous ion pair. The catalytic activity of the chemisorbed $Cp_2ZrCH_3^+$ systems for ethylene polymerization was investigated at both μ_2-O and μ_3-O sites and compared with the analogous $Cp_2ZrCH_3^+H_3CB(C_6F_5)_3^-$ -mediated process in solution. The enchainment mechanism proceeds via ethylene π-complex formation and an α-agostic assisted transition state to yield γ- and β- agostic insertion products. The overall enchainment kinetics are correlated with the energetics of π-complex formation, and we suggest that the differing kinetics of the Cp_2ZrR^+ adsorbates on the various Al_2O_3 coordination sites and the analogous homogeneous species reflect differences in olefin π-complex stabilization energies. These results provide remarkable insight and agree well with experiment, which indicates that only fractions of surface-bound species are catalytically significant. However, these are far more catalytically active than the homogeneous analogues.

Future Plans

To activate polynuclear molecule-based catalysts to new levels of activity, we will investigate more Brønsted acidic supports, seeking catalytic effects only possible via the agency of adjacent catalytic centers. A variety of binuclear catalyst precursors will be chemisorbed and studied. Structural characterization will include solid state NMR and EXAFS/XANES at ANL, with operando studies of catalysts turning over and/or being inhibited. Here, our systems with virtually 100% active sites present a unique opportunity. We also plan investigations of cooperative effects in homogeneous binuclear group 10 catalysts, focusing on transformations that are normally exceeding difficult by virtue of steric congestion and/or unfavorable substrate basicity. Catalysts will include Ni_2, Pd_2, and heterobinuclear NiPd and mixed groups 4 + 10 systems.

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12. Li, Z.; Fredin, L.A.; Tewari, P.; DiBenedetto, S.A.; Lanagan, M.T.; Ratner, M.A.; Marks, T.J. *In Situ* Catalytic Encapsulation of Core-Shell Nanoparticles having Variable Shell Thickness. Dielectric and Energy Storage Properties of High-Permittivity Metal Oxide Nanocomposites, submitted.

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

Bio-inspired Iron Catalysts for Hydrocarbon Oxidations: April 2010 report

Project initiated September 1, 2009; 2009-10 budget: $175,000 total costs
Postdoctoral associates: Praneeth Vijayendran Koombil Kuummaya
Graduate students: Yan Feng, Partha Das

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, Minnesota 55455
Phone: 612 625 0389; fax: 612 624 7029; e-mail: larryque@umn.edu

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 is exploring the use of nonheme iron complexes as catalysts for the oxidation of hydrocarbons using H_2O_2 as terminal oxidant.

Recent Progress

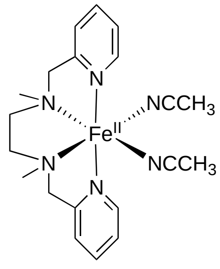
We report three important developments in our work.

1. First example of biomimetic cis-dihydroxylation of naphthalene.

We reported in *Chemical Communications* that $[Fe^{II}(TPA)(MeCN)_2](OTf)_2$, the catalyst we have characterized in greatest detail, can catalyze the *cis*-dihydroxylation of naphthalene, the substrate for naphthalene dioxygenase (NDO), with H_2O_2 as oxidant. 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. ^{18}O-labeling studies to determine the sources of the oxygen atoms incorporated into products showed that Fe(TPA)-catalyzed *cis*-dihydroxylation of naphthalene operates by a water-assisted mechanism, analogous to that we have proposed for olefin *cis*-dihydroxylation. Our results show that one diol oxygen derives from H_2O_2 and the other from water. Indeed the plot for the incorporation of labeled water for naphthalene oxidation as a function of labeled water concentration overlays that previously reported for Fe(TPA)-catalyzed cyclooctene *cis*-dihydroxylation, implicating a common oxidant. Thus, the Fe(TPA)/H_2O_2 combination can oxidize alkanes to alcohols, olefins to epoxides and *cis*-diols, and arenes to *cis*-1,2-dihydrodiols, all with high retention of stereoselectivity. For all oxidations, a short-lived $Fe^{V}(O)(OH)$ species is proposed as the oxidant.

2. Iron-catalyzed ipso-hydroxylation

In our efforts to understand the role that carboxylic acid additives play in modulating the behavior of Fe(TPA) and Fe(BPMEN) complexes that catalyze olefin oxidation, we investigated the effects of benzoic acids. The addition of benzoic acid in these catalytic experiments resulted in stoichiometric *ortho*-hydroxylation to form an Fe(III)-salicylate complex. However, *ortho*-hydroxylation was inhibited in the case of benzoic acids with *ortho* substituents. Instead, *ipso*-hydroxylation occurred with concomitant decarboxylation.



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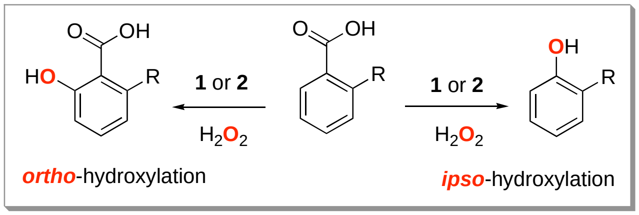
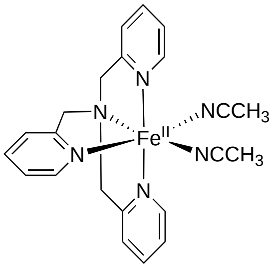
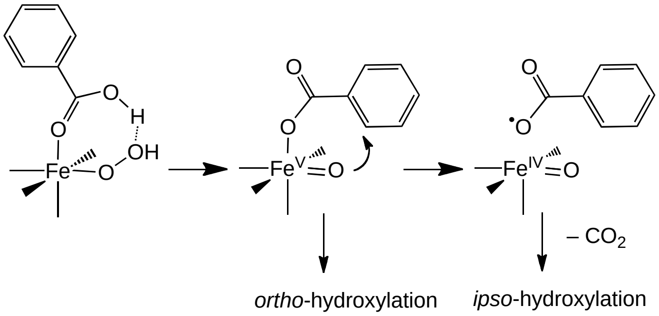
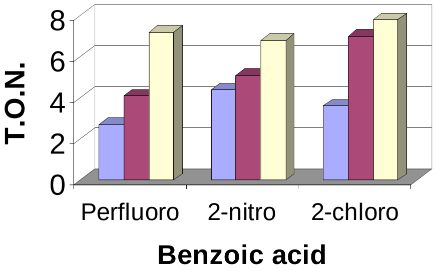




2

These results can be interpreted within the same mechanistic framework as the hydrocarbon oxidation catalysis in item #1 above invoking an Fe^{V}=O oxidant. These results were published in *Chem. Eur. J.*

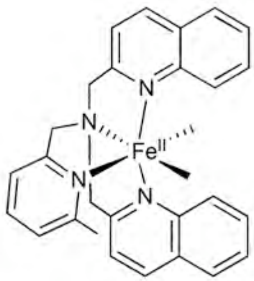


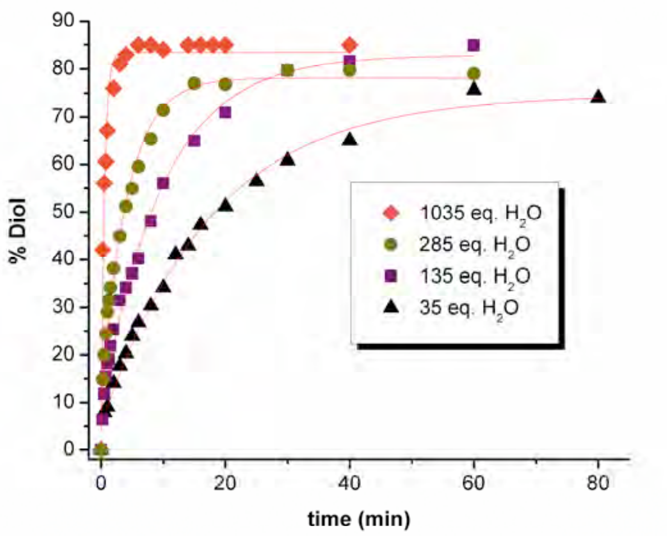


In further ongoing work on benzoic acids with electron withdrawing *ortho* substituents, we have found that *ipso*-hydroxylation can be catalytic, as shown in the bar graph above right (reaction conditions: 1mM Fe catalyst, 10 equiv H_2O_2, varying amounts of added ArCOOH (blue = 10 equiv, maroon = 25 equiv, yellow = 50 equiv), RT, 30 min reaction time). Furthermore, *ipso*-hydroxylation was shown to be competitive with olefin oxidation. The product distributions observed strongly suggest that the $Fe^{V}(O)(O_2CAr)$ oxidant formed can react by undergoing *ipso*-hydroxylation/decarboxylation or by transferring the oxo atom to an olefin.

3. Mechanistic studies of olefin cis-dihydroxylation by bio-inspired Fe catalysts

We have completed a systematic investigation of olefin *cis*-dihydroxylation by iron(II) complexes supported by a family of facial tridentate *N,N,O* ligands, a ligand set that is inspired by the 2-His-1-carboxylate facial triad motif commonly found for mononuclear nonheme iron oxygenases, including the Reiske dioxygenases that catalyze arene *cis*-dihydroxylation. The *N,N,O* ligands are variations of *N*-acylated dipyridin-2-ylmethylamines (R-DPAH), and crystal structures of the iron(II) complexes show that they indeed bind the iron center in a facial tridentate manner. When treated with 10 equiv H_2O_2 in the presence of olefins, the iron(II) complexes catalyze the oxidation of olefin substrates into *cis*-diol products, with as much as 90% of the H_2O_2 oxidant being converted into *cis*-diol products. However, a large excess of olefin is required to achieve the high conversion efficiency. Reactivity and mechanistic comparisons with the previously characterized Fe(TPA)/H_2O_2 catalyst/oxidant combination (TPA = tris(pyridin-2-ylmethyl)amine) lead us to postulate a different mechanism for these Fe(II) catalysts involving a novel $Fe^{IV}(OH)_2$ oxidant that is formed from the activation of H_2O_2 upon interaction with the Fe(II) center. This hypothesis is supported by three sets of observations: a) the absence of a lag phase in the conversion of the H_2O_2 oxidant into *cis*-diol product, thereby excluding the prior oxidation of the Fe(II) catalyst to an Fe(III) derivative as established for the Fe(TPA) catalyst; b) the incorporation of $H_2{}^{18}O$ into the *cis*-diol product, thereby requiring O-O bond cleavage to occur prior to *cis*-diol formation; and c) the formation of *cis*-diol as the major product of cyclohexene oxidation, rather than the epoxide or allylic oxidation products more commonly observed in metal-catalyzed oxidations of cyclohexene, implicating an oxidant less prone to oxo transfer or H-atom abstraction.





Recently, we found [Fe(6-Me-BQPA)$(OTf)_2$] to be a highly effective *cis*-dihydroxylation catalyst for which syringe pumping was not necessary to elicit a high yield of products. The possibility of adding the H_2O_2 oxidant all at once opens the door for much needed kinetic measurements to shed light on the mechanism of *cis*-dihydroxylation. As shown on the right, the reaction kinetics, as monitored by product analysis, exhibits nice exponential behavior for the formation of *cis*-diol. Interestingly, an unexpected accelerative effect of water can be observed. Despite the large water effect, water labeling studies showed no incorporation of labeled water into the diol products from this catalytic system. With kinetic studies now possible for the first time for one of these bio-inspired catalysts, we are poised to gain significant thermodynamic and kinetic insight into how this chemistry works.

Future objectives

Continued detailed mechanistic studies of the reactions of peroxides with nonheme iron(II) complexes to understand the molecular basis for H_2O_2 activation by iron that leads to stereospecific oxidation products.

Development of iron catalysts for olefin *cis*-dihydroxylation reaction for applications in synthetic organic chemistry.

Trapping high-valent intermediates in the iron-catalyzed olefin oxidation reactions

Current support

NIH GM-33162 "Nonheme Iron Oxygen Activation in Enzymes and Models" $1,856,000 total costs for the period 4/1/05-3/31/11

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” $340,000 total costs for the period 9/1/09-8/31/11

2009-2010 Publications

solely supported by US DOE

1. Feng, Y.; Ke, C.-y.; Xue, G.; Que, L., Jr., Bio-inspired arene *cis*-dihydroxylation by a non-haem iron catalyst modeling the action of naphthalene dioxygenase. *Chem. Commun.* **2009**, 50-52 (designated as a HOT paper by journal)
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3. Oldenburg, P. D.; Feng, Y.; Pryjomska-Ray, I.; Tiegs, D.; Que, L., Jr., Olefin *cis*-Dihydroxylation with Bio-Inspired Iron Catalysts. Evidence for an Fe^{II}/Fe^{IV} Catalytic Cycle, submitted to *Journal of the American Chemical Society*

supported by US DOE and other agencies

4. Company, A.; Feng, Y.; Güell, M.; Ribas, X.; Luis, J. M.; Que, L., Jr.; Costas, M., Olefin-Dependent Discrimination Between Two Nonheme HO-Fe^{V}=O Tautomeric Species in Catalytic H_2O_2 Epoxidations. *Chem. Eur. J.* **2009**, *15*, 3356-3362.

DE-FG02-08ER15997 **Melanie S. Sanford**

Catalytic Oxidative Coupling of Arenes and Alkanes: Applications for Efficient Chemical Synthesis and for Hydrocarbon Oligomerization

Additional PI's:	none
Post-doc:	Rebecca Loy
Students:	Kami Hull, Thomas Lyons, Amanda Hickman
Collaborators:	none
Contacts:	University of Michigan, 930 N University Ave, Ann Arbor, MI 48109; mssanfor@umich.edu

Goal

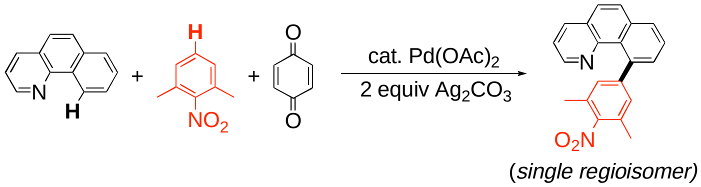
Use mechanistic studies to develop new and highly selective metal catalyzed C–H activation/C–C coupling reactions.

DOE Interest

This research provides an atom efficient and environmentally benign alternative route to the synthesis biaryl compounds, which are critical structures in a wide array of pharmaceuticals and fine chemicals. In addition, similar catalytic strategies can ultimately be applied for the oxidative oligimerization of alkanes, providing a direct and energy efficient route from natural gas to liquid fuels and providing an attractive approach to upgrade low molecular weight by-products of the Fisher Tropsch process.

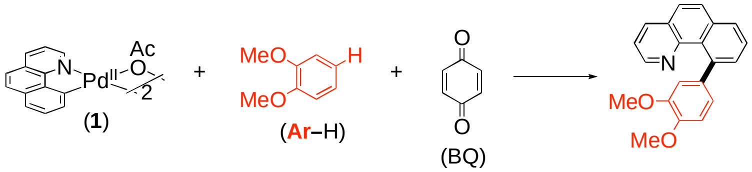
Recent Progress

Development of Pd-catalyzed Ar–Ar' cross-coupling reaction. We have recently developed a Pd-catalyzed reaction for the highly chemo- and regioselective oxidative cross-coupling of aromatic C−H substrates (eq. 1). This transformation involves two discrete C–H activation reactions at Pd – a ligand-directed cyclometalation followed by undirected Ar–H activation.



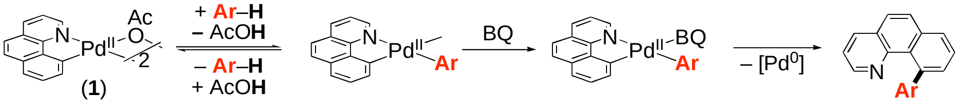
(*1*)

Mechanism of Ar–Ar' oxidative cross-coupling. We have conducted detailed mechanistic investigations of this new transformation. We were particularly interested in understanding the mechanism of the 2nd, non-directed arene activation step; thus we examined the reaction between dimer **1** and 1,2-dimethoxybenzene in detail (eq. 2).



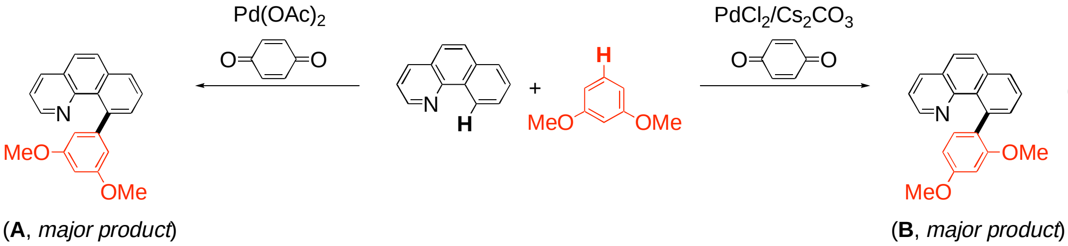
(*2*)

Through a series of experiments, including determination of the order of the reaction in various reagents, H/D exchange studies, kinetic isotope effect investigations, and the evaluation of electronic effects, we proposed a detailed mechanism for these reactions that is summarized in eq. 3. Intriguingly, this work demonstrates that the role of benzoquinone (a key additive for controlling both reactivity and selectivity) is to promote C–C bond-forming reductive elimination from Pd^{II}. This work provides key insights for rationally tuning the reaction conditions in order to control the chemo- and regioselectivity of Ar−Ar′ coupling.



(3)

Control of regioselectivity in Ar–Ar’ oxidative cross-coupling. Very recent studies have shown that the regioselectivity of the Ar-Ar’ cross-coupling reactions can be tuned by modification of reaction conditions. For example, as shown in eq. 4, the use of acetate-based Pd catalysts in the coupling of benzo[*h*]quinoline with 1,3-dimethoxybenzene provides product **A** with high selectivity. However, this selectivity can be completely reversed in the presence of carbonate salts to afford **B** as the major product.



(4)

Developed assay to rapidly screen metal complexes for C–H activation activity. The development of new oxidative coupling reactions will require catalysts that are highly reactive towards arene and alkane activation. In order to rapidly assay potential catalysts, we have developed a procedure to compare diverse group 10 metal complexes in the H/D exchange between benzene and TFA-d_1, AcOD-d_4, TFE-d_3, CD_3OD, D_2O, and other deuterium sources using turnover number (TON) as a standard metric. An initial survey of Pt complexes, including commercial Pt salts ($PtCl_2$, K_2PtCl_4) and Pt chloride complexes containing bidentate and tridentate nitrogen donor ligands, was carried out. This study established that the addition of AgOAc (in TFA-d_1) or $AgBF_4$ (in AcOD-d_4 and TFE-d_3) displaces the Cl ligands on the Pt precatalyst, which leads to dramatically increased turnover numbers. In general, the simple Pt salts provided the fewest turnovers, and Pt complexes containing bidentate ligands afforded higher turnover numbers than those with tridentate ligands. A diimine Pt complex was found to be a top performing catalyst for H/D exchange with all deuterium sources examined. Interestingly, the relative reactivity of many of the catalysts varied dramatically upon changing the deuterium source.

Future Plans

Ar-Ar' oxidative cross-coupling. Determine mechanistic origin of reversal of regioselectivity in cross-coupling reactions in presence of OAc vs CO_3 salts. Examine substrate scope of these reactions and expand them to alkane based-substrates.

Non-directed C–H activation/C–C coupling reactions. Apply insights gained from Ar-Ar' cross-coupling reactions above to the development of new, selective Pd-catalyzed C–H activation/C–C bond-forming transformations.

H/D exchange. Expand H/D exchange assay studies to alkane substrates. Develop detailed structure activity relationship to understand ligand effects in H/D exchange reactions. Use insights gained from H/D exchange studies to develop new catalysts for C–H activation/C–C coupling.

Publications (2008-2010)

K. L. Hull, M. S. Sanford, "Mechanism of Benzoquinone-Promoted Palladium-Catalyzed Oxidative Cross-Couplng Reactions," *J. Am. Chem. Soc.* **2009**, *131*, 9651-9653.

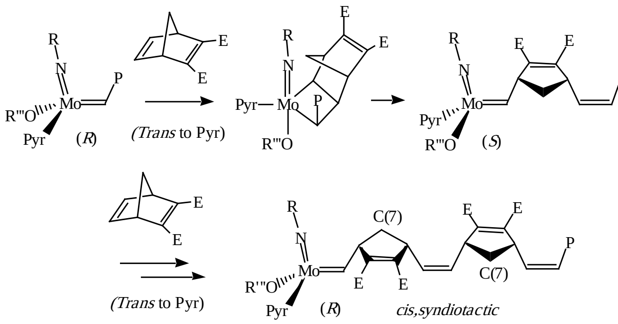
A. J. Hickman, J. A. Villalobos, M. S. Sanford, "Quantitative Assay for the Direct Comparison of Pt Catalysis in Benzene H/D Exchange," *Organometallics* **2009**, *28*, 5316-5322.

T. W. Lyons, M. S. Sanford, "Palladium-Catalyzed Ligand-Directed C–H Functionalization," *Chem. Rev.* **2010**, *110*, 1147-1169.

The ROMP Polymerization of Olefins with New MonoAlkoxidePyrrolide (MAP) Catalysts

Richard R. Schrock, MIT, Department of Chemistry
Cambridge, MA 02139; E-mail: rrs@mit.edu

Approximately two years ago new types of metathesis catalysts (MonoAlkoxidePyrrolide or MAP species) were discovered through treatment of a bispyrrolide complex, e.g., $M(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$, with an alcohol (M = Mo or W). The resulting *syn*-$M(NAr)(CHCMe_2Ph)(Me_2Pyr)(OR)$ species contain four different covalently bound ligands, one of which is involved in a catalytic metathesis reaction. MAP species can be prepared *in situ* and are >100 times more efficient than either bispyrrolides (virtually no activity) *or* bisalkoxides that might be formed in some instances through reactions of the MAP species with a second equivalent of alcohol. As a consequence of the presence of a stereogenic metal center the chirality at the metal center inverts with each metathesis step. Fundamental studies suggest that an olefin adds to the metal *trans* to the pyrrolide to yield a metallacyclobutane complex that contains axial imido and OR''' groups. If OR''' is large enough with respect to NR then all *cis* metallacycles can form and therefore all *cis* polymers. The fact that the metal inverts with each insertion automatically leads to *syndiotactic* polymers, as shown in the example in equation 1 (Pyr = pyrrolide). Pure *cis,syndiotactic* ROMP polymers have never been prepared to our knowledge. We have dubbed the principle that governs the formation of *syndiotactic* polymers "stereogenic metal control." This new principle is believed to be the most powerful determinant of polymer tacticity, with enantiomorphic site control being the next most powerful, and chain end control being the least powerful. The goal is to explore extensively the use of MAP species, hundreds of which are now available in our laboratories as a consequence of their development for enantioselective or Z selective reactions. No examples of control of the structure of ROMP polymers prepared with ruthenium metathesis catalysts has been reported. The synthesis of polymers with a regular structure with Mo or W catalysts strongly depends on the rate of interconversion of *syn* and *anti* isomers, which may be fast (e.g.,100 s^{-1}) or slow (e.g., 10^{-5} s^{-1}) and therefore also on the temperature of the polymerization and the reactivity of the monomer in question.



(1)

Figure 1. Details of forming *cis,syndiotactic* polymer.

We are focussing on the polymerization of 3-methyl-3-phenylcyclopropene (MPC), a new monomer for ROMP polymerization, backed up with various norbornenes and substituted norbornadienes, polymerization of which have been more thoroughly studied with previous catalysts and for which tacticity in a highly regular polymer can be determined through NMR techniques that we have developed. We have been able to make two highly tactic MPC polymers, *both of which have cis structures*. One is formed through enantiomorphic site control using a biphenolate catalyst and the other through stereogenic metal control with a MAP catalyst. We are developing methods that will allow us to prove that (we propose) the former is *isotactic* and the latter *syndiotactic*.

The goal of this project is to control the microstructure of polymers, a key determinant of polymer properties. It would be highly desirable to understand how to prepare all possible regular structures of ROMP polymers (*trans or cis, isotactic or syndiotactic*) through manipulation of sterics and electronics of the imido, pyrrolide, and alkoxide ligands. In the process we will have to synthesize new variations of MAP catalysts and carry out extensive mechanistic studies. The fact that many polymerizations are likely to be living creates many possibilities in terms of block copolymer syntheses.

DE-FG02-93ER14359 Lawrence T. Scott

High Temperature Chemistry of Aromatic Hydrocarbons

Additional PIs:	none
Postdocs:	none
Students:	Aaron Amick, Anthony Belanger, Kristen Curtis, Maria Eliseeva, Eric Fort, Allison Greene, Edward Jackson, Jennifer Quimby, Jonathan Rose, Natalie Smith, Brian Steinberg
Collaborators:	D. M. Grant (University of Utah), R. J. Pugmire (University of Utah), M. A. Petrukhina (University at Albany, SUNY), A. Wakamiya (Kyoto University, Japan), R. LeParc (Université Montpellier, France), V. Jourdain (Université Montpellier, France), C. Joblin (CNRS and Université de Toulouse, France), P. Pilleri (CNRS and Université de Toulouse, France), M. Gerin (Observatoire de Paris et École Normale Supérieure, Paris, France), T. F. Giesen (Universität Köln, Germany), J.-U. Grabow (Universität Hannover, Germany), M. Marcaccio (Università di Bologna, Italy), C. Fontanesi (Università di Modena e Reggio Emilia, Italy), G. Malloci (Osservatorio Astronomico di Cagliari, Capoterra, Italy), S. Brünken (Ecole Polytechnique Fédéralede, Lausanne, Switzerland)
Contact:	Department of Chemistry, Boston College, Chestnut Hill, MA 02467-3860; lawrence.scott@bc.edu

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.

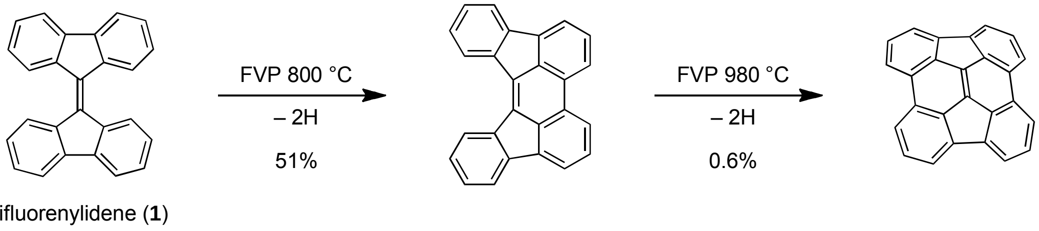
DOE Interest

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

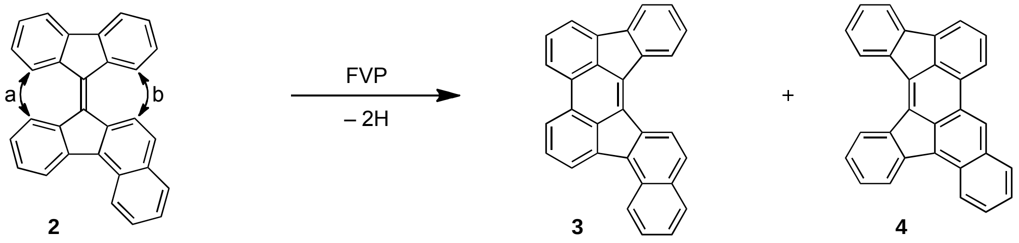
Surprisingly little is known about the mechanism(s) of thermal cyclodehydrogenation reactions, even though they represent ubiquitous transformations in the high temperature formation of condensed carbon-rich products such as fullerenes, soot particles, and discrete PAHs (*e.g.*, benzo[*a*]pyrene, a potent carcinogen). Experimental studies are virtually nonexistent, beyond the work underway in our laboratory, and very little computational work has been published on such reactions. Following up on our successful benzannulation studies on [5]helicene cyclizations, we are conducting analogous studies on the cyclodehydrogenation of bifluorenylidene (Scheme 1). The relative ease of this cyclization has been attributed to the significant relief of strain associated with the twisted double bond in the starting material. The second closure involves a large strain *increase* and has been found to be much more difficult. Our experiments will focus only on the relatively efficient first cyclodehydrogenation.

Scheme 1



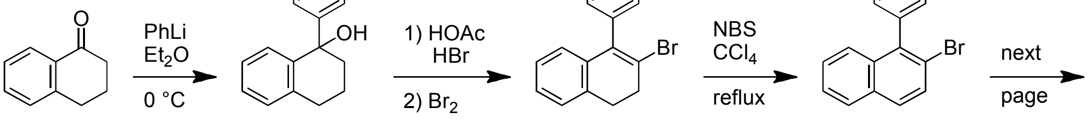
Benzannulation as shown in structure **2** (Scheme 2) sets up an internal competition between cyclodehydrogenation pathways *a* and *b*. Our studies will determine not only the relative rates of cyclization by pathway *a vs* pathway *b*, but also these rates relative to that for cyclization of the parent hydrocarbon (**1**) under the same conditions. From these data, and those obtained in a parallel study of an isomeric benzannulated bifluorenylidene (not shown), we will be able to determine whether such thermal cyclodehydrogenations occur by an electrocyclization mechanism, a hydrogen shift/carbene insertion mechanism, or a C–H cleavage/radical addition mechanism.

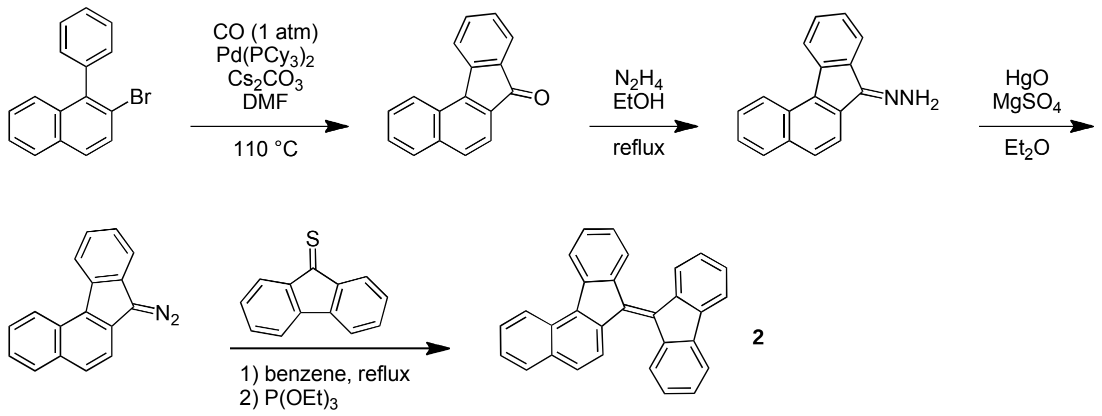
Scheme 2



We have now completed a synthesis of **2** as shown in Scheme 3, and the initial flash vacuum pyrolysis experiments have been initiated. Once conditions have been optimized for thermal cyclodehydrogenation of **2**, the relative rate data will be measured. Results from other projects and collaborations can be found in the publications listed.

Scheme 3





Future Plans

Conditions will be optimized for thermal cyclodehydrogenation of **2**, and the product distribution will be determined. The relative rate data obtained will be compared with that for cyclization of **1**. Parallel experiments on an isomeric benzannulated bifluorenylidene (not shown) will also be performed to elucidate the mechanism(s) of such thermal cyclodehydrogenations that form 6-membered rings.

Publications (2008-2010)

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DE-AC02-05CH11231 **T. Don Tilley**

Transformations of Organic Compounds via Homogeneous Catalysis & Heterogeneous Catalysis with Well-Defined Single Sites

Postdocs: Pat Bazinet, Chris Bradley, Robert Wright
Students: Dan Ruddy, Jennifer McBee, Meredith McMurdo
Collaborators: Alex Bell (LBNL), Odile Eisenstein (U. Montpellier)
Contact: T. Don Tilley, Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; phone: (510) 642-8939; Email: tdtilley@berkeley.edu

Goal

Activities in this program include the development and study of homogeneous and heterogeneous catalyst systems for selective transformations of organic compounds. Molecular-based, homogeneous catalysts are based on early or late transition metals, and are designed to provide novel bond activation pathways that may be incorporated into a catalytic cycle. Another goal of this project is to develop molecular chemistry that allows atomic-level and nanoscopic control over the structures of heterogeneous catalysts, and well-defined, single-site catalysts via chemical reactions on a surface. Such catalysts 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.

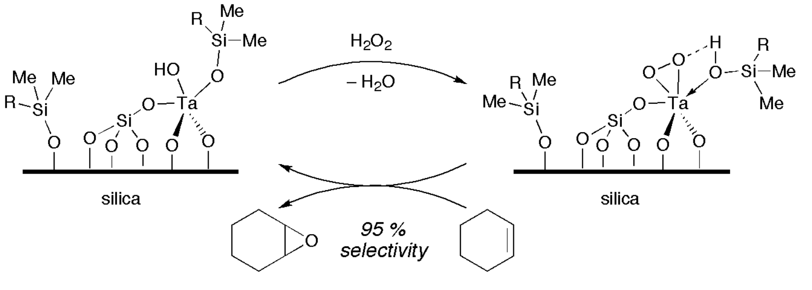
Recent Progress

Homogeneous Catalysis: Hydroaminations of norbornene with arylsulfonamides and weakly basic anilines were achieved using electrophilic Pt(II) bis(triflate) complexes of the type $L_2Pt(OTf)_2$ (L_2 = $^tBu_2bpy$, $^tBuC_6H_4N{=}C(CH_3)C(CH_3){=}NC_6H_4{}^tBu$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, *S*-BINAP [8]. Pseudo first order kinetics reveal little to no dependence of the reaction rate on the ancillary ligand. Mechanistic studies do not favor an olefin coordination mechanism but are instead consistent with a mechanism involving sulfonamide coordination and generation of an acidic proton that is transferred to the norbornene. It is postulated that the resulting norbornyl cation is then attacked by free sulfonamide, and loss of proton from this adduct completes the hydroamination. The platinum-sulfonamide complex readily undergoes deprotonation to give a μ-amido platinum-bridged dimer that was isolated from the reaction solution. These studies also involve use of Me_3SiPh and Me_3SnPh as non-nucleophilic proton traps. Cleavage of the Ph-E bonds was used to detect the acidic, catalytically active species.

The monoanionic, chelating 2-(2-pyridyl)indolide (PyInd) ligand has been found to stabilize coordinatively unsaturated Ir(V) and Rh(V) bis(silyl)dihydride complexes, one of which, the Rh(V) bis(silyl)dihydride $(PyInd)Rh(H)_2(SiEt_3)_2$, mediates the catalytic dehydrochlorinative coupling of chlorobenzene with triethylsilane. A related system, derived from the monoanionic ligand, 3,5-diphenyl-2-(2-pyridyl)pyrrolide (PyPyr), supports analogous, coordinatively unsaturated Ir(V) and Rh(V) bis(silyl)dihydride complexes. Interestingly, one of these Rh(V) bis(silyl)dihydrides, (PyPyr)Rh(H)$_2$(Si^{t}BuPh$_2$)$_2$, was found to undergo silane exchange through a 14-electron intermediate of the type (PyPyr)RhH(Si^{t}BuPh$_2$) [15].

Single-Site Selective Oxidation Catalysis: 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. In one aspect of this work, tantalum centers on the surface of an organically modified silica have been observed to exhibit high selectivities in the epoxidation of olefins with aqueous H_2O_2 [5]. Modified Ta-SBA15 catalysts were prepared to give a hydrophobic surface and Ta-OSiMe$_2$R functionalities. A product selectivity of >95% epoxide is observed for at least 6 h of reaction time versus 11% for the unmodified catalyst. Reactivity studies indicate that the Ta-OSiMe$_2$R group plays an important role in determining this selectivity. 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. The kinetic data are similar to that for 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

The Pt-mediated proton transfer mechanism associated with hydroaminations by sulonamides may have broad implications for bond activation pathways in reactions catalyzed by electrophilic, late transition metal complexes. This possibility will be examined, starting with hydroarylations catalyzed by L$_2$Pt(OTf)$_2$ complexes. Research with single-site oxidation catalysts will focus on attempts to more thoroughly characterize intermediates, for example by EXAFS. Additional mechanistic work involving *in situ* spectroscopic methods will address the formation, stability, and reactivity of Ta(V)(η^2-O$_2$) and related intermediates. Efforts will also be directed toward identification of new, highly selective oxidations, for substrates such as arenes, alkynes, and carbonyl compounds.

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Additional Poster Presentations

Theodore A. Betley -- *Catalytic C–H Bond Functionalization Utilizing Electrophilic Iron Complexes*

T. Brent Gunnoe -- *Development of Transition Metal Catalysts for the Functionalization of Carbon-Hydrogen Bonds: Fundamental Studies of Catalytic Hydroarylation of Olefins*

Daniel J. Mindiola -- *Hydrosilylation Catalysts of Nickel and Carboamination of Aldimines and Alkynes with an Easy-to-Make Titanium Catalyst*

Bahram Moasser -- *Synthetic and Mechanistic Studies of New Metal-Ligand Bifunctional Hydrogenation Catalysts*

Dmitry E. Polyansky -- *New Insights into Mechanism of Catalytic Water Oxidation by Mononuclear Ru Polypyridyl Complexes*

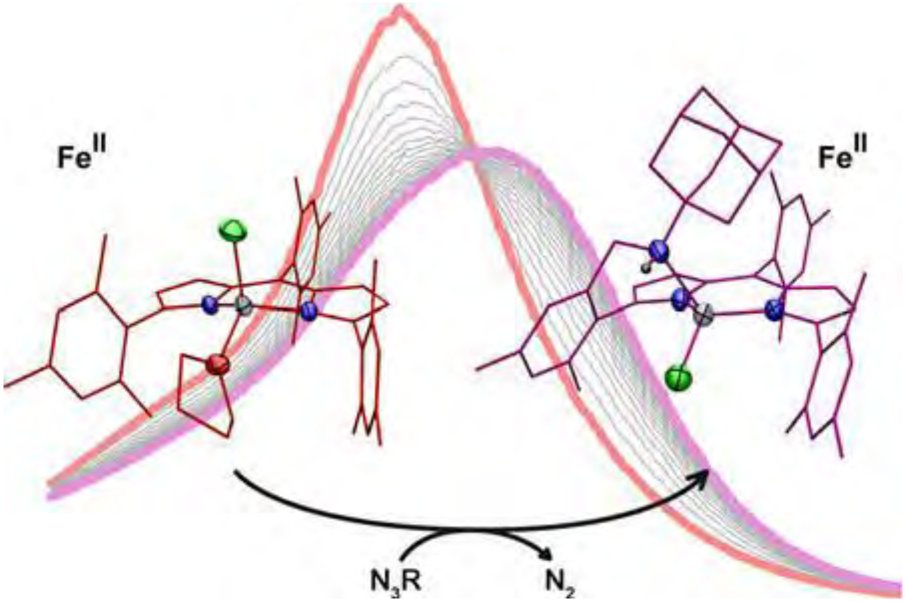
Travis J. Williams -- *Bifunctional Catalysts for Dehydrogenation of Ammonia Borane*

Catalytic C–H Bond Functionalization Utilizing Electrophilic Iron Complexes

Theodore A. Betley, Chemistry Department, Harvard University, 12 Oxford Street, Cambridge, MA 02138

E-mail: betley@chemistry.harvard.edu

The combination of small-molecule activation with C—H bond functionalization represents a significant advance in converting inexpensive chemical feed stocks (e.g. hydrocarbons) to valuable functional molecules with minimal or complete absence of waste generation. We are targeting multi-electron redox transformations by mid-tolate, first row transition metal complexes targeting methods for the functionalization of C–H bonds. Specifically, we have synthesized a class of electrophilic complexes featuring transiently-formed, or metastable metal-ligand multiple bonds capable of mediating C–H functionalization. Dipyrromethene- (or semi-porphyrin) supported ferrous complexes were found to effect a range of intra- and intermolecular C–H bond functionalization reactions - allowing for the construction of new C–N, C–C and C–O bonds from unactivated C–H bonds. Our research has improved our understanding of factors contributing to the promotion of productive C–H bond activation and functionalization, further developing new classes of inorganic/organometallic catalysts to synthesize value-added commodity chemicals via clean reaction routes with minimal waste product.



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

Hydrosilylation Catalysts of Nickel and Carboamination of Aldimines and Alkynes with an Easy-to-Make Titanium Catalyst.

Additional PI's: Dongwhan Lee

Postdocs: Jiyoung Jung and Marlena Washington

Contact: Department of Chemistry, Indiana University, 800 E. Kirkwood Ave.,
Bloomington IN 47405; mindiola@indiana.edu

Goals

Prepare hydrosilylation catalysts for reduction of the carbonyl group using cheap transition metals such as Ni, and which also allow for expansion of the degree of functional group tolerance. We also want to explore the mechanism of a reaction that involves the carboamination of aldimines with alkynes by an easy-to-prepare titanium catalyst. Our studies in this area also expand this methodology to the formation of highly modular α,β-unsaturated imines, in particular monomers that can be readily polymerized or decorated to function as sensors for several analytes or metal ions.

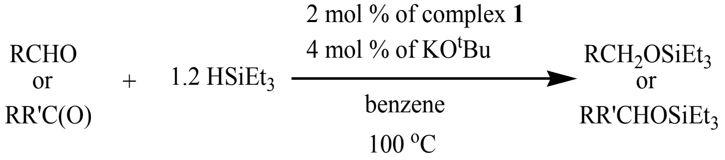
DOE Interest

The reduction of the carbonyl functionality, specifically the aldehyde and ketone groups, to alcohol via hydride transfer is an important transformation in organic synthesis. More importantly, reducing the carbonyl group followed by protection of the alcohol moiety would appeal from a synthetic standpoint if such a substrate is being used for subsequent multistep synthesis. Consequently, metal catalyzed hydrosilylation reactions constitute a practical protocol in synthetic organic chemistry because both the reduction and the protection steps are performed in a single, atom efficient fashion. Traditionally, catalytic hydrosilylation of the carbonyl functionality has been employed with precious, heavy metals ranging from Re, Rh, Ru, to Ir. Our studies focus on the use of cheap and late transition metals such as Ni and Co for hydrosilylation catalysis. We also are studying carboamination reactions promoted by easy-to-make titanium catalysts, and which allow for incorporation of unusual functional group for further transformations such as polymerization. Our studies allow for fundamental understanding of how C=N and C=C bonds are catalytically formed while C=N bonds broken but also provides an energy efficient route to novel and highly conjugated α,β-unsaturated imines. These new organic archetypes offer an excellent opportunity to study their photophysical properties and ability to detect various analytes such as CN^- or metal ions. Our route to these interesting moieties will readily establish their use for polymer formation and ion detection.

Recent Progress

Nickel Hydrosilylation Catalysts: Our group has reported a Ni(II) precursor using amino phosphine chelating ligands, $[(PN)Ni(\mu_2\text{-}Cl)]_2$ (**1**) (Scheme 1) that was capable of

Scheme 1.

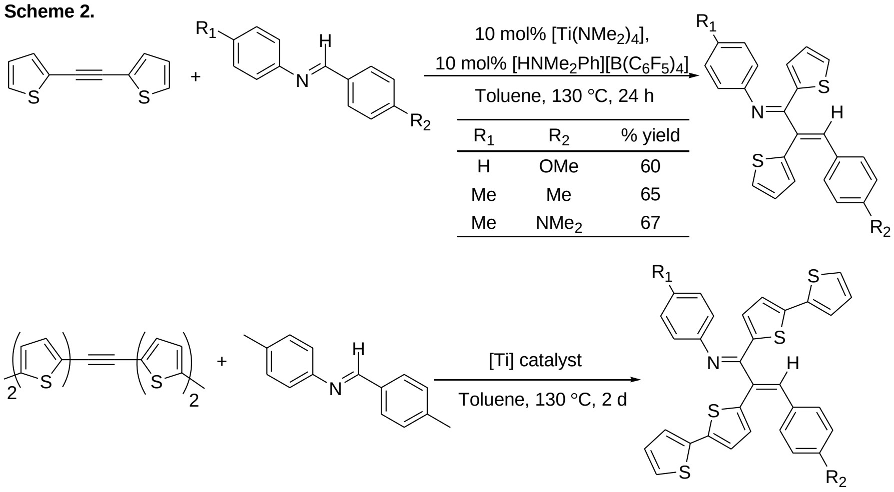


$$\begin{matrix}\text{RCHO}\\ \text{or}\\ \text{RR'C(O)}\end{matrix} + 1.2\ \text{HSiEt}_3 \xrightarrow[\text{benzene}\ \ 100\ ^{o}\text{C}]{\text{2 mol \% of complex } \mathbf{1}\ \ \text{4 mol \% of KO}^t\text{Bu}} \begin{matrix}\text{RCH}_2\text{OSiEt}_3\\ \text{or}\\ \text{RR'CHOSiEt}_3\end{matrix}$$

conducting the hydrosilylation of ketones and aldehydes, utilizing Et_3SiH as the hydride source. In these studies we also detected a transient nickel-hydride as the active species mediating the catalytic hydrosilylation reaction, via a series of independent reactions using various hydride sources. We our now expanding this methodology to Co(II) catalysts as well as exploring Co(II) and Ni(II) boryl complexes as candidates for borylation chemistry.

Carboamination Catalysis: We discovered that protonolysis of the commercially available titanium reagent $Ti(NMe_2)_4$ with $[NHMe_2Ph][B(C_6F_5)_4]$ gives rise to a highly reactive precatalyst, $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$, useful in the carboamination of of aldimines and alkynes. Since our catalyst is an early transition metal it is tolerant to thiophene, dithiophene, and borane substituted alkynes (Scheme 2). Therefore, we can incorporate redox active sites into the α,β-unsaturated framework using a catalytic approach that can be modified readily at the aldimine or alkyne groups.

Scheme 2.



R_1	R_2	% yield
H	OMe	60
Me	Me	65
Me	NMe_2	67

Future Plans

Expand Hydrosilylation Catalysis to Co(II) and Fe(II) Complexes:

We are currently exploring Fe(II) and Co(II) complexes supported with aminophosphine ligands, N-(2-$^iPr_2$-4-methylphenyl)-2,4,6-triisopropylanilide and N-(2-$^iPr_2$-4-methylphenyl)-2,4,6-trimethylanilide as catalysts for hydrosilylation and borylation chemistry. Our goal will be to prepare Co(II) and Fe(II) complexes having a PN and a hydride ligand, and then explore their reactivity towards carbonyl containing groups as well as aromatic and aliphatic C-H bonds. Likewise, we will prepare Co(II) and Fe(II) boryl complexes in low-coordination environments.

Electropolymerization of α,β-Unsaturated Imines:

Having prepared the α,β-unsaturated imines shown in Scheme 2 we will conduct electropolymerization reaction in hopes of preparing polymeric material that can serve as sensor for analytes. Since the the α,β-unsaturated imines are highly modular we will explore imines having donor and acceptor groups since this will promote charge transfer within the organic framework.

Development of more Efficient Carboamination Catalysts:

Although we have reported a facile entry to carboamination catalysts using a combination of commercially available reagents such as $Ti(NMe_2)_4$ and $[HNMe_2Ph][B(C_6F_5)_4]$, we want to further expand this methodology to more efficient titanium(IV) and vanadium(V) catalysts that do not lose their ancillary ligands in the process of metal imide formation.

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Synthetic and Mechanistic Studies of New Metal-Ligand Bifunctional Hydrogenation Catalysts

B. Moasser,* M. Zhu, S.L. Synnott, A.B. Enyong
Georgetown University, Department of Chemistry, Washington, DC, 20057
e-mail: bm276@georgetown.edu

Catalytic hydrogenations involving the concerted transfer of a metal-hydride and a ligand-proton (usually NH) to polar double bonds, such as ketones, have been termed metal-ligand bifunctional. We are interested in exploring the mechanistic scope of the ligand "NH effect" in these reactions, particularly for ketone transfer hydrogenations that are performed in the aqueous medium with sodium formate as the reducing source or in the formic acid/triethylamine azeotropic mixture. We will describe Hammett studies for the transfer hydrogenation of acetophenone in HCO_2H-Et_3N (5:2) using $[RuCl_2(p\text{-cymene})]_2$, a base, and a series of *N*-tosyl-*N*'-*p*-X-C_6H_4-ethylenediamine ligands where the sensitivity of the reaction rate to the substituent at the phenylamino group was consistent with a mechanism involving step-wise catalyst regeneration as the rate determining step. We will also report the activation parameters derived from Eyring analysis, as well as, the preliminary data on catalytic hydrogenations in aqueous/organic biphasic media. We are also interested in developing new synthetic applications of metal-ligand bifunctional catalytic reactions. Thus, we will describe our efforts towards two reactions of considerable practical utility based the type of transfer hydrogenation catalysts discussed here. The first is the selective alkylation of amines with alcohols using recyclable immobilized ruthenium catalysts. The second is the mild catalytic reduction of amides to amines using new hetromultifunctional catalysts that are designed to improve reactivity through multiple noncovalent ligand-substrate interactions.

New Insights into Mechanism of Catalytic Water Oxidation by Mononuclear Ru Polypyridyl Complexes

Dmitry E. Polyansky,[1] Jonathan Rochford,[2] Etsuko Fujita,[1] James T. Muckerman,[1]
Randolph Thummel,[3] and Ruifa Zong[3]

[1] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000

[2] Department of Chemistry, University of Massachusetts, Boston, MA 02125

[3] Department of Chemistry, University of Houston, Houston, TX 77204-5003

e-mail: dep@bnl.gov

We have found that catalytic water oxidation by $[Ru^{II}(L)(4\text{-}pic)_2(H_2O)]^{2+}$ (where L = 4-t-butyl-2,6-di-1',8'-(naphthyrid-2'-yl)-pyridine and pic = picoline) proceeds through the formation of multiple intermediate species in the series of consecutive proton-coupled oxidation events. The first oxidation of the starting complex $[Ru^{II}(L)(4\text{-}pic)_2(H_2O)]^{2+}$ by the ceric ion in acidic solutions (pH < 1) is the rate limiting step and is followed by rapid formation of the two-electron oxidized $[Ru^{IV}(L)(4\text{-}pic)_2(O)]^{2+}$ complex. The estimated rates of the second oxidation are similar in both acidic and basic solutions pointing toward the active role of the free base site of the naphthyridyl ligand. The spectra of the two-electron oxidized species measured in acidic and basic conditions also match very well. However, the exhaustive electrolysis of aqueous solutions of $[Ru^{II}(L)(4\text{-}pic)_2(H_2O)]^{2+}$ at potential only sufficient to produce the $[Ru^{IV}(L)(4\text{-}pic)_2(O)]^{2+}$ complex yields species with the mass matching the structure $[Ru(L)(4\text{-}pic)_2(OO)]^{2+}$ and coulomb counts corresponding to net *four-electron oxidation*. The electrolysis in isotopically labeled water confirmed incorporation of two oxygen atoms into the final product yielding $[Ru(L)(4\text{-}pic)_2(^{18}O^{18}O)]^{2+}$. The observed complex was proposed to be a key intermediate in the mechanism of water oxidation and its exact structure is currently being probed by resonance Raman spectroscopy and high level DFT calculations.

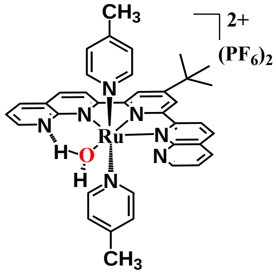


Fig. 1. The structure of $[Ru(L)(4\text{-}pic)_2(H_2O)]^{2+}$ (L = 4-t-butyl-2,6-di-1',8'-(naphthyrid-2'-yl)-pyridine)

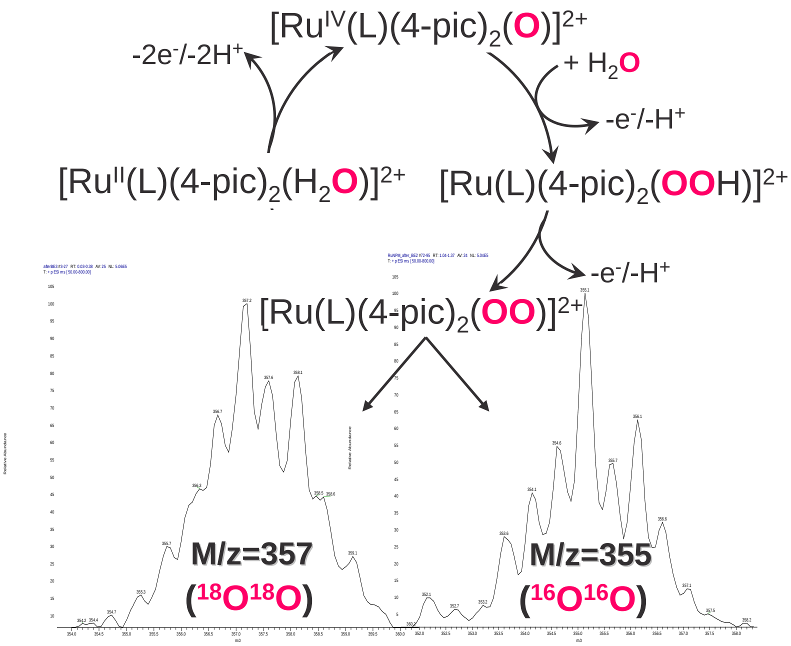


Fig. 2. The observed and proposed intermediates formed during electrochemical oxidation of $[Ru(L)(4\text{-}pic)_2(H_2O)]^{2+}$ at 1050mV (vs. Ag/AgCl) in water.

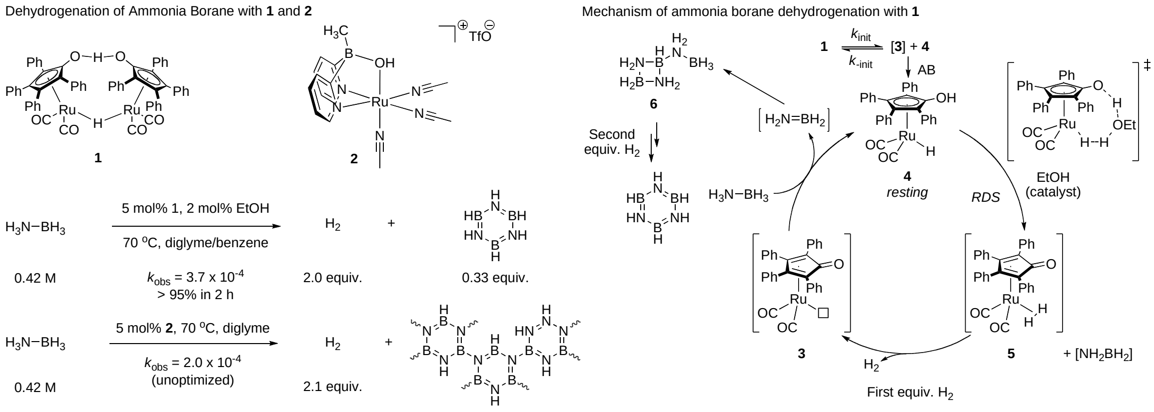
Bifunctional Catalysts for Dehydrogenation of Ammonia Borane

Travis J. Williams* and Brian L. Conley
University of Southern California, Loker Hydrocarbon Research Institute and
Department of Chemistry. Los Angeles, CA 90089-1661
travisw@usc.edu

Abstract

Shvo's cyclopentadienone-ligated ruthenium complex (**1**)[i] and borate-ligated complex[ii] **2** are efficient catalysts for dehydrogenation of ammonia borane (Scheme, left). We have developed a mechanistic model for the early stages of the former reaction (Scheme, right)[iii] and we are currently working to optimize both. Simultaneously with these studies, we are developing conditions for the direct regeneration of the spent ammonia borane by-products of these dehydrogenation reactions with formic acid. This poster will present our mechanistic work, catalyst development studies, and progress toward the regeneration of ammonia borane.

Scheme



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Participant List

Name	Affiliation	Email
Mahdi Abu-Omar	Purdue University	mabuomar@purdue.edu
Aaron Appel	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Vincent Artero	Commissariat à l'Energie Atomique (CEA-Grenoble)	vincent.artero@cea.fr
Stanley Autrey	Pacific Northwest National Laboratory	tom.autrey@pnl.gov
Andreja Bakac	The Ames Laboratory	bakac@ameslab.gov
Bart Bartlett	University of Michigan	bartmb@umich.edu
Louise Berben	University of California Davis	laberben@ucdavis.edu
John Bercaw	California Institute of Technology	bercaw@caltech.edu
John Berry	University of Wisconsin - Madison	berry@chem.wisc.edu
Guy Bertrand	UC Riverside	guy.bertrand@ucr.edu
Theodore Betley	Harvard University	betley@chemistry.harvard.edu
Andrew Bocarsly	Princeton University	bocarsly@princeton.edu
Jeff Brinker	Sandia National Laboratories	cjbrink@sandia.gov
Phillip Britt	Oak Ridge National Laboratory	brittpf@ornl.gov
A. C. Buchanan, III	Oak Ridge National Laboratory	buchananac@ornl.gov
Morris Bullock	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Emilio Bunel	Argonne National Laboratory	ebunel@anl.gov
Don Camaioni	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Siu-Wai Chan	Columbia University	sc174@columbia.edu
Christopher Chang	UC Berkeley/LBNL	chrischang@berkeley.edu
Paul Chirik	Cornell University	pc92@cornell.edu
Suzanne Doucette	Purdue University	sbart@purdue.edu
Daniel DuBois	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Michel Dupuis	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
William Evans	University of California	wevans@uci.edu
Eric Ferreira	Colorado State University	emferr@mail.colostate.edu
Richard Finke	Colorado State University	rfinke@lamar.colostate.edu
Michel Gagne	UNC Chapel Hill	mgagne@unc.edu
Bruce Garrett	Pacific Northwest National Laboratory	bruce.garrett@pnl.gov
David Goldberg	Johns Hopkins University	dpg@jhu.edu
Karen Goldberg	University of Washington	goldberg@chem.washington.edu
Thomas Gunnoe	University of Virginia	tbg7h@virginia.edu
Allexander Harris	Brookhaven National Laboratory	alexh@bnl.gov
John Hartwig	University of Illinois at Urbana-Champaign	jhartwig@scs.uiuc.edu
Nilay Hazari	Yale University	nilay.hazari@yale.edu
Craig Hill	Emory University	chill@emory.edu
Patrick Holland	University of Rochester	Holland#chem.rochester.edu
Jan Hrbek	DOE BES	jan.hrbek@science.doe.gov
Simon Humphrey	University of Texas	smh@cm.utexas.edu
Nancy Jackson	Sandia National Laboratories	nbjacks@sandia.gov
Philip Jessop	Queen's University	jessop@chem.queensu.ca
Marc Johnson	Argonne National Laboratory	mjjohnson@anl.gov
William Jones	University of Rochester	jones@chem.rochester.edu

Name	Affiliation	Email
Christopher Jones	Georgia Institute of Technology	cjones@chbe.gatech.edu
Richard Kemp	University of New Mexico	rakemp@unm.edu
Dorothee Kern	HHMI/Brandeis University	dkern@brandei.edu
Nicolai Lehnert	University of Michigan	lehnertn@umich.edu
Elizabeth Mader	Argonne National Laboratory	mader@anl.gov
Diane Marceau	Department of Energy	diane.marceau@science.doe.gov
Paul Maupin	DOE-BES	paul.maupin@science.doe.gov
John Miller	U. S. Department of Energy	John.miller@science.doe.gov
Daniel Mindiola	Indiana University	mindiola@indiana.edu
Raul Miranda	U.S. Department of Energy - Basic Energy Sciences	raul.miranda@science.doe.gov
Liviu Mirica	Washington University, Dept of Chemistry	mirica@wustl.edu
Bahram Moasser	Georgetown University	bm276@georgetown.edu
Djamaladdin Musaev	Emory University	dmusaev@emory.edu
Jack Norton	Columbia University Department of Chemistry	jrn11@columbia.edu
Justin Notestein	Northwestern University	j-notestein@northwestern.edu
Colin Nuckolls	Columbia University	cn37@columbia.edu
Oleg Ozerov	Texas A&M University	ozerov@chem.tamu.edu
Gerard Parkin	Columbia University	parkin@columbia.edu
Roy Periana	The Scripps Research Institute	rperiana@scripps.edu
Dmitry Polyansky	Brookhaven National Laboratory	dep@bnl.gov
Philip Power	University of California, Davis	pppower@ucdavis.edu
Thomas Rauchfuss	University of Illinois at Urbana-Champaign	rauchfuz@uiuc.edu
Simone Raugei	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Justine Roth	Johns Hopkins University	jproth@jhu.edu
Elena Rybak-Akimova	Tufts University	elena.rybak-akimova@tufts.edu
Aaron Sadow	US DOE Ames Laboratory	sadow@iastate.edu
Gregory Schenter	Pacific Northwest National Laboratory	gregory.schenter@pnl.gov
Ayusman Sen	Pennsylvania State University	asen@psu.edu
Paul Sharp	University of Missouri - Columbia	sharpp@missouri.edu
Wendy Shaw	Pacific Northwest National Lab	wendy.shaw@pnl.gov
Lawrence Sita	University of Maryland	lsita@umd.edu
Jeremy Smith	New Mexico State University	jesmith@nmsu.edu
Jake Soper	Georgia Institute of Technology	jake.soper@chemistry.gatech.edu
Shannon Stahl	University of Wisconsin-Madison	stahl@chem.wisc.edu
Peter Stair	Northwestern University	pstair@northwestern.edu
Licheng Sun	Royal Institute of Technology (KTH)	lichengs@kth.se
Andrzej Sygula	Mississippi State University	asygula@chemistry.msstate.edu
Klaus Theopold	University of Delaware	theopold@udel.edu
Christine Thomas	Brandeis University	thomasc@brandeis.edu
William Tolman	University of Minnesota	wtolman@umn.edu
Dean Toste	University of California	fdtoste@berkeley.edu
Gerard van Koten	Utrecht University, Debye Institute	g.vankoten@uu.nl
Andrei Vedernikov	University of Maryland	avederni@umd.edu

Name	Affiliation	Email
David Vicic	University of Hawaii	vicic@hawaii.edu
Timothy Warren	Georgetown University	thw@georgetown.edu
Bradford Wayland	Temple University	bwayland@temple.edu
Marcus Weck	New York University	marcus.weck@nyu.edu
Travis Williams	University of Southern California	travisw@usc.edu
L. Keith Woo	Ames Laboratory	kwoo@iastate.edu
Jenny Yang	Pacific Northwest National Laboratory	donna.sturdevant@pnl.gov
Yan Zhao	Iowa State University	zhaoy@iastate.edu

Author Index