

Western New York Inorganic Symposium

(WNYIS)

Saturday June 2nd, 2018

Cornell University

120 Physical Sciences Building

Ithaca, NY



WNYIS 2017 - Schedule of Events

Time	Details
9:40 – 10:00 AM	Coffee and Poster Set-Up
10:00 – 10:10 AM	Opening Remarks
10:10 – 11:30 AM	Student Talks Session #1
11:30 – 12:10 PM	Poster Session #1 (Rochester)
12:10 – 1:00 PM	Lunch in PSB Atrium
1:00 – 2:20 PM	Student Talks Session #2
2:20 – 3:00 PM	Poster Session #2 (Cornell and Buffalo)
3:20 – 4:30 PM	Student Talks Session #3
4:30 – 4:40 PM	Closing Remarks Group Photo Poster and Talks Awards

Talk 1 [10:10 – 10:30 AM]

Isolation and characterization of in-situ species formed in iron-catalyzed cross-coupling reactions with aryl nucleophiles

Stephanie H. Carpenter and Michael L. Neidig*

Department of Chemistry, University of Rochester, Rochester NY, USA

Kochi first proposed the use of simple iron salts and Grignard reagents for iron-catalyzed cross-coupling reactions in the early 1970s.¹ Since the 1970s, iron-catalyzed reactions have become increasingly popular as iron catalysts offer a cheaper and safer alternative to the well studied precious metal catalysts. However, there is limited mechanistic understanding of iron-catalyzed cross-coupling reactions. This gap in knowledge has led to many mechanistic proposals, where the oxidation state of the catalytically relevant species is not agreed upon.²⁻⁴ Previous work in the group provides significant evidence for the catalytically relevant iron species, $\text{Fe}_8\text{Me}_{12}^-$, in reactions involving simple iron salts and MeMgBr .⁵ Characterization of the $\text{Fe}_8\text{Me}_{12}^-$ via electron paramagnetic resonance (EPR) and magnetic circular dichroism (MCD) is consistent with the $S = 1/2$ species Kochi originally reported.⁵ These studies help advance the understanding of iron-catalyzed cross-coupling using simple iron salts and MeMgBr , yet there is limited mechanistic understanding when aryl Grignard reagents are used. This presentation will cover current efforts and insight obtained through isolating and characterizing intermediate iron species formed in-situ from simple iron salts and aryl Grignard reagents and evaluating their reactivity towards electrophiles. Characterization techniques include X-ray crystallography, Mössbauer spectroscopy, EPR, MCD, and gas-chromatography (GC) studies.

References

- (1) Tamura, M.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1487.
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- (3) Fürstner, A.; Krause, H.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 440.
- (4) Fürstner, A.; Martin, R.; Krause, H.; Seidel, G.; Goddard, R.; Lehmann, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 8773.
- (5) Muñoz, S. B.; Daifuku, S. L.; Brennessel, W. W.; Neidig, M. L. *J. Am. Chem. Soc.* **2016**, *138*, 7492.

Talk 2 [10:30 –10:50 AM]

Externally Regulated Polymerizations and Their Application in Copolymer Synthesis

Veronika Kottisch, Quentin Michaudel, Brian M. Peterson, Michael J. Supej, and Brett P. Fors

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, USA

The use of external stimuli, such as pH, pressure, and light, as tools in organic synthesis has vastly expanded the scope of materials design in polymer chemistry. Specifically, light serves as an inexpensive, abundant, and adaptable stimulus to induce chain growth. With the advent of photocontrol, chemists are now able to reversibly commence and halt chain growth. Until recently, this level of control had been mainly confined to radical processes. Only over the last few years, photocontrol has been expanded to polymerizations with cationic intermediates. Employing photocatalysts which are highly oxidizing in their excited state allowed us to successfully develop a novel cationic photocontrolled polymerization of vinyl ethers. The method exhibits living characteristics, good chain-end fidelity, and spatial and temporal control over chain growth – all mediated by light. Utilizing a variety of analytical methods, such as UV-Vis spectroscopy, electron-spin resonance, and time-resolved fluorescence spectroscopy, enabled us to elucidate the mechanism of our photocontrolled cationic polymerization. Additionally, we found a strong link between the electrochemical properties of the photocatalysts and the degree of temporal control we can achieve. This allowed us to determine two cationic iridium complexes as superior photocatalysts that facilitate improved temporal control. Furthermore, we investigated other external stimuli to promote cationic polymerization and found electrochemical and chemical control as viable, and importantly, orthogonal alternatives to light. The latter allowed us to switch between photocontrolled radical polymerization and chemically controlled cationic polymerization in one pot to synthesize multiblock copolymers.

Talk 3 [10:50 – 11:10 AM]

Excited-State Charge Transfer in V₂O₅/Quantum Dot Type II Heterostructures

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Efficient charge separation following photoexcitation is the key to harness solar energy efficiently by semiconductor heterostructures. Cadmium chalcogenide quantum dots (QDs) interfaced with V₂O₅ nanowires provide a promising system for solar energy conversion or photocatalysis. The type II interface between QDs and V₂O₅ promotes spatial separation of charge carriers in different components of the heterostructure (electrons in V₂O₅ and holes in QDs). We prepared V₂O₅/CdSe heterostructures via linker-assisted assembly (LAA) and successive ionic layer adsorption and reaction (SILAR) and studied charge-transfer dynamics in these heterostructures. Attachment of CdSe QDs onto V₂O₅ NWs was confirmed by transmission electron microscopy (TEM) and Raman spectroscopy. Charge-transfer dynamics in CdSe/V₂O₅ heterostructures was studied by transient absorption spectroscopy. The transient absorbance (TA) spectrum of QD/V₂O₅ heterostructures revealed a new induced absorption band when CdSe QDs were present on the nanowire as opposed to V₂O₅ NW alone. This new induced absorption band was attributed to the charge-separated state in which electrons were localized in the CB of V₂O₅ NWs and holes in the VB of CdSe QDs. Ultrafast TA measurements revealed that the charge separation occurred within picoseconds for SILAR- and LAA-derived heterostructures. The charge-separated state decayed on microsecond timescales with lifetimes of 1.4 μ s and 3.4 μ s for SILAR- and LAA-derived heterostructures, respectively. Thus, SILAR assembled heterostructure showed faster charge separation compared to LAA assembled heterostructure, as well as faster charge recombination, which is consistent with intimate contact between QDs and V₂O₅ NWs in SILAR prepared heterostructures as compared to LAA prepared structures. Both types of QD/NW heterostructures underwent excited-state interfacial charge transfer and are therefore promising for applications in light-harvesting and solar energy conversion.

Talk 4 [11:10 – 11:30 AM]

Hydrogen Evolution from Water Catalyzed by Cobalt-Mimochrome VI*a, a Synthetic Mini-Protein

Jennifer M. Le, Vincenzo Firpo, Vincenzo Pavone, Angela Lombardi, and Kara L. Bren

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Cobalt mimochrome VI*a (CoMC6*a) is a synthetic enzyme that electrocatalytically reduces protons to hydrogen (H₂) in water at neutral pH under aerobic conditions. CoMC6*a is a mini-protein with a cobalt deuteroporphyrin within a scaffold of two synthetic peptides covalently bound to the porphyrin. Comparison of the activity of CoMC6*a to that of cobalt microperoxidase-11 (CoMP11-Ac), a cobalt porphyrin catalyst with a single “proximal” peptide and no organized secondary structure, reveals that CoMC6*a has significantly enhanced stability, yielding TONs exceeding 230,000, in comparison to 25,000 for CoMP11-Ac. Furthermore, comparison of cyclic voltammograms of CoMC6*a and CoMP11-Ac indicates that the trifluoroethanol-induced folding of CoMC6*a lowers the overpotential for H₂ evolution by up to 100 mV. These results demonstrate that even a minimal polypeptide scaffold can enhance stability and efficiency of a H₂-evolution catalyst.

1) Polyoxovanadate-Alkoxide Clusters as Precursors to Colloidal VO_x Nanocrystals

Jordan W. Andrews and Kathryn E. Knowles

Department of Chemistry, University of Rochester

This poster describes the preliminary studies of the use of polyoxovanadate-alkoxide ($[V_6O_7(OCH_3)_{12}]^n$) clusters as precursors to VO_x nanocrystals. Several studies have shown that the oxidation state of the vanadium centers within the clusters are easily manipulated through chemical oxidants/reductants, which may be used to control the valency of the nanocrystal product. VO_x nanocrystals are known to exist in several valencies, thus the use of clusters may provide a robust and selective method for the synthesis of stoichiometrically well-defined VO_x products.

2) Identification of key intermediates in iron-catalyzed C-H functionalization

Tessa M. Baker, Theresa E. Iannuzzi, Stephanie H. Carpenter and Michael L. Neidig

Department of Chemistry, University of Rochester

Significant research has been focused towards the development of non-precious base metal catalysts which directly activate and functionalize C-H bonds in order to circumvent multi-step synthetic methods. Iron catalysts are particularly attractive due to their low cost, high availability, limited toxicity, and rich oxidation chemistry. Recently, iron-based catalytic systems have successfully directed C-H transformations via cross-coupling C-H bonds with organometallic reagents under oxidative conditions. Synthetic and spectroscopic techniques were utilized to elucidate the nature of *in-situ* iron speciation, with specific focus on identifying the structures of key intermediates, operative in Nakamura et al. iron-catalyzed C(sp²-H) activation, as well as, Ackermann and co-workers' iron-catalyzed arylation of aryl C(sp²-H) bonds by triazole assistance. Identification of such intermediates will provide molecular level insight into the nature of the active iron catalytic species, including detailed electronic structure-activity relationships, and the mechanism of the underlying iron C-H functionalization catalytic cycle.

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3) Solvothermal Synthesis of Hematite Nanocrystals as Electrochemical Models for Elucidation of Band-Bending

David Brewster and Kathryn E. Knowles*

Department of Chemistry, University of Rochester

Metal oxide semiconductors are promising photoelectrodes for photoelectrochemical transformations, such as water oxidation and carbon dioxide reduction. Although the theoretical capacity for a semiconductor photoelectrode to catalyze a redox transformation increases with its surface area, such geometry changes can also affect the thermodynamics and kinetics of photocarrier extraction at the interface between a semiconductor and a liquid electrolyte. Colloidal metal oxide nanocrystals can serve as useful model systems to investigate the photoelectrochemical behavior of nanostructured semiconductors as a function of their surface area to volume ratio. These investigations require a combination of synthetic techniques to control nanocrystal size and electrochemical analysis to reveal interfacial electronic dynamics as a function of the size and morphology of nanocrystals. This presentation describes a ligand-based strategy for controlling the size of isotropic pseudocubic hematite nanocrystals from synthesized using a solvothermal method. The formation of smaller nanocrystals from reactions containing longer-chain aliphatic iron-carboxylate precursors is attributed to the lower solubility of these precursors in the polar solvents leading to faster nanocrystal nucleation. Ongoing measurements of photocurrent generated by dispersions of hematite nanocrystals with diameters ranging from 20-1000 nm in solutions containing a sacrificial hole quencher and a redox electrolyte will explore the possible evolution of band-bending behavior with decrease surface area to volume ratio.

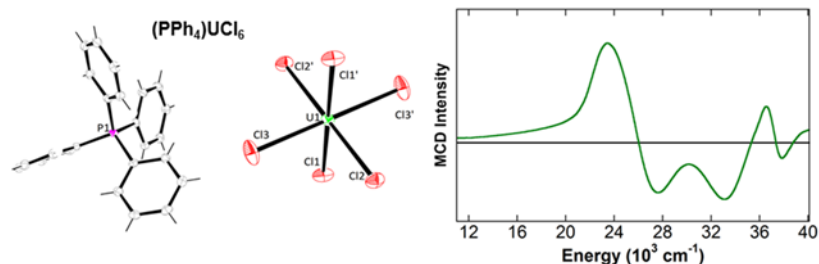
4) Spectroscopic and computational tools for the study of novel f-element complexes

Valerie E. Fleischauer and Michael L. Neidig

Department of Chemistry, University of Rochester

The chemistry of f-elements plays a critical role in the environmental, chemical separation, and energy fields. Despite the importance of these applications, the fundamental electronic structure and bonding of relevant f-element complexes remains poorly defined, especially when compared to d-block chemistry. To remedy this lack of understanding, electronic structure studies along with

investigation of well-defined and in situ generated species are required. Magnetic circular dichroism (MCD) is a particularly useful technique for the study of well-defined complexes and can be used to determine electronic structure characteristics including ground and excited states, polarization of transitions, and the effects of spin orbit coupling. Combined with theoretical studies this work provides a detailed electronic structure evaluation of the octahedral UCl_6^- ion in the UV-Vis spectral region as a baseline for the study of more complex f-block molecules.



5) Heterometal Installation into Polyoxovanadate-Alkoxide Clusters

Rachel Meyer and Ellen Matson*

Department of Chemistry, University of Rochester, Rochester, NY

Polyoxovanadate (POV) clusters are a class of polyoxometalates that exhibit fascinating magnetic, optical, and electrochemical properties. Multiple methods can be employed to tune the properties of these clusters. In particular, installation of heterometals into the POV framework is of interest as it can both tune the redox properties as well as provide a binding site for substrates to allow for cooperative bifunctional reactivity between the heterometal and the POV scaffold. However, the synthesis of heterometal-functionalized POV clusters is challenging as the structural flexibility of vanadium favors the formation of homometallic, cage-like structures.

With the goal of developing a general understanding of heterometal into POV clusters, a series of Lindqvist POV-alkoxide clusters, $(\text{VO})_5\text{O}(\text{OCH}_3)_{12}\text{MCl}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Ga}$), were synthesized. Trivalent salts of iron and gallium, which have similar ionic radii, can be used as precursors for these clusters, while a divalent chromium salt is needed to obtain the chromium-POV cluster. Attempts at installing divalent manganese using similar methods as the chromium installation results in the formation of cyclic $[(\text{VO})(\text{OCH}_3)_2]_6\text{Cl}$ cluster, where the chloride acts as a template for the POV ring. These results indicate that other physical properties besides the size of the heterometal ion are affecting the installation of these ions. Furthermore, preliminary studies using

$\text{VO}(\text{OC}_2\text{H}_5)_3$ in place of $\text{VO}(\text{OCH}_3)_3$ as a precursor allows for the formation of $(\text{VO})_4\text{O}(\text{OC}_2\text{H}_5)_{12}(\text{MnCl})_2$, suggesting that the type alkoxide ligands along with the heterometal precursor may influence the kinds of clusters that form.

6) Polyoxovanadate-Alkoxide Clusters as Molecular Models for the Investigation of Oxygen Vacancy Formation in Reducible Metal Oxides

Brittney Petel and Ellen Matson*

Department of Chemistry, University of Rochester, Rochester, NY

Reducible metal oxides (RMO) are widely used compounds in heterogeneous catalysis as active supports for novel transformations. Theoretical investigations have modeled the role of RMOs and found they traditionally follow a mechanism in which the generation of an oxygen-atom vacancy is crucial for the high reactivity of the bulk material. However, limited spectroscopic techniques for *in situ* analysis of RMOs has restricted experimental investigations on the formation and reactivity of these surface defects. This research investigates the use of Lindqvist polyoxovanadate-alkoxide (POV-alkoxide) clusters ($[\text{V}_6\text{O}_7(\text{OCH}_3)_{12}]^{-1}$) as homogenous models for metal oxides in heterogeneous catalysis. POV-alkoxide clusters are uniquely qualified to serve as molecular models for RMOs due to their comparable structures and fascinating physical and electronic properties. Herein, we present the generation of an oxygen-atom vacancy on the POV-alkoxide cluster *via* addition of a reductant. Generation of the reduced POV-alkoxide cluster ($[\text{V}_6\text{O}_6(\text{OCH}_3)_{12}]^{-1}$) has presented us with the opportunity to study the effects of vacancy formation on the electron delocalization of the cluster as well as reactivity with oxyanions and small gaseous molecules.

7) Elucidating the Role of TMEDA in Iron Catalyzed Cross-Coupling Reactions

Jeffrey D. Sears and Michael L. Neidig*

Department of Chemistry, University of Rochester, Rochester, NY

Many iron catalyzed cross-coupling methods exhibit significantly enhanced reactivity and selectivity from the use of nitrogen-based additives and supporting ligands. Tetramethylethylenediamine (TMEDA) has been reported to improve selectivity in several carbon-carbon cross-coupling reactions utilizing Grignard reagents as nucleophiles. Mechanistic investigations aimed at elucidating the role of TMEDA in iron catalyzed cross-coupling reactions have

been limited. Bedford and coworkers concluded that while TMEDA-ligated transmetallated iron species (e.g. (TMEDA)FeMes₂) selectively generate cross-coupled product from MesMgBr and *n*-octylbromide, they were not as reactive as homoleptic iron complexes (e.g. tris-mesityliron(II) ferrate, [FeMes₃]). Therefore, the reason for the suppression of undesirable reactivity, such as β-hydrogen elimination, by TMEDA remains elusive. To investigate the role of ligand additives such as TMEDA further, a synthetic physical-inorganic approach is highly desirable. Using ⁵⁷Fe Mössbauer spectroscopy and gas chromatographic monitoring of organic products during catalytic cross-coupling of phenyl Grignard reagents and alkyl electrophiles, insight into the precise role of TMEDA in iron speciation and cross-coupled product distributions has been obtained. Additionally, several TMEDA-ligated species have been identified by single crystal X-ray diffraction and their individual reactivities investigated. The results of this study contradict previously reported mechanistic proposals and provide significant insight to aid in the design and development of future iron catalyzed cross-coupling methodologies utilizing TMEDA and similar additives.

8) Electrocatalytic Reduction of Nitrite by a Cobalt Metallopeptide

*Jesse R. Stroka, Yixing Guo, Kara L. Bren**

Department of Chemistry, University of Rochester, Rochester, NY

A cobalt metallopeptide (CoGGH) inspired by the amino terminal copper- and nickel-binding (ATCUN) motif has been found to catalyze the six-electron reduction of nitrite to ammonia in water. The electrocatalytic reaction has a Faradaic efficiency greater than 90%, indicating high selectivity for the ammonium product. The catalytic peak potential for this process in 50 mM MOPS buffer in water at pH 7.2 was found to be -0.98 V vs. Ag/AgCl (1 M KCl). CoGGH has also been shown to be active towards hydroxylamine and nitric oxide reduction to ammonia, both of which are proposed intermediates. The half-catalytic peak potential for nitrite reduction was found to shift towards more negative potentials with increasing pH, whereas the half-catalytic peak potential for hydroxylamine reduction becomes less negative with increasing pH. This behavior suggests the presence of at least one proton-coupled electron transfer, and a complex relationship of catalytic behavior with pH. Ongoing research also involves evaluation of other biorelevant catalysts for similar catalytic activity.

9) Redox Chemistry of Cuprous Oxide Nanocrystals

*Mehrin Tariq, Jordan W. Andrews and Kathryn E. Knowles**

Department of Chemistry, University of Rochester, Rochester, NY

Cuprous oxide (Cu_2O) is a *p*-type semiconductor, with a bandgap of ~ 2.2 eV, that has many potential applications, including as an electrode material in lithium ion batteries, as a catalyst for the water–gas shift reaction to produce hydrogen and for the conversion of carbon monoxide to methanol, and as a photocathode for the photoelectrochemical reduction of protons to form hydrogen under visible irradiation. Although, the electronic structure and optical properties of these nanocrystals are chemically tunable, due to the multiple accessible oxidation states of copper as well as nanoscale size and shape effects, these properties are not yet well understood. Complete synthetic control of nanocrystal size, shape, and crystal structure as well as a thorough understanding of their redox behavior is required for the optimization of their performance as catalysts and photocatalysts. This poster presents preliminary investigations into the synthesis and characterization of colloidal cuprous oxide (Cu_2O) nanocrystals and aims to understand the redox behavior of these nanocrystals under both ambient and inert conditions using spectroscopic techniques such as UV-vis spectroscopy, X-ray photoelectron spectroscopy, spectroelectrochemistry and cyclic voltammetry.

10) Myoglobin Catalyzed C-H Functionalization of Unprotected Indoles

David A. Vargas, Antonio Tinoco, Vikas Tyagi, and Rudi Fasan*
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Functionalized indoles are recurrent motifs in several biologically active alkaloids and pharmaceuticals. While transition metal catalyzed carbene insertion have provided an attractive route to afford C3-functionalized indoles, these protocols are viable only in the presence of N-protected indoles, due to competition from the more facile indole N-H insertion reaction. Here, a biocatalytic strategy for enabling the direct C-H functionalization of unprotected indoles is reported. Engineered variants of myoglobin provide efficient biocatalysts for this reaction, which has no precedents in the biological world, enabling the transformation of a broad range of indoles in the presence of α -diazoacetate to give the corresponding C3-chemoselectivity. This strategy could be exploited to develop a concise chemoenzymatic route to afford the nonsteroidal anti-inflammatory drug indomethacin.

11) Synthesis of Unstable Homoleptic Uranium Complexes

Nikki J. Wolford, Jeffrey D. Sears and Michael L. Neidig*

Department of Chemistry, University of Rochester, Rochester, NY

Homoleptic organouranium complexes have been of interest to the chemical community since the early 1940s. Specifically, uranium alkyl complexes were of interest prior to the Manhattan project for their potential use as volatile compounds for isotope separation in uranium enrichment processes. This focus has since shifted to obtaining a fundamental understanding of the electronic structure and bonding of uranium. Previous attempts towards synthesizing these types of alkyl complexes in the absence of stabilizing ligands (such as TMEDA) have been unsuccessful due to the instability of the resulting products. Use of benzyl potassium has shown success in the synthesis of the four-coordinate uranium species, $U(CH_2C_6H_5)_4$, which contain η -type coordination to the aryl rings for stabilization. Previous work in the Neidig group has utilized low temperature synthesis and crystallization techniques to elucidate the speciation of iron-catalyzed reactions. Using these same techniques, we have been able to access several unsupported homoleptic alkyl and aryl uranium species using lithium nucleophiles. These unusual complexes can be used to obtain a better understanding of the electronic structure and bonding of uranium.

Talk 1 [1:00 – 1:20 PM]

Development of Macrocyclic Fe(III) T₁ MRI Contrast Agents

Didar Asik, Eric Snyder, Samira M. Abozeid, Janet R. Morrow*
Department of Chemistry, University at Buffalo, Buffalo NY

Magnetic resonance imaging (MRI) is an immensely important, non-invasive and high resolution biomedical imaging technique. There are significant concerns about the potential toxicity of highly successful clinically approved Gd(III) based MRI contrast agents, particularly in long-term exposure and the indications related to Nephrogenic Systemic Fibrosis (NSF). High spin complexes of Mn(II) and Fe(III) are considered as potential alternatives to Gd(III) contrast agents because their relatively long electronic relaxation times lead to enhanced T₁ relaxation enhancement. Our aim is to design new triazacyclononane based macrocyclic Fe(III) T₁ MRI contrast agents. Our lead complexes have alkoxide donors that stabilize the Fe(III) complexes. A third group contains with a coordinating or a non-coordinating group. For example, a benzyl or a benzoate pendant group was used for increasing binding to serum albumin and thus the rotational correlation time of the complexes. Alternatively, Fe(III) complexes with coordinating amide groups were prepared. The inner and second sphere water interactions were studied and water exchange rates were calculated by using variable temperature ¹⁷O NMR spectroscopy. In vitro and in vivo imaging experiments were performed on a 4.7 T MRI scanner. Our results show human serum albumin (HSA) binding to certain complexes enhances T₁ relaxivity. Lead complexes show strong enhancement and good in vivo clearance from mice. The complexes in this study are the first macrocyclic Fe(III) based agents that produce T₁ relaxivity values that are similar to those of Gd(III) agents at 4.7 T field strength. Preliminary results are promising and encouraging in the development of safe, cost effective alternatives to clinically used Gd(III) T₁ contrast agents.

Talk 2 [1:20 – 1:40 PM]

Expanded Macrocycles for the Selective Chelation of Large Metal Ions

Nikki A. Thiele, Justin J. Wilson*

Department of Chemistry and Chemical Biology, Cornell University

The development of chelating scaffolds that can selectively bind large alkaline earth, lanthanide, and actinide metal ions can be leveraged for several important applications including targeted cancer therapy ($^{223}\text{Ra}^{2+}$, $^{135}\text{La}^{3+}$, $^{225}\text{Ac}^{3+}$), radionuclide decorporation and remediation ($^{90}\text{Sr}^{2+}$, $^{226}\text{Ra}^{2+}$), and barite scale removal in petroleum processing (Ba^{2+}). The stable chelation of these large ions, however, is challenging due to the predominance of electrostatic character in their binding interactions with ligands, which become weaker with increasing ionic radius of the metal ion. Ligand design efforts in our lab for the chelation of large metal ions have been focused on the development of a series of diaza-18-crown-6 macrocycles bearing different pendent donor arms. This presentation will provide an overview of the synthesis of these ligands, their thermodynamic affinities for the alkaline earth and lanthanide ions, the kinetic inertness of the resulting metal-ligand complexes, and their radiolabeling properties with therapeutically-useful nuclides.

Talk 3 [1:40 –2:00 PM]

Mechanism-guided design of efficient P450 catalysts for C-H amination via nitrene transfer

Viktoria Steck, Rudi Fasan*

Department of Chemistry, University of Rochester, Rochester, NY

Cytochrome P450s were recently identified as viable systems for catalyzing C-H amination reactions via nitrene transfer, a synthetically valuable transformation for forging new C-N bonds that is not found in nature. Despite this progress, the catalytic efficiency of P450s in these non-native reactions is limited and significantly inferior to that exhibited in their native monooxygenase function. Guided by mechanistic hypotheses concerning non-productive pathways operating during P450-catalyzed C-H amination, rationally designed mutations were introduced to targeting the native proton shuttle pathway and thus disfavoured byproduct formation during the C-H amination reaction. This strategy led to the development of engineered P450 variants with dramatically enhanced C-H amination activity (>5,000 turnovers) as well as improved chemoselectivity, corresponding to the most efficient C-H amination biocatalyst reported to date. Kinetic isotope effect experiments revealed that the mechanism proceeds with C-H bond activation as the rate limiting step and provided insights into the competition between productive versus non-productive nitrene transfer pathways. The substrate scope of these improved C-H amination biocatalysts could be extended to azide-based substrates not efficiently processed by the parent enzyme. These studies demonstrate the value of mechanism-guided rational design for the development of efficient P450 catalysts for non-native group transfer reactions.

Talk 4 [2:00 – 2:20 PM]

Impact of Inner- and Second-Sphere Structure on the Reactivity of Heme P460 Cofactors

Meghan A. Smith, Kyle M. Lancaster*

Department of Chemistry and Chemical Biology, Cornell University

Ammonia-oxidizing bacteria (AOB) and archaea (AOA) derive total energy for life from the multi-electron, proton-coupled oxidation of ammonia (NH_3) to nitrite (NO_2^-). The relevant pathway—nitrification—constitutes a major sink of NH_3 applied to soil to improve crop yields. Additional consequences of unchecked nitrification include production of harmful wastewater and gaseous pollutants. Enzymes known to participate in biological nitrification include the copper-containing membrane monooxygenase ammonia monooxygenase (AMO) and the multi-heme containing hydroxylamine oxidoreductase (HAO). Mechanistic study of the enzymes driving this chemistry would inform more efficient and sustainable agricultural practices. Our lab has studied cytochrome (cyt) P460, which contains the same unique active site as HAO, but without the additional electron transfer hemes that can interfere with spectroscopic analysis. Recently, we have shown a direct link between cyt P460 and the agriculture-based production of the potent greenhouse gas nitrous oxide (N_2O) through the oxidation of hydroxylamine (NH_2OH). We are now interested in exploring the specific characteristics that allow for this activity. The cyt P460 cofactor is a unique c-type heme, which in addition to the two thioether linkages common to all c-type hemes contains a third covalent cross-link between a heme meso carbon and lysine side chain nitrogen. The exact role of the cross-link is unknown, but is believed to potentially play a part in defining heme distortions (i.e. ruffling), rigidity, and electronic structure. We have also identified a specific residue near the heme cofactor that is essential for NH_2OH -oxidation catalyzed by cyt P460.

12) Utilizing Orthogonal Stimuli To Switch Between Radical and Cationic Polymerization Mechanisms in Situ

Brian Peterson, Michael J. Supej, Veronika Kottisch, Brett Fors*

Department of Chemistry and Chemical Biology, Cornell University

Controlled “living” polymerizations allow for the synthesis of polymers with narrow molecular weight distributions of predictable size. Development of polymerizations in which initiation, propagation, and termination are controlled via external stimuli, such as light, electrical potential, or ultrasound, provide handles for non-invasive control over these polymerizations. Moreover, by pairing two mechanistically distinct polymerizations, controlled by orthogonal stimuli, selective regulation of monomer incorporation can be achieved. Thus a stimuli-gated switch could allow for the synthesis of more advanced polymer architectures. By utilizing small molecule electrochemical mediators, we have developed cationic polymerizations of vinyl ether and styryl monomers controlled via electrical potential. The polymerizations can be initiated and reversibly terminated by application of an oxidizing and reducing potential, respectively. Pairing this new method with a photochemically controlled radical polymerization of methyl acrylate, we demonstrate a photochemically-electrochemically gated polymerization of multi-block copolymers in one pot.

13) Combinatorial synthesis and anticancer activity of rhenium tricarbonyl complexes

Charlene Konkankit, Justin J. Wilson

Department of Chemistry and Chemical Biology, Cornell University

Novel rhenium tricarbonyl complexes were synthesized using a combinatorial approach and screened for anticancer activity in ovarian cancer cells using a high-throughput method. These complexes maintained high cytotoxicity between wild-type and cisplatin-resistant cell lines, and the lead compound was further explored for its mechanism of action. Mechanisms explored include reactive oxygen species generation, mitochondrial membrane depolarization, apoptosis, cell cycle dependence, necrosis by membrane disintegration, and glutathione independence involved in cisplatin resistance. Confocal Raman

microscopy and X-ray fluorescence spectroscopy are currently being used to determine compound accumulation in the cell. Results indicate that the lead compound acts via a necrotic pathway and circumvents cisplatin resistance.

14) Establishing a Structure-Activity Relationship for Bioactive Co(III) Schiff Base Complexes

A. Paden King and Justin J. Wilson*

Department of Chemistry and Chemical Biology, Cornell University

Cobalt complexes containing Schiff base ligands are promising antiviral and anticancer agents that operate via enzyme inhibition. To date, however, few studies have investigated the role of the Schiff base ligand on mediating the biological activity of this class of complexes. The goal of this project is to probe how the Schiff base ligand affects the physical properties, namely the ligand substitution kinetics and electrochemistry, and biological activities of complexes of the type $[\text{Co}(\text{Schiff base})(\text{L})_2]^+$. We have synthesized complexes bearing three different Schiff base equatorial ligands with the axial ligands comprising either ammonia or benzylamine. We show that by varying both the Schiff base and axial ligands, it is possible to tune the reactivity of the complexes toward reduction and ligand exchange, thus modifying their efficacy for enzyme inhibition and anticancer activity. This study provides a basis for future design of improved Co(III)-Schiff base complexes as enzyme inhibitors or cytotoxic agents.

15) Investigating the Mechanism of Cytochrome P460 From the Methanotroph *Methylococcus capsulatus* (Bath)

Sean H. Majer and Kyle M. Lancaster*

Department of Chemistry and Chemical Biology, Cornell University

Methanotrophs, bacteria which oxidize methane (CH_4) as their sole source of carbon and energy, share two hydroxylamine (NH_2OH) oxidizing enzymes with nitrifiers: hydroxylamine oxidoreductase (HAO) and cytochrome (cyt) P460. Methanotrophs lack the necessary electron carriers to extract electrons from NH_2OH oxidation for respiration. However, their ability to oxidize NH_2OH is physiologically reasonable: particulate methane monooxygenase (pMMO),

which oxidizes CH_4 to CH_3OH , also oxidizes isoelectronic ammonia (NH_3) to NH_2OH . Enzymatic machinery to eliminate this cytotoxic NH_2OH burden is essential when under high NH_3 -tensions.

While the methanotrophic HAO has not been purified or studied extensively, cyt P460 from *Methylococcus capsulatus* (Bath) has been purified from the native organism

and reported to oxidize NH_2OH to nitrite (NO_2^-) at a much faster turnover rates than the nitrifier homologii.² With respect to their amino acid sequences, cyt P460 from *M. capsulatus* bears little identity to the nitrifier homolog (~24%). All things being equal, these findings suggest that the discrepancy in reactivity may be linked to the structure of the enzyme.

Based on our lab's studies of NH_2OH oxidation by the nitrifier *N. europaea*³, we sought to investigate the methanotrophic cyt P460. Under anaerobic turnover conditions, the nitrifier cyt P460 yields an observable $\{\text{FeNO}\}^5$ by rapid NH_2OH -oxidation. This $\{\text{FeNO}\}^5$ intermediate reacts with another equivalent of NH_2OH to form N_2O . While we are able to generate the nitrifier intermediates through shunting experiments, anaerobic steady-state kinetics of the *M. capsulatus* cyt P460 suggest NH_2OH oxidation is the rate determining step, contrary to *N. europaea*. While these homologs show a characteristic Soret maximum at 460 nm in their ferrous states, they appear to be spectroscopically distinct from each other. Namely, the methanotrophic aquo-enzyme shows a 20 nm blue shift of the Soret maximum relative to the nitrifier as well as a more axial EPR signal. Differences in the local structure at the heme P460 cofactor may manifest themselves as these pronounced spectroscopic differences and by extension tune the different NH_2OH -oxidase activity.

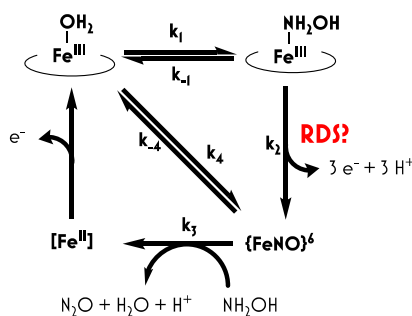
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16) Understanding the Effects of Organelle-Specific Singlet Oxygen and Radiation Damage Using Rhenium and Technetium Complexes

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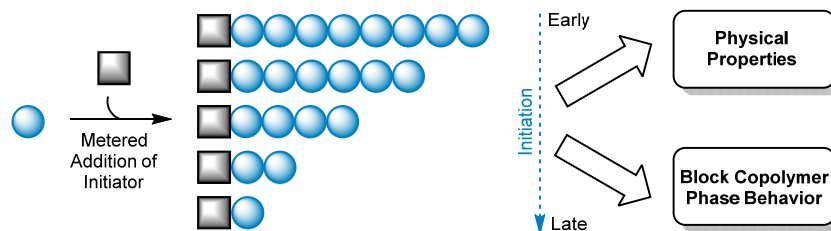
Photodynamic and radiotherapy are among the most frequently used approaches for the treatment of cancer. For example, approximately 50% of all cancer patients receive some form of either internal or external radiotherapy. However, the precise intracellular targets of these treatment approaches that contribute to their success are poorly understood. The goal of the research described in this presentation is to probe the biological effects resulting from specific organelle damage induced by singlet oxygen or Auger electrons. This knowledge will enable the design of improved photodynamic and radiotherapeutic agents for the treatment of cancer. To this end, we have synthesized tridentate ligands designed to carry either photodynamic therapeutic rhenium or Auger electron-emitting technetium complexes to specific organelles. The rhenium complexes have distinct phototoxicity depending on the nature of the targeted organelle, suggesting that subcellular targeting may be an important aspect for the future development of photodynamic and radiotherapeutic agents.

17) Molecular Weight Distribution Shape as a Handle to Tune Polymer Properties

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Molecular weight distributions (MWDs) heavily influence polymer properties from bulk macroscale features such as viscoelasticity to the morphological phase behavior of their self-assembled nanostructures. Gaining synthetic control of the shape of these MWDs offers a modular strategy for tuning the properties of polymeric materials, but this area has been underexplored due to the lack of robust methods that provide absolute control over the entire MWD. To address this challenge, we have developed a versatile strategy enabling deterministic control of MWD shape through temporal regulation of polymer chain initiation. Remarkably, we find that MWD skew has a profound impact on a diverse repertoire of physical properties from processability and Young's Modulus to morphological characteristics such as domain spacing and morphology. We anticipate that these findings will provide a platform for using MWD shape to tune polymer function in advanced materials applications.



18) Electronic structure and bonding in 1st row hetero-bimetallic complexes probed via multi-edge X-ray absorption spectroscopy

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Department of Chemistry and Chemical Biology, Cornell University

Metal-metal (M–M) bonds between 1st row early and late transition metals have gained significant attention owing to their potential applications in catalysis. Hetero-bimetallic complexes featuring direct M–M bonds between Ti and Fe (using double-decker phosphinoamide ligand) and between Ti and Ni (using double-decker phosphinopyrrolide ligand) along with their redox counterparts have recently been synthesized by the Lu and Tonks groups, respectively. However, the assignment of metal oxidation states to each metal in these multiply bonded systems often seem to be a daunting task since multiple resonance structures can be equally possible for a particular complex. Conventional spectroscopic techniques such as NMR, EPR, Mössbauer, X-Ray crystallography etc. frequently fail to resolve these ambiguities. This poster will present element specific multi-edge X-Ray absorption spectroscopy data in combination with time dependent density functional theory (TD-DFT) calculations to interrogate these systems towards accurately assigning the physical oxidation states of the metals and understanding the nature of M–M bond and associated electronic structures.

19) Quantification of the deviation from idealized hapticity of Lewis base adducts of manganocene

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We have synthesized and characterized several mono- and bidentate Lewis base adducts of manganocene (Cp₂ Mn) using pyridine and polypyridine ligands. These complexes exhibit ring slippage, which is similar to other adducts of manganocene. It is difficult to determine the extent of ring slippage in ionic metallocenes because the extent of slippage does not fall into traditional integer haptic environments. Therefore, we have addressed this challenge by parametrizing the extent of ring slippage. Furthermore, we have found a correlation between the ring slippage and the steric bulk of the adduct. This correlation supports the hypothesis that the haptotropic shifts in ionic metallocenes are caused by the steric properties of the coordinating adduct.

20) Rhenium(I) Phosphazane Complexes and their Applications Towards Catalytic CO₂ Reduction

Matthew R. Crawley and Timothy R. Cook*

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To date, a wide range of rhenium(I)-based CO₂ reduction catalysts have been studied in the literature; however, very few feature phosphorus-donors, and none feature phosphazane ligands. Phosphazane ligands exhibit far greater tunability both in terms of electronic structure as well as steric demand, in comparison to other supporting ligands currently in use. Our work looks to expand the library of ligands currently utilized in CO₂ reduction as well as other forms of small-molecule activation. A series of Re(I) chelating-phosphazane (PNP) complexes supported by polypyridyl and carbonyl ligands have been designed, synthesized, and in addition to routine spectroscopic characterization, their structural and electrochemical properties have been examined via single-crystal X-ray diffraction studies and cyclic voltammetry. Findings show that the monomeric Re(dppa)(bpy)(CO)₂OTf (dppa =

bis(diphenylphosphino)amine, bpy = 2,2'-bipyridine) complex reduces CO₂ to CO and water in the presence of trifluoroethanol (TFE) with excellent catalyst performance both in terms of catalytic rate constant as well as longevity in controlled potential electrolysis (CPE) experiments. Additionally, functionalized analogues of dppa have been synthesized and the ramifications of the phosphazane ligands on electrocatalytic performance were assessed.

21) Hydroxypyridinonates (HOPOs) as ancillary ligands for Fe(III) MRI contrast agents: towards Fe(II) responsive agents

Vusumuzi Hove, Akanksha Patel, Janet R. Morrow*

Department of Chemistry, University of Buffalo, Buffalo, NY

Magnetic Resonance Imaging (MRI) is a diagnostic procedure used in the field of radiology to obtain high-resolution images of soft tissue. MRI uses the ¹H NMR signal of water molecules located in the body. MRI takes advantage of the differences in the density of protons (water content) and the longitudinal (T₁) and transverse (T₂) relaxation times of the protons in tissue. By means of the administration of paramagnetic contrast agents, typically Gd³⁺ complexes, the image contrast is improved. The Morrow group has synthesized Fe³⁺ macrocyclic complexes as a promising new class of MRI contrast agents. HOPO ligands, a class of compounds that are heterocyclic and possess a hydroxyl group ortho to a ketone, are known iron chelators. Studies will be presented on derivatizing these HOPOs, and coupling them to the macrocyclic Fe(III) complex, to make labile iron pool-responsive contrast agents that can be used in MRI imaging. Studies to determine the selectivity of metal ion binding and the effect of the HOPO on the MRI relaxivity of the iron complexes will be discussed.

22) The Assembly of Covalently Linked Quantum Dot Heterostructures on Metal Oxide Thin Films: Towards the Characterization of Charge-Transfer Dynamics of a Multilayer System.

Caitlin R. McGranahan, Alejandro Falca, and David F. Watson*

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Semiconductor quantum dots (QDs) are prime candidates for solar energy conversion in QD-sensitized solar cells (QDSSCs) due to their size-dependent optical properties and high molar absorption coefficients along with the possibilities to undergo multi-exciton generation and hot carrier extraction.

Recent efforts have established the validity of utilizing carbodiimide coupling chemistry to facilitate the formation of bilayers of QDs through the formation of an amide bond between capping ligands of two different QDs on substrates. Having a covalently linked bilayer of QDs on a wide bandgap semiconducting material such as titanium dioxide (TiO₂) would allow stepwise excited-state charge transfer processes to occur, resulting in extended separation of photogenerated electrons and holes. This project focuses on (1) the assembly of covalently-tethered CdS-CdSe and covalently-tethered CdSe-CdTe heterostructures on TiO₂ and zirconium dioxide (ZrO₂) as a control; (2) characterization of the QDs deposited onto the metal oxide thin films and ligand-exchange processes; and (3) spectroscopic characterization of excited-state charge-transfer processes. Deposition of the first layer of QDs onto the TiO₂ thin film was confirmed using UV-VIS and FTIR. The carbodiimide coupling chemistry was performed on TiO₂-adsorbed thioglycolic acid (TGA) capped-CdS or CdSe QDs by reacting N,N'-dicyclohexylcarbodiimide (DCC) and N-hydroxysuccinimide (NHS), which yielded activated NHS-ester-capped CdS or CdSe and was characterized using FTIR. Prior to the assembly of the heterostructures, 4-aminothiophenol (4-ATP) and thiophenol (TP) ligand-exchanges were performed on the secondary QD for each system (CdSe or CdTe) and characterized using ¹H NMR. The activated CdS or CdSe films were then soaked in ligand-exchanged CdSe or CdTe, respectively, to yield the CdS-CdSe and CdSe-CdTe heterostructures on both TiO₂ and ZrO₂. The presence of the secondary QD was characterized using UV-VIS and FTIR. The resulting heterostructure-modified thin films were characterized using time resolved-emission where dynamic quenching was observed.

23) Mid-Gap States Mediated Photoelectrochemical Hydrogen Generation in CdSe Quantum Dots/ β -Pb_{0.33}V₂O₅Nanowires Heterostructures

Nuwanthi Suwandarathne, David Watson*

Department of Chemistry, University of Buffalo, Buffalo, NY

To enhance the efficiency of photoelectrochemical (PEC) water splitting, more attention has been focused on designing photocatalysts with new engineering strategies. Here, we interfaced CdSe quantum dots (QDs) and β -Pb_{0.33}V₂O₅ nanowires (NW) together to form CdSe/ β -Pb_{0.33}V₂O₅ heterostructures as a promising candidate for PEC water-splitting. The intercalation of Pb²⁺ ions in the crystal structure of V₂O₅ NWs gives rise to mid-gap states which lie energetically slightly positive of the water oxidation potential (+1.23 Vvs NHE), and have a significant overlap with the valence band (VB) of CdSe QDs. To investigate the

role of mid-gap states in charge transfer process for effective proton reduction, we performed photocurrent measurements on CdSe/ β -Pb_{0.33}V₂O₅ heterostructures and compared it to CdSe/V₂O₅ heterostructures with no mid-gap states. CdSe/ β -Pb_{0.33}V₂O₅ heterostructures exhibited an enhanced photocurrent density of 25 μAcm^{-2} at 0 V vs reversible hydrogen electrode (RHE) at low pH, which was 5 fold greater than that of CdSe/V₂O₅ heterostructures with similar loading of QDs under white LED light illumination (45 mW). Moreover, photocathodes based on CdSe/ β -Pb_{0.33}V₂O₅ heterostructures showed good stability and very high Faradaic efficiency (95%) for H₂ generation. These results suggest that the CdSe/ β -Pb_{0.33}V₂O₅ heterostructures are indeed promising architectures for light harvesting and photoelectrochemical water splitting.

24) Novel Tacn-Based Macrocycles for Radiometal Chelation

William T. Schumacher and Justin J. Wilson*

Department of Chemistry and Chemical Biology, Cornell University

Selective chelation of first row transition metals in aqueous solution presents an interesting challenge in ligand design. We have begun the synthesis of a library of 1,4,7-triazacyclononane (TACN) based ligands to select for these smaller ions, over a variety of metals with larger ionic radii, in efforts to create new opportunities for radiotherapy and diagnostics. Our efforts have focused on the synthesis and implementation of oxygen donor ligands on these macrocyclic scaffolds in efforts to accommodate oxophilic first row metals, and evaluating their potential for stability in aqueous solution. Ongoing work is focused on evaluating the scope, properties, and feasibility of these moieties.

Talk 1 [3:10 – 3:30 PM]

Coordination-Driven Self-Assembly of Multiple Chromophore Systems: Discovering Structures to Create Emergent Photophysical Properties

Cory E. Hauke, Dr. Yuzhen Zhang and Dr. Timothy R. Cook*

Department of Chemistry, University at Buffalo, Buffalo, NY

Natural light harvesting systems often incorporate multiple chromophores into supramolecular complexes. The spatial and energetic arrangement of these chromophores lead to emergent photophysical properties such as enhanced absorption and emission along with directional energy and/or electron transfer. Herein, we use coordination-driven self-assembly as a facile synthetic method to organize multiple chromophores based on molecular ruthenium and platinum complexes in specific orientations and distances from one another in discrete metallacycles and cages. We discuss the effects self-assembly on absorption, energy and/or electron transfer, and emission of these cages and cycles as compared to the standalone chromophore building blocks to examine the emerging photophysical properties of these architectures.

Talk 2 [3:30 –3:50 PM]

Advances in polyoxovanadate-alkoxide cluster synthesis with application in nonaqueous redox-flow batteries

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Effective integration of renewable energy from intermittent sources (i.e. solar and wind) requires the development of efficient energy storage systems which can function in tandem with the electrical grid. Non-aqueous redox-flow batteries have emerged as promising systems for large-capacity, reversible energy storage capable of meeting the variable demands of the electrical grid. The use of non-aqueous solvents increases the energy density of these systems, however there are few electrolytes with sufficient solubility and electrochemical stability to function in organic media. In this work, we investigate the potential for Lindqvist polyoxovanadate-alkoxide (POV-alkoxide) clusters to serve as both the anolyte and catholyte for symmetric, non-aqueous redox-flow batteries. POV-alkoxide clusters display numerous, highly reversible redox events, and demonstrate significant solubility and electrochemical stability in organic solvents. These bulky compounds also demonstrate the ability to mitigate species crossover and membrane fouling, thereby improving the energy efficiency and lifetime of flow battery cells. The application of POV-alkoxides as electrolytes in organic media demonstrates that the remarkable redox properties of multimetallic clusters can be harnessed for non-aqueous energy storage applications, and represents an important new direction for the generation of high performance redox-flow batteries.

Talk 3 [3:50 –4:10 PM]

New Cell-Permeable Inhibitor for the MCU and its use for the Treatment of Ischemia/Reperfusion Injury

Joshua J. Woods, Justin J. Wilson*

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Cardiovascular disease is the leading cause of death worldwide. Ischemia/reperfusion injury (I/R-injury) is a detrimental condition that occurs in patients who experience myocardial infarction and is a significant contributing factor to patient mortality. This phenomenon arises from initial arterial occlusions, which impede the flow of blood to the effected organ. This in turn causes a decrease in cellular oxygen levels and a drop in cytosolic pH. Clearing the obstruction restores physiological conditions, but also triggers biochemical pathways that cause cell death and tissue damage, which are characteristic features of I/R-injury. There are no clinically available treatments for I/R-injury, and therefore a critical need exists for preventative drugs.

Inhibiting mitochondrial Ca^{2+} uptake is a promising therapeutic strategy for the prevention of I/R-injury as it prevents the initiation of cell death pathways that occur when the mitochondria are flushed with Ca^{2+} ions upon reperfusion.

Our group has developed a novel ruthenium compound, Ru265, that can protect against I/R-injury by inhibiting mitochondrial calcium uptake. We will describe our efforts to synthesize and evaluate Ru265 as a mitochondrial calcium uptake inhibitor. These results demonstrate that ruthenium compounds hold exciting therapeutic properties for the treatment of I/R-injury.

Talk 4 [4:10–4:30 PM]

Organomanganese phenolic-pincer complexes; Synthesis, Coordination chemistry, and Catalysis

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Homogeneous catalysis using ruthenium and iridium based pincer complexes have been extensively studied and reported. Very recently, manganese based pincer complexes gained interest among the catalysis community. Starting from 2016, several PNN and PNP pincer complexes with manganese have been well studied and reported as catalysts for various organic transformations including hydrogenation and dehydrogenation reactions. However, POP pincer complexes of manganese remain unexplored. We have synthesized several new organomanganese complexes using a phenol based POP pincer ligand. This new ligand platform revealed interesting coordination chemistry with manganese and yielded various mono and multi-nuclear complexes. The reactivity of these compounds towards acids and bases were also investigated. Finally, we explored the ability of these complexes in catalyzing various organic transformations.

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