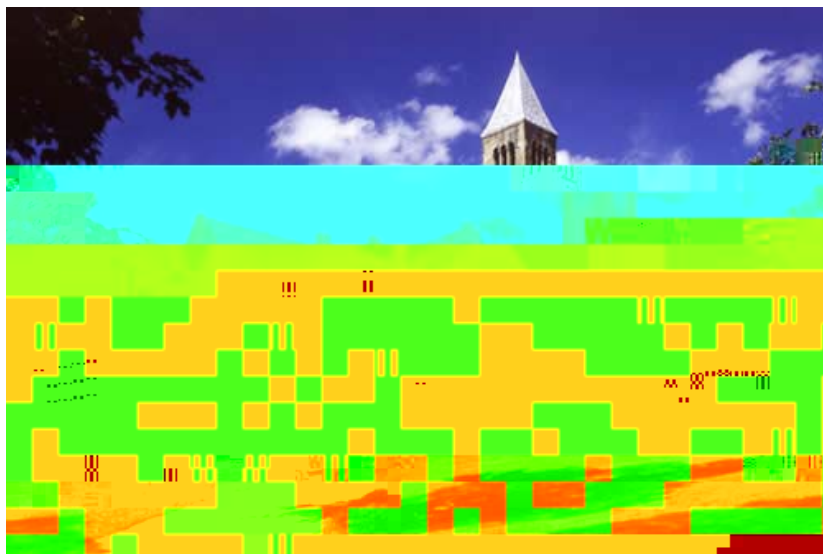


Western New York Inorganic Symposium

(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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- (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.

Oral Presentation Session I [10:10– 11:30PM]

Talk 3 [10:50– 11:10AM]

Excited State Charge Transfer in V_2O_5 /Quantum

Talk 4 [11:10 – 11:30 AM]

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

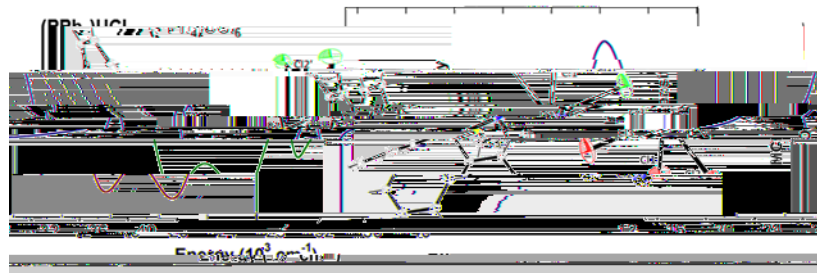
Jennifer M. Le, Vincenzo Firpo, Vincenzo Pavone, Angela
Lombardi, and Kara L. Bren

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

Cobalt mimochrome VI*a (CoMC6*a) is a synthetic enzyme that electrocatalytically reduces protons to hydrogen ($H_{2Tc@003>TJTD0Tis}$)

Gu, Q.;

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, $(VO)_5O(OCH_3)_{12}MCl$ ($M = Cr, Fe, Ga$), 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 $[(VO)(OCH_3)_2]_6Cl$ 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

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

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. Large their their of

large

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

Figure.

Oral Presentation Session 2

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.

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. ~~o003Tj/TT101Tf.45M.03Tj/TT31Tf.o003Tj/TrTD.850TD0Tc0003Tj/TT3~~



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

Anthony F. Cannella,¹ Suman Kr Dey,¹ Samantha N. MacMillan,² David.C. Lacy^{1*}

1. *Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, United States E mail: dclacy@buffalo.edu*

2. *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States*

We have synthesized and characterized several mono- and bidentate Lewis base adducts of manganocene (Cp₂Mn) 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*

Department of Chemistry, University of Buffalo, Buffalo, NY

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 spectr

in

A

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

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

role of mid gap states in charge transfer process for effective proton reduction, we performed photocurrent measurements on CdSe/ $\text{Pb}_{0.33}\text{V}_2\text{O}_5$ heterostructures and compared it to CdSe/ V_2O_5 heterostructures with no mid

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

Oral Presentation Session 3 [3:10 – 4:30 PM]

Talk 2 [3:30 – 3:50 PM]

Advances in polyoxovanadate alkoxide cluster synthesis with application in nonaqueous 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*

Department of Chemistry, University of Buffalo, Buffalo, NY

Cardiovascular disease is the leading cause of death worldwide. Ischemia/reperfusion injury (I/R injury) is a detrimental condition that occurs ~~io~~ occurs

Talk 4 [4:10–4:30 PM]

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

Karthika J. Kadassery,[†] Samantha N. MacMillan,[§] David C. Lacy*[†]

*† Department of Chemistry, University at Buffalo, State University
of New York, Buffalo, New York 14260, United States*

*§ Department of Chemistry and Chemical Biology, Cornell
University, Ithaca, New York 14853, United States*

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

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