



MAISIS

Mid-Atlantic Seaboard Inorganic Symposium

Schedule of Events

- 9:00 – 10:00 **Registration**, Department of Chemistry's Chem '73 Building
- 10:00 – 10:05 **Introduction**, Stiteler Hall, Room B6
- 10:05 – 10:30 **Kayleigh Jones, Temple University, PI: Ann Valentine**
Biological and Environmental Implications of the Interactions of Ti(IV) with the Siderophore Desferrioxamine B
- 10:30 – 10:55 **Davit Jishkariani, University of Pennsylvania, PI: Christopher Murray**
Tuning of Optical, Magnetic and Colloidal Properties of Nanoparticles with Dendritic ligands
- 10:55 – 11:10 **Break**
- 11:10 – 11:35 **Alain Charly Tagne Kuate, Rutgers University – Newark, PI: Frieder Jäkle**
Ferrocene-Based Planar Chiral Lewis Pair Systems
- 11:35 – 12:00 **Jan Paulo Zaragoza, Johns Hopkins University, PI: David Goldberg**
Mn-oxo and Re-oxo Porphyrinoid π -Radical Cation Complexes and the Influence of Lewis Acids and Oxidants on Reactivity
- 12:00 – 12:25 **Jennifer Eddy, University of Delaware, PI: Joel Rosenthal**
Oxygen Reduction to Water and Hydrogen Peroxide with Cobalt Tetrapyrrole Complexes
- 12:25 – 2:00 **Lunch**
- 2:00 – 2:25 **Ian McKendry, Temple University, PI: Michael Zdilla**
Synthetic Strategies for Enhancing Properties of 2D Materials

- 2:25 – 2:50 **James Hodges, The Pennsylvania State University, PI: Raymond E. Schaak**
Colloidal Strategies for Controlling the Morphology, Composition, and Crystal Structure of Inorganic Nanoparticles
- 2:50 – 3:10 **Break**
- 3:10 – 3:35 **Rui Cao, Johns Hopkins University, PI: Kenneth Karlin**
Formation and Characterization of Binuclear Copper Superoxide and Peroxynitrite Complexes
- 3:35 – 4:00 **Abolghasem Bakhoda, Georgetown University, PI: Timothy Warren**
Elusive Terminal Copper-Arylnitrene Intermediates
- 4:00 – 4:20 **Break**
- 4:20 – 4:45 **Lan Wang, University of Delaware, PI: Klaus Theopold**
Curious Structure, Stability and Reaction of Binuclear Alkyl Hydrides of Chromium
- 4:45 – 5:10 **Lauren Grant, University of Pennsylvania, PI: Daniel Mindiola**
Titanium Nitrides: Exploring Nucleophilic Reactivity and Redox Chemistry
- 5:10 – 5:35 **Joseph Becica, Temple University, PI: Graham Dobereiner**
Lewis Acid Acceleration in the Pd-mediated N-Arylation of Amides
- 5:35 – 8:00 **Poster session and dinner, Department of Chemistry's Chem '73 Building**

We thank the following sponsors for their generous support of MASIS 2016



Abstracts for Oral Presentations

1. Kayleigh Jones, Temple University, PI: Ann Valentine

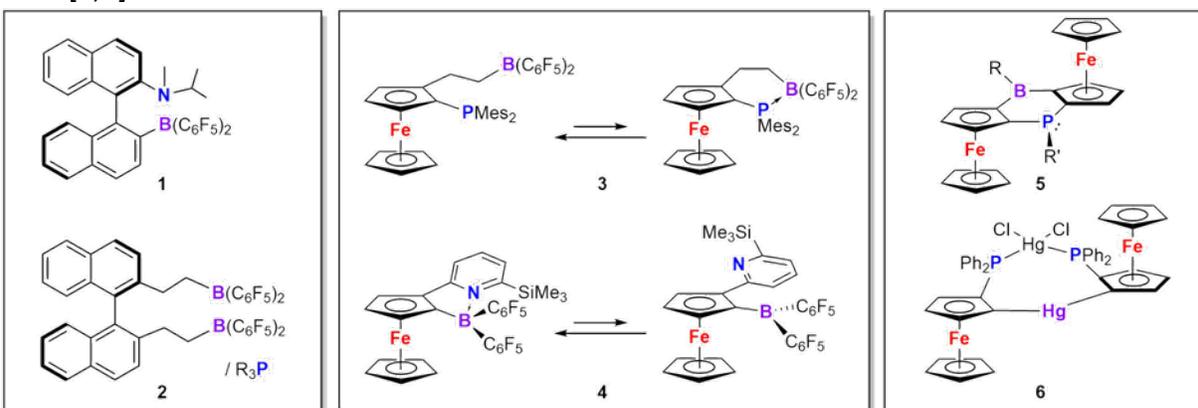
Biological and Environmental Implications of the Interactions of Ti(IV) with the Siderophore Desferrioxamine B

Transition metals play an important role in many biological processes. Iron is essential for almost every organism, but its availability is limited due to low solubility of Fe(III) in aqueous environments. Siderophores solubilize and sequester iron(III). Ti(IV) is chemically similar to Fe(III), and the use of generally-inert TiO₂ is increasing in products such as sunscreens and paint. TiO₂ also forms as a passivating coating on Ti and alloys used in joint replacements. In solution, siderophores like desferrioxamine B (DFOB) are avid binders of Ti(IV). This research explores how DFOB interacts with Ti(IV) in aqueous solutions and can solubilize Ti(IV) from the surface of solid TiO₂. Such dissolution might render bioactive Ti(IV) biologically available, and might interfere with Fe(III) biogeochemical cycling. Spectrophotometric techniques and isothermal titration calorimetry were used to determine the speciation of Ti(IV)-DFOB and the proton-independent stability constant for Ti(IV)-DFOB when in competition with EDTA. Complementary computational methods were employed to predict the structure of Ti(IV)-DFOB, since no crystal structure has been determined thus far. Dissolution studies of TiO₂ in the presence of DFOB were monitored by UV/Vis and confirmed with ICP-OES to determine the kinetics of Ti(IV)-DFOB formation. Further investigative studies were conducted using SEM, TEM, ATR-IR and MS to determine the surface interactions of TiO₂ with DFOB. Kinetic data confirmed that dissolution of Ti(IV) with DFOB is a two step process, with one faster, less extensive step and a slower step involving additional Ti(IV). Understanding these interactions is necessary to determine the effects of binding, the interactions of these complexes in aqueous environments and how they behave chemically in biological systems.

3. Alain C. Tagne Kuate, Rutgers University – Newark, PI: Frieder Jäkle
Ferrocene-Based Planar Chiral Lewis Pair Systems

Alain C. Tagne Kuate, Jiawei Chen, Roger A. Lalancette, Frieder Jäkle

Since the initial breakthroughs on the reactivity of unquenched Lewis acids and bases, a new era in materials chemistry and catalysis has opened and offered to scientists a large spectrum of potential applications. Accordingly, small molecule fixation, bond activation, and the development of transition metal-free catalysts have been among the many attractions of Lewis pair chemistries.[1] Owing to the great importance of asymmetric synthesis in organic transformations, Lewis pairs incorporating chirality have naturally emerged and the most recent findings include the chiral intra- and intermolecular amine- and phosphine-borane Lewis pairs **1** and **2**. [2,3]



Ferrocene represents an ideal and attractive ligand support for the attachment of Lewis pairs at its edge with the possibility to fine-tune the Lewis acidity by redox chemistry and to investigate the response in reactivity. We and others have recently introduced planar chiral ferrocene-based Lewis pairs, **3** [4] and **4** [5], that establish an equilibrium between the open and the closed form in solution. In this contribution, we wish to present our recent work in this field including the development of new planar-chiral ferrocene-based Lewis pair systems such as **5** [6] and **6**.

Bibliography:

- [1] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 2.
- [2] M. Lindqvist, K. Borre, K. Axenov, B. Kótai, M. Nieger, M. Leskela, I. Pápai, T. Repo, *J. Am. Chem. Soc.* **2015**, *137*, 4038.
- [3] S. Wei, H. Du, *J. Am. Chem. Soc.* **2014**, *136*, 12261.
- [4] X. Wang, G. Kehr, C. G. Daniliuc, G. Erker, *J. Am. Chem. Soc.* **2014**, *136*, 3293.
- [5] J. Chen, R. A. Lalancette, F. Jäkle, *Chem. Eur. J.* **2014**, *20*, 9120.
- [6] a) J. Chen, D. A. Murillo Parra, R. A. Lalancette, F. Jäkle, *Angew. Chem. Int. Ed.* **2015**, *54*, 10202 ; b) J. Chen, A. C. Tagne Kuate, R. A. Lalancette, F. Jäkle, *Organometallics* **2016**, in press, DOI: 10.1021/acs.organomet.6b00272.

4. Jan Paulo T. Zaragoza, Johns Hopkins University, PI: David Goldberg

Mn-oxo and Re-oxo Porphyrinoid π -Radical Cation Complexes and the Influence of Lewis Acids and Oxidants on Reactivity

Interest in metalloporphyrinoid complexes with radical character arises from the occurrence of species such as $\text{Fe}^{\text{IV}}(\text{O})(\text{porph}^{\bullet+})$ (compound I) in the catalytic cycles of heme-containing enzymes. We have shown that binding of Lewis acids ($\text{LA} = \text{Zn}^{\text{II}}, \text{B}(\text{C}_6\text{F}_5)_3, \text{H}^+$) in the secondary coordination sphere of the $\text{Mn}^{\text{V}}(\text{O})$ corrolazine (Cz) leads to stabilization of a valence tautomer, a metastable $\text{Mn}^{\text{IV}}(\text{O}) \pi$ -radical-cation complex. The reactivity of $\text{Mn}^{\text{IV}}(\text{O-LA})(\text{Cz}^{\bullet+})$ is significantly different from $\text{Mn}^{\text{V}}(\text{O})(\text{Cz})$, with the metal-oxo unit and redox-active Cz ligand functioning together to carry out H-atom transfer and O-atom transfer reactions. Kinetic analyses, including Hammett plots and substrate steric effects, provide insights into the origins of the difference in rate constants for the different valence tautomers. A $\text{Re}^{\text{V}}(\text{O})(\text{Cz})$ complex was also prepared as an isoelectronic analog of $\text{Mn}^{\text{V}}(\text{O})(\text{Cz})$. Addition of strong Brønsted acids does not lead to stabilization of a valence tautomer in this case, but rather the reversible protonation of a remote site on the ligand to form $\text{Re}^{\text{V}}(\text{O})(\text{CzH})^+$. This N-*meso* protonated complex was characterized by various spectroscopic techniques and revealed a strengthening of the Re–O bond upon protonation. It is shown that the redox-active Cz ring can participate in electron-transfer and H-atom transfer reactions without the involvement of the rhenium-oxo unit. The H-atom transfer reactivity for the one-electron-oxidized $\text{Re}^{\text{V}}(\text{O})(\text{Cz}^{\bullet+})$ is also shown to be strongly dependent on the nature of the external one-electron oxidant through a surprising observation of zero-order kinetics.

5. Jennifer Eddy, University of Delaware, PI: Joel Rosenthal

Oxygen Reduction to Water and Hydrogen Peroxide with Cobalt Tetrapyrrole Complexes

Jennifer Eddy, Tian Qiu, Glenn P. A. Yap, Joel Rosenthal

The selective $4\text{e}^-/4\text{H}^+$ reduction of molecular oxygen to water is an important reaction that takes place at the cathode of fuel cells. The partial reduction ($2\text{e}^-/2\text{H}^+$) of molecular oxygen to hydrogen peroxide is less desired as more than half a volt of energy is squandered by this incomplete reduction. While platinum materials are excellent catalysts for the $4\text{e}^-/4\text{H}^+$ reduction of O_2 , the cost of such materials is incompatible with the wide spread implementation of fuel cell devices. As such, the search for alternatives to platinum that can be used at fuel cell cathodes is an active area of current research. Cobalt macrocycles, particularly cobalt porphyrins, have been widely explored as less expensive catalyst alternatives for the oxygen reduction reaction (ORR). Our group has developed an efficient synthetic strategy for a variety of related tetrapyrrole macrocycles that display sp^3 hybridization at various meso positions. The cobalt complexes of these ligands were probed for their ability to selectively promote the ORR towards water production over hydrogen peroxide production. Analysis of data from rotating ring disk electrode experiments shows a higher selectivity towards water over hydrogen peroxide than most previously studied mono-cobalt macrocycles.

6. Ian McKendry, Temple University, PI: Michael Zdilla

Systematic modification of layered manganese-oxide complexes for cheap and efficient water-oxidation catalysis.

Cheap and efficient water-oxidation catalysts remain one of the major hurdles in the implementation of a hydrogen economy. A promising solution to this hurdle is the use of inexpensive oxide minerals, particularly manganese oxides due to its low cost, large abundance, and ability to easily tune its physical and chemical properties. Through experimental and theoretical interaction, we have explored the roles of oxidation states, lattice dopants, and interlayer species on the material's properties and water oxidation capabilities. Our findings suggest increasing manganese(III) and cobalt(III) content as well as introduction of harder, redox active species in the interlayer greatly enhance water oxidation activity through charge delocalization and increase of high energy frustrated water activity that rivals that of ruthenium and iridium oxide OER catalysts can be achieved.

7. James Hodges, The Pennsylvania State University, PI: Raymond E. Schaak

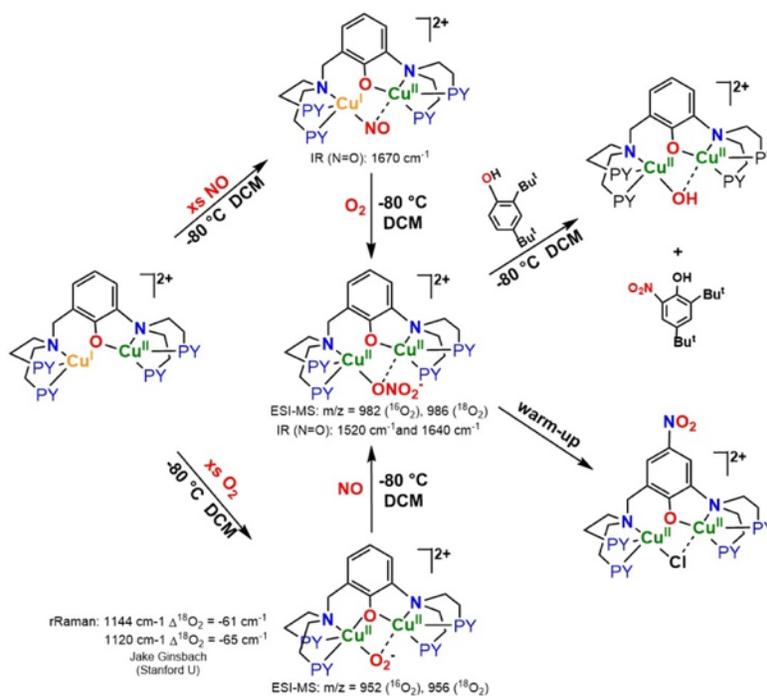
Colloidal Strategies for Controlling the Morphology, Composition, and Crystal Structure of Inorganic Nanoparticles

Colloidal nanochemistry is one of the most effective methods for generating high quality, monodisperse nanocrystals with diverse structural features and highly complex architectures. However, traditional colloidal approaches require a precise balance of crystal nucleation, particle growth, and redox potential of chemical reagents, which can be difficult to synchronize in complex chemical environments. For this reason, many important material systems are not accessible as monodisperse and/or shape-controlled colloidal nanocrystals. Solution-mediated ion exchange transformations have recently emerged as powerful alternatives to conventional colloidal approaches, which circumvent complex nanoparticle formation processes. Importantly, structural characteristics of the starting nanotemplate, such as morphology and crystal symmetry, can be retained during these transformations, offering unique chemical routes to synthetically challenging nanomaterials. In this presentation, I discuss some of the recent strategies that we have developed for improving control of the morphology, composition, and crystal structure of colloidal nanomaterials using nanoscale ion exchange approaches. Specifically, I will show how anion and cation exchange chemistry can be integrated into one reaction sequence to accomplish a complete nanomaterial transformation, where the final product does not contain any of the original constituent elements, although the original morphology is retained, thereby decoupling morphology and composition control. Additionally, I will show how cation exchange can be used to synthesize interesting crystal polymorphs that are inaccessible using direct methods. The ability to decouple control of the morphological and structural features of colloidal nanoparticle products is anticipated to provide new capabilities for accessing materials with precisely targeted features.

8. Rui Cao, Johns Hopkins University, PI: Kenneth Karlin

Formation and Characterization of Binuclear Copper Superoxide and Peroxynitrite Complexes

Oxygenation of $[\text{Cu}_2(\text{UN-O}^-)(\text{DMF})]^{2+}$ (**1**), a structurally characterized dicopper Robin-Day class I mixed-valent Cu(II)Cu(I) complex, with UN-O^- as a binucleating ligand and where dimethylformamide (DMF) binds to the Cu(II) ion, leads to a superoxo-dicopper(II) species $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{O}_2^{\bullet-})]^{2+}$ (**2**). Complex **2** can be reversibly reduced to the peroxide species $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{O}_2^{2-})]^+$, using varying outer-sphere ferrocene or ferrocenium redox reagents. A Nernstian analysis could be performed by utilizing a mono-diphenylamine substituted ferrocenium salt to oxidize the peroxo complex, leading to an equilibrium mixture with $K_{\text{et}} = 5.3$ (-80°C); a standard reduction potential for the superoxo-peroxo pair is calculated to be $E^\circ = +130$ mV vs SCE. A literature survey shows that this value falls into the range of biologically relevant redox reagents, e.g., cytochrome *c* and an organic solvent solubilized ascorbate anion. The peroxide complex and the superoxide complex are characterized by rRaman spectroscopy, respectively. The superoxide complex further reacts with excess nitric oxide gas to form a peroxynitrite complex $[\text{Cu}^{\text{II}}_2(\text{UN-O}^-)(\text{O}_2\text{NO}^-)]^{2+}$ (**3**) which is characterized by low temperature electrospray ionization mass spectrometry (ESI-MS) and infrared spectroscopy. Additionally, the mixed-valent Cu(II)Cu(I) complex reacts directly with nitric oxide to form a copper nitrosyl complex which can be best described as a mixed valence $[\text{Cu}^{\text{I,II}}(\text{UN-O}^-)(\text{NO})]^{2+}$ (**4**) based on the N-O stretching at 1670 cm^{-1} . This mixed valence copper nitrosyl complex **4** can generate the same peroxynitrite complex upon removing excess nitric oxide and adding excess dioxygen gas. The peroxynitrite complex **3** that is produced by either process shows full nitration in the presence of the substrate 2,4-di-*t*-butyl phenol on the ortho position. Direct warm up of the peroxynitrite complex **3** results in nitration on the para position of the phenol group of the ligand and a chloride bridged dipper complex.



9. Abolghasem Bakhoda, Georgetown University, PI: Timothy Warren

Elusive Terminal Copper-Arylnitrene Intermediates

Terminal copper-nitrene species $[\text{Cu}]=\text{NR}$ have been proposed as key intermediates in many alkene aziridation and sp^3 C-H amination reactions. Although such $[\text{Cu}]=\text{NR}$ species have been demonstrated as intermediates based on kinetic analysis of C-H amination of isolable dicopper nitrenes $[\text{Cu}]_2(\mu\text{-NR})$,^{1,2} the isolation such terminal copper nitrenes has proven elusive. In this presentation, we report our recent attempts to isolate copper aryl nitrenes by reaction of copper(I) β -diketiminato complexes $[\text{CuI}]$ with arylazides N_3Ar . A number of interesting structures result including a dinuclear Cu(II) ketimide species (**1**) formed by coupling of the *p*-C atoms of the N-aryl group to make a new $\text{sp}^3\text{-sp}^3$ C-C bond. Dinuclear **1** serves as a source of the mononuclear, terminal copper nitrene $[\text{Cu}]=\text{NAr}$ through reversible C-C bond cleavage, capable of transfer the nitrene group to both nucleophiles such as phosphines and isocyanides as well to strong sp^3 C-H bonds of hydrocarbons such as ethylbenzene.

References

1. Badieli, Y. M.; Krishnaswamy, A.; Melzer, M. M.; Warren, T. H. *J. Am. Chem. Soc.*, **2006**, *128*, 15056–15057.
2. Badieli, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 9961–9964.

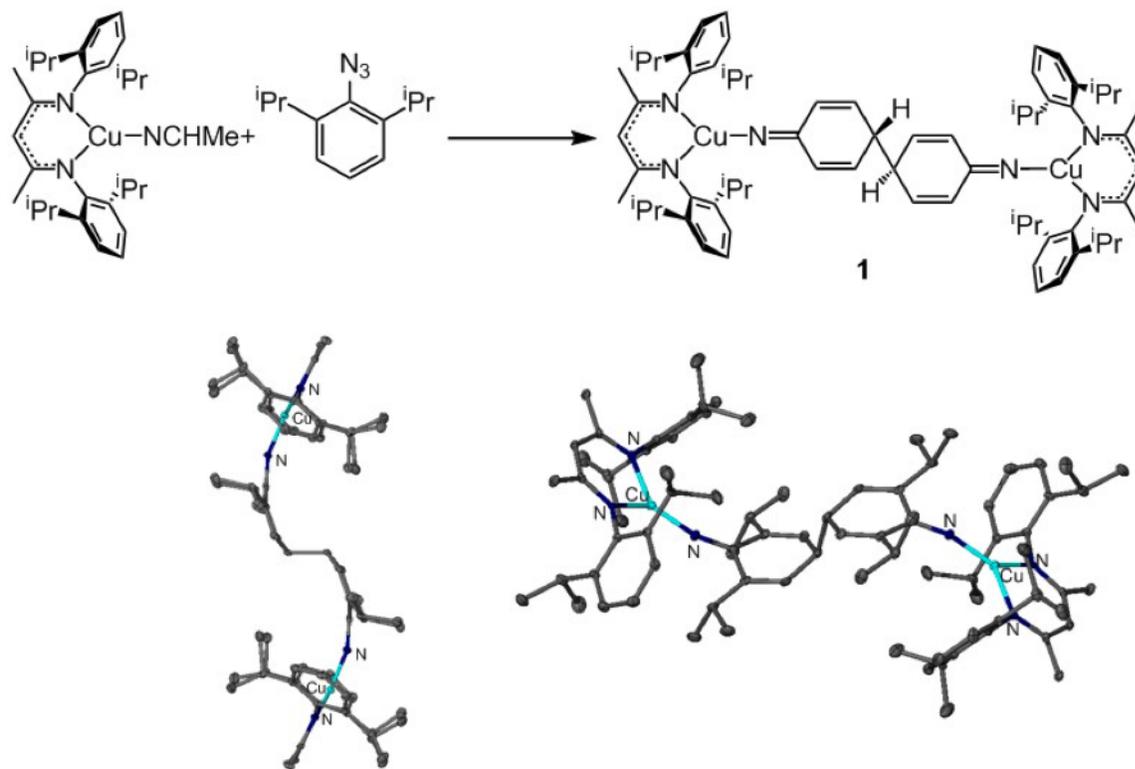


Figure 1 X-ray crystal structure of **1**.

10. Lan Wang, University of Delaware, PI: Klaus Theopold

Curious Structure, Stability and Reaction of Binuclear Alkyl Hydrides of Chromium

We have previously encountered binuclear chromium alkyl hydrides supported β -diketiminato ligand (Nn), which resist reductive elimination even upon heating.[1] Recently, we have established general routes for the synthesis of chromium alkyl hydride complexes (where alkyl = trimethylsilylmethyl, phenyl, benzyl and neopentyl) for both β -diketiminato and α -diimine ligand systems (a notoriously 'redox-ambiguous' ligand which was unexplored). Notably, the chromium neopentyl hydride with Nn reacts with benzene, toluene and tetramethylsilane to afford the correspondent alkyl hydride complexes. This is an apparent C-H activation. And the complexes supported by α -diimine ligand provides a novel system with unexpected structures and curious stabilities. The synthesis, structures and exploration of the reactivities of the chromium alkyl hydrides will be discussed.

[1] (a) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. A stable alkyl hydride of a first row transition metal. *Chem. Commun.* 2003, 1164-1165, (b) Monillas, W.; Yap, G. P. A.; Theopold, K. A Tale of Two Isomers: A Stable Phenyl Hydride and a High-Spin ($S=3$) Benzene Complex of Chromium. *Angewandte Chemie International Edition* 2007, 46, 6692-6694

11. Lauren Grant, University of Pennsylvania, PI: Daniel Mendiola

Titanium Nitrides: Exploring Nucleophilic Reactivity and Redox Chemistry

Mononuclear, terminally bound early transition metal nitrides have largely evaded isolation until recently due to the reactive nature of this highly polarized metal-ligand multiple bond. This presentation will discuss the reactivity and characterization of the terminally bound anionic dinuclear titanium nitride, $[\mu_2\text{-K}(\text{OEt}_2)]_2[(\text{PN})_2\text{Ti}\equiv\text{N}]_2$, (PN- = (N-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide). Featured reactivity includes access of rare imide scaffolds, complete N-atom transfer, and redox reactivity.

12. Joseph Becica, Temple University, PI: Graham Dobereiner

Lewis Acid Acceleration in the Pd-mediated N-Arylation of Amides

The cross coupling of amides and aryl halides via a Pd/xantphos catalyst is demonstrated to be accelerated by Lewis acid co-catalysts. With the goal identification of the role of the Lewis acid in catalysis, a kinetic study has been performed and our mechanistic inferences will be presented.

Abstracts for Poster Presentations

13. Mark R. Zierden, Jean P. Gaffney, Temple University, PI: Ann Valentine

Ferrireductase Activity of Nicatransferrin, a Monolobal Transferrin from the Ascidian Ciona intestinalis

A monolobal transferrin, nicaTf, was identified in the primitive ascidian species *Ciona intestinalis*. Fe(III)-bound nicaTf displays significant spectral differences from other Fe(III)-bound transferrins, which are likely the consequence of differences in metal coordination. NicaTf does not exhibit a tyrosine-to-Fe(III) charge transfer band near 460 nm as do most transferrins. It instead shows an unassigned shoulder at around 330 nm. Unlike typical transferrins, nicaTf as-isolated reduces Fe(III) to Fe(II) stoichiometrically in the absence of external electron donors as measured by the detection of Fe(II) with Ferrozine and 1-10 phenanthroline. The reduction is modeled as a sequential two-step process. The data are interpreted in terms of these three spectroscopic species.

14. Siqi Yu, Lehigh University, PI: David Vasic

Accessing perfluoroalkyl nickel(II),(III), and (IV) complexes bearing a readily attached [C₄F₈] ligand

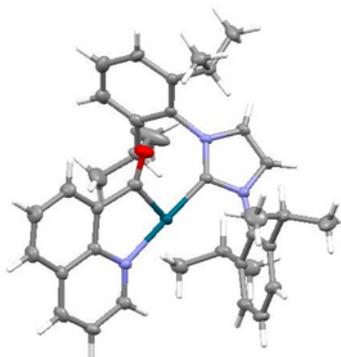
In recent years, nickel complexes have been proved very successful in catalyzing cross-couplings reactions. However, cross-coupling reactions involving perfluoroalkyl groups remain challenging due to the difficulty of reductive eliminations. Oxidatively inducing reductive eliminations of perfluoroalkyl groups may be possible with first-row metals. Here, we present our efforts to prepare high valent terpyridyl nickel complexes bearing perfluoroalkyl ligands so that the factors influencing reductive eliminations can be better understood. The [C₄F₈] ligand was found to stabilize nickel complexes in +2 and +3 oxidation states. Our electrochemical studies provide insight into how nickel complexes can be modified to facilitate oxidation of Ni(III) to Ni(IV). Reactivity studies show that eliminations at these high valent complexes are indeed possible.

15. Derek Wozniak, Temple University, PI: Graham Dobereiner

Structure and Catalytic Activity of a T-Shaped Cationic Pd(II) Acyl Complex

Novel cationic Pd(II) acyl complexes, including a nominally 3-coordinate species, have been synthesized and characterized by NMR and single-crystal x-ray diffraction. DFT studies have revealed that weak arene-Pd and anagostic C-H...Pd interactions are present in the 3-coordinate compound, helping to stabilize what would normally be a highly reactive complex. This complex is so desperate for electron density that it can, in fact, bind methylene chloride, an exceptionally poor ligand. Considering the high reactivity usually associated with low-coordinate complexes, catalytic activity for the isomerization of olefins was investigated, using 1-hexene as the model

substrate. While the catalyst does indeed facilitate the isomerization of 1-hexene to 2-hexene, it was found that the addition of Lewis Acid $[B(C_6F_5)_3]$ was required for the reaction to occur at an appreciable rate. NMR kinetics studies were performed on this reaction in an attempt to elucidate the mechanism.



16. Alexander B. Weberg, University of Pennsylvania, PI: Neil C. Tomson

Electrostatic Activation of Small Molecules: Ligand Design and Application

Alexander B. Weberg, Xiujing Xing, Andrea J. C. Tam, Brian C. Manor, Patrick J. Carroll, Neil C. Tomson

Transition metal mediated small molecule activation has become an area of great interest in organometallic chemistry, with invaluable application to synthetic and industrial processes. A recent and often overlooked area of study with regard to these catalysis deals with using electrostatic fields to affect the potential orbital energies of small molecules in key transition states, hereby activating them towards lower energy conversion pathways. However, the majority of work in this area primarily centers around either computational studies, or the use of unconstrained π -acid cations. We are interested in developing a range of ligand frameworks that incorporate localized point charges (phosphoniums, ammoniums, borates, etc.) at different distances from, and in different geometries around novel transition metal catalysts. The ligand frameworks discussed within will have the effect of producing specific and possibly unique binding orientations of small molecules, and will provide a high degree of electrostatic field tunability that could activate a range of small molecules towards otherwise kinetically unfavorable transformations.

17. Qiuran Wang, University of Pennsylvania, PI: Neil C. Tomson

Redox-Active Macrocycles as Model Systems for Heterogeneous Catalysis

Qiuran Wang, Laura M. Thierer, Peng Cui, Samuel P. McCollom, Brian C. Manor, Patrick J. Carroll, Neil C. Tomson

Redox active macrocyclic ligands using pyridinediimine and naphthyridinediimine frameworks are of appropriate size to form complexes containing clusters of 2-4 transition metal centers. The

arrangement of the clusters in these macrocyclic complexes is aimed at modeling different possible active sites of heterocatalysts, while the redox active ligands in such complexes could incorporate the cooperative electronics from the extended heterocatalytic metal surface. So far, strontium pyridinediimine macrocycles with ethylene and propylene linkers have been successfully synthesized. The transmetalation reactions between the CuCl_2 or AgNO_3 afford a Ag complex with a polymeric spiral structure, while characterization of the resulting Cu(II) product is ongoing.

18. Stephanie Velardo, University of Delaware, PI: Joel Rosenthal

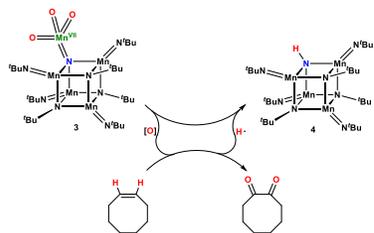
CO₂ Reduction Using 3D Printed Flow Electrolysis

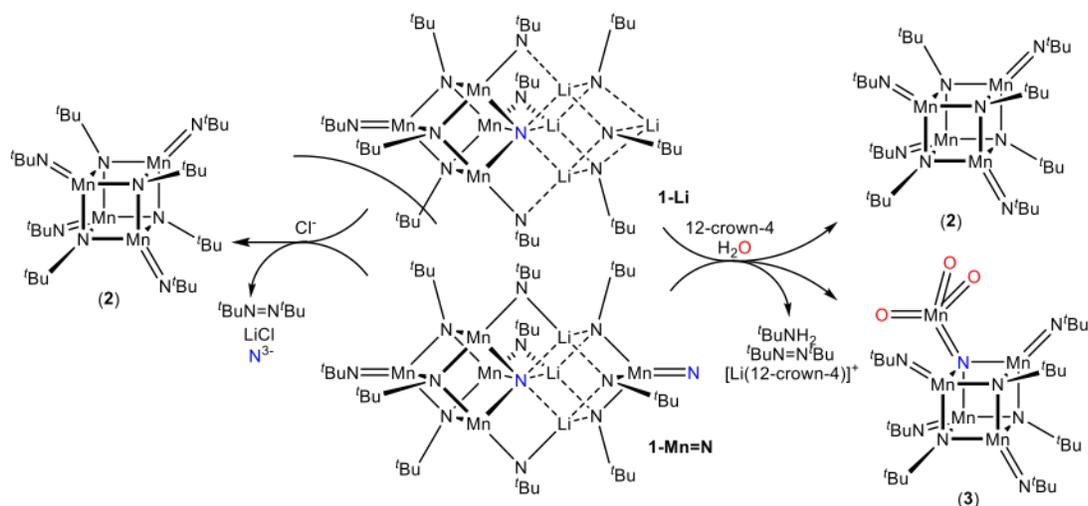
The development of inexpensive electrolyzer platforms capable of efficient and rapid reduction of CO_2 to CO provide a route to solar fuel production when driven by renewable electricity generated from a PV assembly. Our laboratory has developed a bismuth-carbon monoxide evolving catalyst (Bi-CMEC) using an electrodeposition strategy. This Bi-CMEC catalyst promotes the conversion of CO_2 to CO at rates and selectivities comparable to those historically observed for precious metals such as silver and gold. In an effort to improve the scalability of the Bi-CMEC platform we have developed a streamlined method by which solutions of Bi^{3+} salts may be drop cast onto large two-dimensional electrode supports. These modified electrodes have been utilized in conjunction with 3D-printed flow cell assemblies to enable the large scale production of CO. This new CO_2 electrolyzer may be directly integrated with PV assemblies to drive to production of CO using solar energy and serves to underscore the feasibility of rapid solar fuel generation.

19. Shivaiah Vaddypally, Temple University, Michael J. Zdilla

Manganese cubane clusters and their reactivities: Isolation of reactive pendant Mn=O moiety, a model of S₄ state of oxygen evolving center in Photosystem II

The structure of the OEC in the dark-adapted S_1 state has been reproduced in several crystal structures.^{1,2} The structure is described as a Mn_3CaO_4 heterocubane cluster with a 4th “dangler” or “pendant” manganese atom. Inspired by the OEC, we have isolated four-coordinate cubane clusters with high oxidation states of IV, V and VII. The heterodicycubane cluster $\text{Li}_3\text{Mn}_4\text{M}(\mu_3\text{-N}^t\text{Bu})_6(\mu\text{-N}^t\text{Bu})_3(\text{N}^t\text{Bu})(\text{N})$ (1), by reaction with Li^+ ion scavengers (${}^t\text{Et}_4\text{NCl}$, 12-crown-4) yields the clusters $(\text{Mn}_4^{\text{IV}}(\mu_3\text{-N}^t\text{Bu})_4(\text{N}^t\text{Bu})_4)$ (2) and $\text{Mn}_4^{\text{IV}}(\mu_3\text{-N}^t\text{Bu})_3(\text{N}^t\text{Bu})_4(\mu_3\text{-NMnO}_3)$ (3) respectively by reductively eliminating azo-tert-butane. The compound 2 undergoes one electron oxidation by using Ferrocene to yield $\text{Mn}_3^{\text{IV}}\text{Mn}^{\text{V}}(\mu_3\text{-N}^t\text{Bu})_4(\text{N}^t\text{Bu})_4$ (4). Compound 3, upon reaction with cyclooctene gives $(\text{Mn}_4^{\text{IV}}(\mu_3\text{-N}^t\text{Bu})_3(\mu_3\text{-NH})(\text{N}^t\text{Bu})_4)$ (5). Compounds 1 to 5 represent a family of cubane type of clusters structurally exhibiting to the natural OEC system along with high oxidation states. Compound 3 represents the S_4 state of oxygen evolving complex due to presence of reactive Mn=O moiety





20. Olivia Stepanic, Temple University, PI: Ann Valentine

Deferasirox as a Ti(IV) Delivery System

Titanium is a bioactive material, and some Ti(IV) compounds have shown potential as anticancer drugs. One of the issues with Ti(IV) concerns its transportation and uptake. Deferasirox (DSX), a synthetic ligand initially developed as an orally active tight binder of Fe(III) for treatment of iron overload, was investigated as a potential binder of Ti(IV) through spectrophotometric methods. Ti(IV) binds DSX in a 2:1 ratio with two species, Ti(DSX)HDSX⁻ and TiDSX₂²⁻, in a pH-dependent equilibrium. The behavior of these complexes was explored, as was the potential release of Ti(IV) from this compound to human serum transferrin (hsTf) and albumin (hsA).

21. Vaidehi Shastri, Marianne Donley, Villanova University, PI: Deanna L. Zubris

Ligand Development for Iron Catalyzed Atom Transfer Radical Polymerization

Inorganic chemistry plays an important mechanistic role in Atom Transfer Radical Polymerization (ATRP), where a metal-based catalyst helps to mediate a controlled ("living") free-radical polymerization yielding polymers with precisely controlled polymer molecular weights. Copper-based ATRP catalysts dominate the ATRP field. These copper catalysts are typically prepared in situ and structural elucidation for the metal-ligand complexes is generally not emphasized. Iron-based ATRP catalysts have potential advantages over copper-based systems due to iron's high natural abundance, low cost, and biocompatibility. Our group is working to refine guiding principles for successful iron-based ATRP, in particular with respect to ligand design. Herein we describe recent efforts to prepare (imino)pyridine iron(II)bromide complexes and a new chelating ligand that contains an electron-donating N-heterocyclic carbene.

22. Evan Samples, Temple University, PI: Graham Dobereiner

Polyketones for Hole Transport Materials

Polyketones are easily synthesized from carbon monoxide and terminal olefins using robust palladium catalysts. The resulting polymer contains a 1,4-diketone moiety that is highly reactive making the polymer ideal for post-polymerization functionalization reactions that could yield new materials useful for Perovskite solar cells (PSCs). Achievements in conversion efficiency of Perovskite solar cells have established PSCs as a credible alternative to liquid electrolyte solar cells, but these cells typically contain spiro-OMeTAD, a solid hole transport material (HTM), which is very expensive to fabricate. The search for efficient replacement HTMs at lower cost is necessary for lowering the cost of the PSCs. Polymers synthesized so far have been modified to polyfurans and polypyrroles through Paal-Knorr condensations, and the oxidation potentials have been compared to those known for spiro-OMeTAD.

23. Sima Sakhaei, Georgetown University, PI: Timothy Warren

Mechanistic Insight into Nitrite to Nitric Oxide Conversion at Copper(I) and Copper(II) Sites

Nitric oxide (NO) is an important cellular signaling molecule involved in many physiological and pathological processes. Nitrite (NO_2^-) represents a tightly regulated and important circulating source of NO in biological systems. We seek to understand factors responsible for the release of NO from nitrite at low coordinate copper centers. While copper enzymes and model complexes have been shown to generate RO-NO bonds via reductive nitrosylation from NO via Cu^{2+} in the presence of HOR (R = H or alkyl), the reverse process is less understood, despite the important production of NO from nitrite in the enzyme copper nitrite reductase. Employing a unique three coordinate copper(I) $\kappa^1\text{-N}$ bound nitrite complex, and its redox couple, we examine the addition of reductants such as PPh₃ and 2,6-dimethylphenylisocyanide to the [Cu]-nitrite complex to trigger the loss of NO and provide more insight into the coordination environment dependence of transformations involved in nitrite/ nitric oxide chemistry. Our results show the reduction of nitrite at Copper(II) center and inertness of Copper(I) site towards NO release. This finding suggests that the oxidation state of the copper center plays an important role in the reactivity of the copper site in nitrite reduction.

24. Patrick Rogler, Johns Hopkins University, PI: Kenneth D. Karlin

Varying Reactivity of Low-Spin Heme-Peroxo-Copper Species Towards a Reductant (Me_{10}Fc) Plus a Phenolic Acid: Covalently Attached Versus Exogenous Heme Axial Bases

Patrick J. Rogler,[†] Savita K. Sharma,[†] Andrew W. Schaefer,[‡] Suzanne Adam,[†] Isaac Garcia-Bosch,[†] Edward I. Solomon^{*‡} and Kenneth D. Karlin^{*†}

[†]Johns Hopkins University, Baltimore, Maryland 21218, United States

[‡]Department of Chemistry, Stanford University, Stanford, California 94305, United States

A recurring interest of our group is to better understand the chemistry relevant to the four electron (e^-), four proton (H^+) reduction of dioxygen to water via reductive O-O bond cleavage, as occurs in the heme a_3 / Cu_B containing active site of cytochrome *c* oxidase. Here, heme-copper derived dioxygen complexes, which have been designed, ligands synthesized and complexes generated at low temperature, have been studied with respect to their reactivity towards a one electron reductant, decamethylferrocene ($Me_{10}Fc$), and a phenolic acid proton source, *para*-nitrophenol (PNP). Specifically, this work describes the spectroscopic characterization (UV-Vis, rRaman, 2H -NMR, EPR, DFT) and a reactivity comparison between two low-spin heme-peroxo-copper adducts. These are the newly developed species $[(P^{Im})Fe^{III}-(O_2^{2-})-Cu^{II}(AN)]^+$ (**1**) and the previously reported complex $[(DCHIm)(F_8)Fe^{III}-(O_2^{2-})-Cu^{II}(AN)]^+$ (**2**). Complexes **1** and **2** are structurally distinct in terms of their heme environment; in the case of complex **1**, the axial base ligand is covalently attached to the porphyrin periphery while in **2** the axial ligand (1,5-dicyclohexylimidazole) was added exogenously. We find that alterations to the heme environment can affect peroxo reactivity towards a weak phenolic acid (*p*-NO₂-PhOH) and an electron source ($Me_{10}Fc$). Only copper(II) reduction occurs on addition of reductant to complex **1**, yielding an end-on ferric heme peroxo product $[(P^{Im})Fe^{III}-(O_2^{2-})]^-$ (**1b**). By contrast, **2** doesn't react with reductant independently however two-electron O-O PCET cleavage occurs when the proton source is added to system with reductant present. We conclude that variations in the heme environment can significantly change the reactivity of our heme-copper dioxygen adducts, providing us with progressing valuable insights into reductive O-O bond cleavage chemistry, which is of fundamental importance.

25. Mahdi Raghibi Boroujeni, Subrata Kundu, Georgetown University, PI: Timothy Warren
Electrocatalytic Ammonia Oxidation with Molecular Copper Complexes

Ammonia (NH_3) is a commodity chemical produced in over 140 M tons a year, primarily to fertilize crops that feed our planet's population. It is also an attractive carbon-free chemical fuel, nearly on par with hydrogen (H_2) in terms of thermodynamic reactivity with O_2 . Indeed, some vehicles have been equipped with ammonia-fueled internal combustion engines. To most efficiently harness the chemical energy contained in ammonia, however, fuel cells must be employed that electrochemically oxidize NH_3 at the anode concurrent with O_2 reduction at the cathode. While electrochemical O_2 reduction catalysis represents an area of intense study, the corresponding electrocatalytic oxidation of NH_3 has been sparsely investigated. We report our initial studies on electrocatalytic ammonia oxidation with copper(I) β -diketiminato complexes. Based on our lab's experience with reactive, oxidized copper(II) amides $[Cu^{II}]-NHR$ in C-H amination, we have found that some such species are unstable towards N-N coupling to diazenes $RN=NR$ (via hydrazines $RNH-NHR$) with concomitant reduction of the copper center to $[Cu^I]$. Thus, related $[Cu^{II}]-NH_2$ intermediates may allow for the key N-N bond forming step crucial to ammonia oxidation. We report cyclic voltammetry experiments that suggest catalytic oxidation of ammonia at modest potentials (+ 80 mV vs. Fc/Fc^+) along with mechanistic studies that indicate that cationic copper(II) complexes $\{[Cu^{II}](NH_3)_x\}^+$ ($X = 1$ or 2) are unstable towards reduction to copper(I) in the presence of excess ammonia.

26. David A. Quist, Daniel E. Diaz, Johns Hopkins University, PI: Kenneth D. Karlin

Stabilization Effect of H-bonding Moieties on Cupric Superoxide Complexes

Many enzymatic and synthetic studies have shown that hydrogen bonding (H-bonding) in the secondary coordination sphere can increase O₂-binding affinity to low valent metal ions and stabilize reactive metal-dioxygen species. One such primary Cu^I/O₂ adduct is best described as a cupric superoxide complex Cu^{II}(O₂^{•-}). It is generally accepted that these carry out hydrogen-atom transfer from substrate in certain copper-containing monooxygenases (PHM, DβM, and TβM), which carry out C-H hydroxylation reactions. Many cupric superoxide model complexes have been reported to date, with only one containing an H-bonding motif in the secondary coordination sphere. To better understand the effect of H-bonding on cupric superoxide stability, a series of previously reported copper complexes, with and without H-bonding groups, has been synthesized. The reactivity of LCu^I complexes with O₂ at low temperature (-135 °C, in MeTHF) has been carried out. Interestingly, LCu^I complexes show varying reactivity with O₂, leading to differing types of LCu^{II}(O₂^{•-}), LCu^{II}(O₂²⁻)Cu^{II}L, or LCu^{III}(μ-O²⁻)₂Cu^{III}L species, depending on the presence of an H-bonding group, despite having similar reduction potentials as indicated by electrochemical data obtained from analog azido [LCu^{II}-N₃]⁺ complexes. The cupric superoxide complexes that form do possess secondary coordination sphere H-bonding groups; these have been characterized via UV-Vis spectroscopy. Preliminary studies show these new cupric superoxides react with *p*-OMe-2,6-di-*tert*-butylphenol at low temperature giving 2,6-di-*tert*-butyl-1,4-benzoquinone, as verified by ¹H NMR spectroscopy. The implication of the work described will be discussed.

Acknowledgements: Research support was obtained from the National Institutes of Health.

27. Tian Qiu, University of Delaware, PI: Joel Rosenthal

Developing cobalt tetrapyrrole catalysts that display multielectron redox property for oxygen reduction reaction (ORR)

The oxygen reduction reaction (ORR) is the most essential process in nature. It is also the cathode reaction of a hydrogen fuel cell which couples the oxidation of H₂ to O₂ reduction. This reaction can proceed through two pathways which are the O₂ to H₂O₂ two electron reduction and the O₂ to H₂O four electron reduction. The four electron reduction pathway is more attractive as it releases more energy than the two electron reduction. Current fuel cells utilize platinum based catalysts to achieve four electron reduction of oxygen. It is very important to develop inexpensive catalysts that can selectively and efficiently facilitate four electron ORR. Cobalt porphyrins can activate O₂. Monomeric cobalt porphyrins are limited to the two electron ORR. Cofacial cobalt porphyrins and cobalt hangman porphyrins that perform four electron ORR require laborious synthetic routes and are inconvenient to prepare on large scales. In confronting this limitation, we have developed a series of novel cobalt tetrapyrrole catalysts for ORR. By incorporating sp³ hybridized carbon centers, a rich multielectron redox chemistry is enabled for the new complexes, which is important for four electron ORR catalysis.

28. Yusen Qiao, University of Pennsylvania, PI: Eric Schelter

Lanthanide Tris-guanidinate Complexes: Synthetic, Structural, Spectroscopic and Theoretical Studies

Yusen Qiao, Haolin Yin, Brian C. Manor, Patrick J. Carroll, Eric Schelter

A series of lanthanide tris-guanidinate complexes, $\text{Ln}^{\text{III}}[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2]_3$ (Ln = La, Ce, Pr, Tb), have been prepared by treatment of LnI_3 with $\text{Na}(\text{THF})[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2]$ in order to investigate their electronic structures. Molecular geometries have been elucidated by X-ray diffraction studies. Electrochemical studies revealed one quasi-reversible oxidation wave at ca. -0.2 V versus $\text{Cp}_2\text{Fe}^{+/0}$ for the Ce(III) and Pr(III) compounds, while at ca. -0.4 V versus $\text{Cp}_2\text{Fe}^{+/0}$ for the La(III) and Tb(III) compounds. The cerium(III) compound showed $4f \rightarrow 5d$ absorptive transitions at ca. 3 eV, whereas the other lanthanide(III) compounds showed only ligand-to-metal charge transfer (LMCT) bands above ca. 4 eV. Chemical oxidation of $\text{Ce}^{\text{III}}[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2]_3$ with $[\text{Cp}_2\text{Fe}^{\text{F}}][\text{BAR}^{\text{F}}_4]$ ($\text{BAR}^{\text{F}}_4 = [3,5\text{-bis(trifluoromethyl)phenyl}]_2\text{borate}$) afforded a dark green cerium(IV) complex, $\{[(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Ce}^{\text{IV}}[\text{BAR}^{\text{F}}_4]\}$, whose molecular structure has also been determined. The electronic structure of this cerium(IV) compound has been investigated in detail by a combination of electronic absorption spectra measurements, magnetic studies and density functional theory calculations, suggesting that this cerium(IV) compound has an unusual multi-configurational ground state.¹

1. Walter, M. D.; Booth, C. H.; Lukens, W. W.; Andersen, R. A. *Organometallics* **2009**, *28*, 698–707.

29. Lauren Profitt, Temple University, PI: Ann Valentine

Active Modes of Inhibition for Titanium Compounds

Titanium's biological application has been minimally valued, yet its presence has been identified in humans' skin and lungs. Titanium is bioactive, giving rise to studies of its medicinal value in terms of anti-cancer and anti-inflammatory effects but very little is known about the mechanism of bioactivity of Ti(IV) complexes. It is theorized that these titanium drug complexes work in the same DNA binding manner as platinum centered chemotherapy drug cisplatin, but other proposals have been little explored. Titanium complexes may work as protein kinase inhibitors or DNA topoisomerases inhibitors. The exact mode of activity for titanium-centered complexes, such as titanocene dichloride, titanium citrate, titanium ascorbate, and titanium bound to hydroxybenzyl ethylenediamine (HBED), is of great interest and coupled with hydrolysis toxicity reports could lead the way for enhanced drug design.

30. Andrea Potocny, Maxwell Martin, University of Delaware, PI: Joel Rosenthal

Synthetically Accessible Tetrapyrrole Metal Complexes as Efficient Photosensitizers of Singlet Oxygen

Tetrapyrroles, including derivatives of porphyrins, phthalocyanines, chlorins, and bacteriochlorins, have been extensively studied as photosensitizers for singlet oxygen production. Although a number of these compounds can sensitize singlet oxygen in high quantum yields, they often require arduous or low yielding synthetic processes, display poor solubility in aqueous environments, or absorb weakly at the longer wavelengths of light most useful in photodynamic therapy. To address these challenges, we have developed a linear tetrapyrrole construct (DMBil) using a modular synthetic strategy that can support a variety of transition metals. Complexes of this tetrapyrrole with appropriately selected late transition metals are capable of generating singlet oxygen with impressive quantum yields upon irradiation with $\lambda > 500$ nm light. Additionally, certain positions of this tetrapyrrole ligand scaffold are easily addressable which has enabled the development of several water-soluble DMBil derivatives with ancillary polyethylene glycol or dextran groups. The synthesis, photophysical properties, and translation of this system from organic to aqueous and biological environments will be detailed.

31. Thomas Pangia, Johns Hopkins University, PI: David Goldberg

Evidence of Radical Rebound in a Non-Heme Model Complex

The heme enzyme Cytochrome P450 is known to hydroxylate C-H bonds using an iron (IV)-oxo π -cation radical species in a radical rebound mechanism. Hydrogen atom transfer is followed by oxygen rebound to form a C-O bond and the reduced iron product. Non-heme iron enzymes such as the α -ketoglutarate dependent dioxygenases perform similar oxidations utilizing iron (IV)-oxo species. In the case of heme and non-heme model complexes, this rebound mechanism is not widely studied. It has been suggested that some non-heme iron model complexes favor a non-rebound mechanism to perform these oxidations. Evidence has also been indirectly observed by others to suggest that a rebound mechanism may be possible in other non-heme iron complexes. Herein is described the synthesis of a new 5-coordinate derivative of N_4Py with a phenolate appendage and a labile 6th coordination site, $[Fe^{II}N_3PyO_2Ph(MeCN)]^+$. Exposure to oxygen in methanol produces the methoxo non-heme iron complex, $[Fe^{III}N_3PyO_2Ph(OMe)]^+$ which provides a platform to directly observe rebound activity. Reaction between this Fe^{III} complex and the organic carbon-based triphenylmethyl radical ($Ph_3C\bullet$) formed the expected rebound product triphenylmethyl methyl ether (Ph_3COMe). Monitoring by UV-vis, EPR, and 1H NMR produced direct evidence of rebound.

32. Grace Panetti, University of Pennsylvania, PIs: Patrick Walsh, Eric Schelter

Using the ZnEt Shibasaki framework $[RE(ZnEtTHF)_3BINOLate_3]$ for the synthesis of chiral propargylic alcohols

The asymmetric alkylation of aldehydes is a versatile synthetic tool for the production of natural products and pharmaceuticals, however previous attempts to perform this reaction using

catalytic amounts of zinc has proved challenging^{1,2}. By using the ethyl zinc analog of Shibasaki's Rare Earth alkali Metal BINOLate (REMB) framework previously reported by our group, we have succeeded in performing the first asymmetric alkylation of aldehydes catalytic in Zinc³. Most often REMB frameworks are used for Lewis acid-Bronsted-base or Lewis acid-Lewis base catalysis in reactions like chiral Michael additions and similar aldol reactions⁴. Using this protocol, we observe excellent conversion to product and enantio excesses (between 70-99%) with moderate catalyst loadings of 5-10 mol%. These results exceed the previous work done by Trost of enantioselective alkylation in both scope and atom economy⁵. This work paves the way for using modified REMB frameworks for more varied reactivity.

1. Frantz, D. et. al. *Acc. Chem. Res.* **2000**, *33*, 373-381.
2. Trost, B. M.; Quintard, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 6704-6708.
3. Nieto, I. et. al. *Organometallics* **2013**, *32*, 7431-7439.
4. Robinson, J. R. et. al. *J. Am. Chem. Soc.* **2014**, *136*, 8034-8041
5. Trost, B. M. et. al. *Chem. Eur. J.* **2012**, *18*, 16498-16509.

33. Owen O'Sullivan, Temple University, PI: Michael Zdilla

Synthesis of Novel Manganese(II)-tetrazole Clusters as Potential High-energy Density Materials (HEDMs)

There is a current need for novel high-energy-density materials (HEDMs) for the national defense that possess increased shattering potential for focused target strikes to decrease collateral damage. Current high energy materials are primarily CHNO based molecular or ionic species containing low-oxidation state atoms (carbon, amine-nitrogens) in close proximity to high-oxidation state atoms (nitro-nitrogens) creating a redox-frustrated compound. Release of energy occurs upon atoms reaching their most stable oxidation states in the products, liberating heat and work. In order to breach the theoretical ceiling for energy density in CHNO-based explosives, inclusion of stronger oxidative moieties is necessary. In comparison to nitro-groups, high-oxidation state transition metals are able to store more energy and thus increase the energy-density of these compounds. A series of manganese(II)-tetrazole clusters have been synthesized through protolysis of amine-functionalized tetrazoles with manganese bis(trimethylsilyl)amide. Tetrazoles are nitrogen-rich ligands possessing good thermal stability as well as containing multiple donor sites to promote bridging interactions for aggregation into clusters. Even though these compounds do not possess high-oxidation state manganese, they have already shown initial promise as energy dense materials. Characterization, thermal stabilities, and explosive properties will be discussed.

34. Joshua Nelson, University of Pennsylvania, PI: Eric J. Schelter

H₃TriNO_x Derivatives for Improved, Simplified Separation of Rare Earth Elements

Rare earth (RE) metals are crucial components of many types of modern technology, including smartphones, wind turbines, and electric vehicles. The increased use of these technologies and the supply risk for the metals calls for strategies to recycle end of life materials containing them. New recycling methods have become essential, as recently stated by both the U.S. Department

of Energy, and the E. U. Commission.¹ Our group has recently reported the TriNOx³⁻ ligand framework, which has been found to induce the dimerization of certain rare earth element complexes from RE(TriNOx)(THF) into [RE(TriNOx)]₂.² We have found that differences in solubility for the dimer and monomer can be exploited for separations, due to large differences in the equilibrium constant for the dimerization.² In this work, the synthesis of a series of substituted [{"(2-RNOH)C₆H₄CH₂}N] (H₃TriNOx^R) ligands, where R = Ad, Ph, *p*-MeOPh, *p*-CF₃Ph is reported. It is expected that substitution of the *t*-butyl moiety of the ligand framework will perturb the geometry of the hydroxylaminate aperture in RE(TriNOx^R) complexes, thus altering the dimerization equilibria to achieve the separation of other rare earth elements, such as yttrium and europium, as well as tune the electronic properties of the complexed metal to achieve new reactivity.

- (1) U.S. Department of Energy, Critical Materials Strategy, Washington, DC, 2011, 1–191.
- (2) Bogart, J. A.; Lippincott, C. A.; Carroll, P. J.; Schelter, E. J. *Angew. Chem.* **2015**, *127* (28), 8340–8343.

35. Kim Mullane, University of Pennsylvania, PI: Eric Schelter

Synthesis of a Uranium(IV) Terminal Imido Metallacycle Complex: Uranium Coordination Chemistry with a PN Pincer Ligand

Uranium(IV) complexes supported by a pincer ligand, PN⁻ = (*N*-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide), were synthesized and characterized. The PN ligand used here was developed by the Mindiola group and has been used to support the first discrete titanium nitride moiety. We have now used the PN ligand to support a uranium(IV) terminal imido complex. Complex (PN)₂U^{III}I (**1**) showed a high propensity for disproportionation reactions. Upon reaction of **1** with one equivalent of sodium azide (PN)₂U^{IV}(N₃)₂ (**2**) was formed, presumably accompanied by deposition of uranium metal. To give more rational reactivity, we synthesized (PN)₂U^{IV}Cl₂ (**3**), which gave **2** through a salt metathesis reaction with two equivalents of sodium azide. Reaction of **2** with potassium graphite yielded [K(THF)₃][U(=NH)[PⁱPr₂(C₆H₅Me)N(C₆Me₂CH₂)](PN)] (**4**), a uranium(IV) metallacycle with a terminal imido moiety. The most likely reaction pathway for the production of **4** involves the formation of a uranium(IV) nitride, which then deprotonates the mesityl ring to form the uranium(IV) imido metallacycle. Prospects for reactivity of this unusual terminal imide will also be discussed.

36. Jeremy McGale, Johns Hopkins University, PI: David Goldberg

Exploring Mechanistic Details for Arene Hydroxylation by a Nonheme Iron Complex: Pursuit of an Fe(III)OH

An FeIV(O) was previously trapped and characterized at -20 °C using pentadentate ligand with strategically designed fluorinated arene groups in the second coordination sphere. Upon warming of the FeIV(O) complex, an unprecedented arene C–F hydroxylation reaction occurs. In the pursuit of an FeIII(OH) complex to clarify the electronic pathway of this reaction, reactivity of

the related FeIOH complex was explored. Herein four novel structures are reported from these oxidation reactions and their potential for future work involving halogenase modeling.

37. Jeffrey McCall, Temple University, PI: Michael Zdilla

X-ray diffraction solution to a previously unsolvable manganese(VI) dimer $[Mn(NBu^t)_2(\mu-NBu^t)]_2$

The neutral manganese(VI) dimer $[Mn(NBu^t)_2(\mu-NBu^t)]_2$ **1** was a twinned crystal that previously could not be solved via X-ray diffraction by Danopoulos and Wilkinson. It has now been solved using modern software techniques. This poster will illustrate the problems faced by crystallographers and the tools available to them to overcome them. A new synthetic route for preparation of **1** through reaction of $[Li(thf)]_2[Mn(N)(NBu^t)_3] \cdot LiCl$ with 1,3-di-*tert*butyl-5-amino-tetrazolium perchlorate is also examined.

38. Gabriel Andrade, University of Delaware, PI: Joel Rosenthal

The Development of Electrochemiluminescent Platforms for Detection of Biomolecule Binding

Gabriel Andrade, Rachel C. Pupillo, Alize Marangoz, Jiyeon Kim, Wenbo Wu, Joel Rosenthal

Many biological activities, including cell division, cell death, immune response and intercellular communication rely on a cascade of complex non-covalent interactions between DNA, proteins and other biomolecules. Current efforts in our lab are aimed at development of new platforms to detect and monitor these interactions using a combination of electrochemical and spectroscopic techniques. Toward this end, we are developing the fundamental chemistry required to build multielectrode arrays onto which large biomolecules such as DNA and transcription-factor binding proteins can be immobilized onto optically transparent conducting surfaces. The success of such bioconjugate interfaces is reliant on the use of robust and well-defined linkages that have topologies that we have identified as being optimal for interfacial charge transfer. Similarly, we have worked to develop methods to incorporate redox and photochemically active probes onto these conducting surfaces and the biomolecules anchored on these platforms. Recent progress on the construction of these platforms and their incorporation into multielectrode arrays will also be highlighted.

39. Jennifer Lee, University of Pennsylvania, PI: Christopher B. Murray

Bimetallic Nanocrystals for Hydrodeoxygenation of 5-Hydroxymethylfurfural

The 2,5-dimethylfuran (DMF), as a promising candidate for biofuel application, is obtained from the hydrodeoxygenation (HDO) of 5-hydroxymethylfurfural (HMF). A suitable catalyst is the keystone for realizing this process with high yield, in which the bimetallic catalysts have been emerging as one of the most promising materials with enhanced selectivity. In this contribution, monodisperse Pt and Pt-M (M = Mn, Fe, Co, Ni) nanocrystals (NCs) with tunable compositions are synthesized via solvothermal methods. Plasma cleaning and thermal annealing are applied on

carbon supported NC catalysts to remove surface ligands and facilitate the reacting surface area. A complete understanding of the composition dependent catalytic activity of as-prepared NC catalysts is confirmed through a continuous flow reactor and a strong correlation between HDO catalytic activities and the composition was observed, and particularly, a selectivity of 98% for DMF was achieved under optimized reaction condition. This work provides the insight of how variation in composition of bimetallic catalysts gives us the possibility of tailoring the selectivity for DMF.

40. Subrata Kundu, Georgetown University, PI: Timothy H. Warren

Mechanistic Insights into NO to N₂O transformation at a Mononuclear Nickel Site

Nitrous oxide (N₂O) is a long-lived (~114 years) greenhouse gas with 298 times global warming potential per molecule as compared to that of CO₂. Global emission of N₂O is mainly attributed to biological denitrification and fossil fuel combustion. The most critical step in microbial denitrification route for N₂O formation is the transition metal mediated reductive coupling of two nitric oxide (NO) molecules. During denitrification, either iron or copper containing nitrite reductase (NiR) enzymes catalyze the reduction of nitrite (NO₂⁻) to nitric oxide (NO). Surprisingly, Cu-NiR exhibits dual-activity and can also participate in reductive N-N coupling of two NO moieties leading to N₂O under high NO flux. The X-ray crystal structure of Cu-NiR active site shows a side-on {CuNO}¹¹ complex; however, the previously reported model Cu-nitrosyl complexes are found to be end-on. To demonstrate the role of non-covalent interactions in governing the transition-metal nitrosyl binding modes, we employ an electron-poor β-diketiminato-Ni core that allows to synthetically access a {NiNO}¹⁰/[{NiNO}¹¹]⁻ redox-couple. Specifically, one-electron reductions of the neutral {NiNO}¹⁰ species by KC₈ in presence of different cryptands, such as 18-crown-6, [2.2.2]-cryptand afford anionic {NiNO}¹¹ cores with corresponding [K⁺] counter-cations ([K⁺] = K⁺[cryptand]). X-ray diffraction analyses on these [K⁺]{NiNO}¹¹ complexes exhibit the involvement of both side-on and end-on anionic {NiNO}¹¹ cores depending on the solvation of the potassium cation by 18-crown-6, [2.2.2]-cryptand, respectively. Addition of one equivalent of NO to these well-defined anionic {NiNO}¹¹ complexes result immediate formation of anionic [Ni](κ²-O₂N₂) species, thereby demonstrating that {MNO}¹¹ cores are prone to undergo N-N reductive coupling with NO and form *cis*-hyponitrite complexes [M](κ²-O₂N₂). Finally, protonation of the anionic [Ni](κ²-O₂N₂) species results in a quantitative N₂O evolution.

41. Connor Koellner, Temple University, PI: Michael Zdilla

Reactive Unchelated Manganese Cluster Biomimics of the Oxygen Evolving Complex

We hypothesize that manganese clusters with lower coordination numbers and reduced chelation will produce systems with unprecedented multi-Mn reactivity and uncover fundamental reactivity properties relevant to the oxygen evolving complex. We propose the use of imido ligands (RN²⁻), which are isolobal and isovalent to O²⁻ and offer a similarly sized heteroatom. Imido ligands can be tuned through organic (R) groups to vary sterics and electronics resulting in alteration of the corresponding coordination chemistry. Current studies have

examined the reaction of $\text{Li}_2\text{N}^t\text{Bu}$ with MnF_3 . When reaction conditions include THF and a 1:1 mixture of THF and toluene, $\text{MnLi}_2(\text{NH}^t\text{Bu})_4$ is observed. This product is supported by crystal structures and suggests C-H bond activation through the reduction of Mn(III) to Mn(II); proposed mechanisms of reactivity will be discussed.

42. Hyun Kim, Johns Hopkins University, PI: Kenneth D. Karlin

The Synthesis of New Porphyrin to Model Systems for Cytochrome c Oxidase

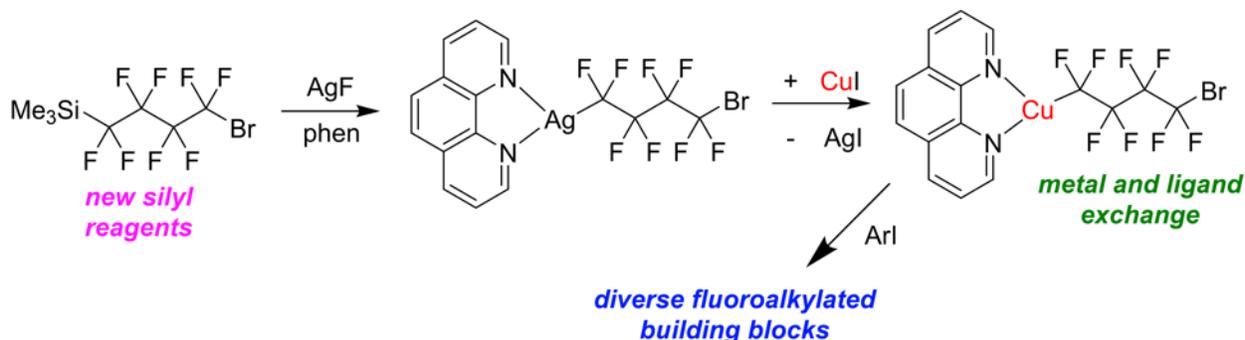
Cytochrome c oxidase (CcO), a terminal enzyme of the respiratory chain of mitochondria and many bacteria, is a key enzyme of aerobic respiration that catalyzes dioxygen reduction coupled with a proton-pumping process. The O_2 reduction site includes a high-spin heme A (heme a_3) and a copper ion (Cu_B). CcO takes electrons from a soluble iron-containing electron transfer protein, cytochrome c, and passes them on to dioxygen which is reduced to water following the reaction: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. The heme a_3/Cu_B binuclear active site in CcO, where O_2 reduction occurs involving O-O cleavage, has been of much interest. Cu_B is chelated with three histidine residues, one of which is covalently cross-linked to a tyrosine that is believed to be responsible for O-O cleavage as a H-atom donor. To contribute to a better understanding of the chemistry occurring at the CcO active site, we have carried out studies where we synthesize biomimetic heme and copper complexes and study their reactivity toward O_2 . We describe here the design of a binucleating ligand, P^{ImH} , possessing a partially fluorinated tetraaryl porphyrinate and with a covalently linked tridentate chelate which includes a histamine moiety. The structure of a Fe(II) complex of P^{ImH} , $[(\text{P}^{\text{ImH}})\text{Fe}^{\text{II}}]$, has been determined by single crystal X-ray crystallography, where the tethered imidazolyl donor is axially bound to the Fe^{II} center. $[(\text{P}^{\text{ImH}})\text{Fe}^{\text{II}}]$ reacts with dioxygen to form a low-temperature stable Fe(III) superoxo intermediate $[(\text{P}^{\text{ImH}})\text{Fe}^{\text{III}}(\text{O}_2^{\bullet-})]$, which was characterized by UV-Vis and NMR spectroscopy. Insertion of copper(I) into $[(\text{P}^{\text{ImH}})\text{Fe}^{\text{II}}]$ led to changes in the UV-Vis and ^1H -NMR spectra, indicating that the complex $[(\text{P}^{\text{ImH}})\text{Fe}^{\text{II}}\text{Cu}^{\text{I}}]^+$ formed and is in a high-spin state, having THF as an axial ligand base. We have focused and will present data concerning the heme-peroxo-copper complex dioxygen binding and reduction chemistry, when paired with appropriate reagents for transferring of protons and/or electrons.

43. Peter Kaplan, Lehigh University, PI: David A. Vicic

Versatile Route to Arylated Fluoroalkyl Bromide Building Blocks

Metal mediated processes have been shown to be effectual pathways for installation of fluoro- and trifluoromethyl- moieties onto organic molecules. However, fluorinated molecules containing repeating difluoromethylene groups are still forthcoming. Recently, routes to symmetrically disubstituted fluoroalkyl chains and fluoroalkyl-containing ring systems have been reported, but the preparation of building blocks for the construction of unsymmetrically disubstituted chain derivatives remains challenging. Here, we report novel difunctionalized fluoroalkylated reagents for the synthesis of arylated fluoroalkyl bromide building blocks. These silyl reagents can be used to prepare isolable $[(\text{phen})\text{Ag}(\text{CF}_2)^n\text{Br}]$ intermediates capable of transferring both the phenanthroline ligand and the fluoroalkyl bromide chain to copper iodide,

eliminating the need for a preligated copper salt precursor. The copper species can then go on to react with aryl iodides to form the targeted building blocks. The methodology is compatible with various chain lengths of the fluoroalkyl halide functionality.



44. Yi Jin, University of Pennsylvania, PI: Eric J. Schelter

Hexachlorocerate(III) Complexes as Photoreductants for Aryl Halides

Yi Jin, Haolin Yin, Kimberly C. Mullane, Jerald E. Hertzog, Patrick J. Carroll, Brian C. Manor, Jessica M. Anna, Eric J. Schelter

The utilization of light energy to drive organic transformations relies on the efficient photochemical generation of important radical intermediates.¹ Aryl radicals, owing to their considerably low redox potentials (for example, $\text{PhCl}^-/\text{PhCl}$, -3.28 V vs. $\text{Cp}_2\text{Fe}^{+/0}$ in DMF), pose a challenge for the majority of reported molecular photoreductants.^{2,3} As such, attention has been focused on the development of strongly reducing photoreductants. Previous work by our group has shown that luminescent Ce(III) complexes possess strongly reducing metalloradical character in their excited states, affording photochemical halogen atom abstraction reactions from sp^3 and sp^2 C–X (X = Cl, Br, I) bonds.⁴ In this work, further investigation into reducing ability, benchtop stability and synthetic simplicity of Ce(III) species has resulted in the discovery of the UVA photosensitizing ability of $[\text{NET}_4]_3[\text{Ce}^{\text{III}}\text{Cl}_6]$ in acetonitrile. The $[\text{Ce}^{\text{III}}\text{Cl}_6]^{3-}$ anion, characterized by single crystal X-ray diffraction and cyclic voltammetry, exhibits a high quantum yield of 0.61(4), low excited-state reduction potential of -3.45 V (versus $\text{Cp}_2\text{Fe}^{+/0}$) and fast quenching kinetics towards organohalogenes. It has been shown that $[\text{Ce}^{\text{III}}\text{Cl}_6]^{3-}$ is the active species involved in the reductive dehalogenation, while UVA light is thermodynamically required to access the low reduction potential of aryl chlorides.

References:

- (1) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., *Chem. Rev.* **2013**, *113*, 5322-5363.
- (2) Pause, L.; Robert, M.; Savéant, J.-M., *J. Am. Chem. Soc.* **1999**, *121*, 7158-7159.
- (3) a) Harkins, S. B.; Peters, J. C., *J. Am. Chem. Soc.* **2005**, *127*, 2030-2031;
b) Sattler, W.; Ener, M. E.; Blakemore, J. D.; Rachford, A. A.; LaBeaume, P. J.; Thackeray, J. W.; Cameron, J. F.; Winkler, J. R.; Gray, H. B., *J. Am. Chem. Soc.* **2013**, *135*, 10614-10617.
- (4) Yin, H.; Carroll, P. J.; Anna, J. M.; Schelter, E. J., *J. Am. Chem. Soc.* **2015**, *137*, 9234-9237.

45. Sarah Jenny, Villanova University, PI: Deanna L. Zubris

Synthesis and Characterization of Iron(II) Catalysts for Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) uses a metal catalyst, often based on copper, to mediate controlled radical polymerization and produce styrenic and acrylic polymers with a narrow polydispersity. Prior studies by Gibson revealed that imino(pyridine) and amino(pyridine) iron (II) complexes can have modest ATRP activity, where the most electron-rich ligands in these studies displayed the highest ATRP activity. Our group has targeted a set of iron(II) complexes with electron-rich nitrogenous ligands with the goal of achieving ATRP utility. We have isolated and characterized examples of monomeric, dimeric, and bis-ligated cationic iron(II) complexes, and have tested these as polymerization catalysts for styrene. Our work suggests Catalytic Chain Transfer (CCT) is a competing mechanism versus ATRP when using these complexes. Current work is focused on identifying the parameters that help favor ATRP versus CCT for our catalysts to help drive future catalyst development.

46. Christine Iseley, Georgetown University, PI: Timothy H. Warren

{M(NO)}¹¹ Metal-Nitrosyls in cis-Hyponitrite and N₂O Formation

During the process of denitrification, copper nitrite reductase converts nitrite (NO₂⁻) to nitric oxide (NO) at type 2 copper active sites found in types of proteobacteria.¹ At high concentrations of NO, however, N₂O is formed via disproportionation of NO. This behavior has been previously modeled with tris(pyrazolyl)borate copper complexes TpCu(NO) which possess a {Cu(NO)}¹¹ configuration.² Based on recent work with β-diketiminato [{Ni(NO)}¹¹]⁻ species, we have identified that such species may possess novel η² “side-on” bonding as well as react instantaneously with NO to form cis-hyponitrite complexes {[Ni](κ²-O₂N₂)}. In this work we explore our hypothesis that {M(NO)}¹¹ complexes are inherently unstable towards reaction with NO to form cis-hyponitrites {M(κ²-O₂N₂)}.¹¹ In a combined synthetic and computational study, we employ tripodal tris(pyrazolyl)borate (Tp) and tris(pyrazolyl)methane (Tpm) ligands as well as planar terpyridine (terpy) and 2,6-pyridinediamide (PDA) to examine nickel and copper {M(NO)}¹⁰ and {M(NO)}¹¹ complexes and their conversion to cis-hyponitrite species [M](κ²-O₂N₂).

- 1) Maia, L.B.; Moura, J.J. *Chem. Rev.* (2014) 114, 5273.
- 2) Merkle, A.C.; Lehnert, N. *Dalton Trans.* (2012) 41, 3355.

47. Valiallah Hosseininasab, Alexander Gee, Georgetown University, PI: Timothy H. Warren

Interconversion of Nitrite and S-Nitrosothiols at Zinc

Nitric oxide (NO) is an important signaling molecule which plays numerous biological roles such as vasodilation, angiogenesis and other significant biological functions. Recently, it has been

found that H₂S also serves as signaling molecule exhibits cross talk with NO under biological conditions, ultimately generating HNO.¹ Moreover, reaction of H₂S with NO as well as nitrite (NO₂⁻)² under acidified conditions leads to the formation of simplest S-nitrosothiol, HSNO.³

Since carbonic anhydrase which possesses a His₃Zn²⁺ active site has been shown to convert nitrite to NO, we have been interested in modeling this behavior with tris(pyrazolyl)borate zinc complexes TpZn(NO₂). We have previously shown that ^{iPr}2TpZn(NO₂) reacts with thiols RSH to give ^{iPr}2TpZn-SR and RSNOs which thermally decay to NO.⁴ Thus, we have begun to examine the possibility of HSNO formation at zinc that may lead to the thionitrite anion (SNO⁻), enhanced by Lewis acid activation of bound nitrite. We will describe our efforts to generate HSNO at TpZn complexes involving TpZn(NO₂), TpZn-SH, and TpZn-OH complexes as well as their additional activation with the potent Lewis acid B(C₆F₅)₃.

References:

- [1] Eberhardt, M.; Dux, M.; Namer, B.; Miljkovic, J. L.; Cordasic, N.; Will, C.; Kichko, T. I.; de la Roche, J.; Fischer, M.; Suárez, S. A.; Bikiel, D.; Dorsch, K.; Leffler, A.; Babes, A.; Lampert, A.; Lennerz, J. K.; Jacobi, J.; Martí, M. A.; Doctorovich, F.; Högestätt, E. D.; Zygmunt, P. M.; Ivanovic-Burmazovic, I.; Messlinger, K.; Reeh, P.; Filipovic, M. R. *Nat. Commun.* **2014**, DOI: 10.1038/ncomms5381.
- [2] Filipovic, M. R.; Miljkovic, J. L.; Nauser, T.; Royzen, M.; Klos, K.; Shubina, T.; Koppenol, W. H.; Lippard, S. J.; Ivanovic-Burmazovic, I. *J. Am. Chem. Soc.* **2012**, *134*, 12016-12027.
- [3] Ivanova, L.V.; Anton, B. J.; Timerghazin, Q. K., *Phys. Chem. Chem. Phys.*, **2014**, *16*, 8476-8486.
- [4] Cardenas, A. J. P.; Abelman, R.; Warren, T.H, *Chem. Commun.* **2014**, *50*, 168-170.

48. Nicholas J. Greybush, University of Pennsylvania, PI: Christopher B. Murray and Cherie R. Kagan

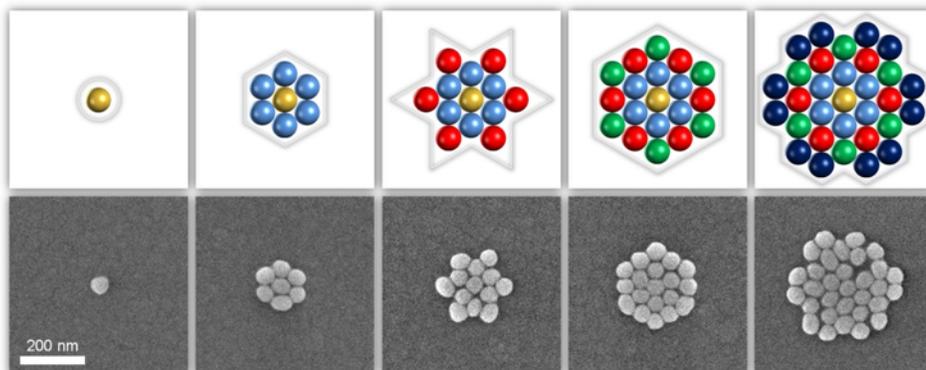
Plasmon Resonances in Self-Assembled Two-Dimensional Au Nanocrystal Metamolecules

Nicholas J. Greybush¹, Iñigo Liberal², Ludivine Malassis³, James M. Kikkawa⁴, Nader Engheta^{1,2,4,5}, Christopher B. Murray^{1,3}, and Cherie R. Kagan^{1,2,3}

Department of Materials Science and Engineering¹, Department of Electrical and Systems Engineering², Department of Chemistry³, Department of Physics and Astronomy⁴, Department of Bioengineering⁵, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

We explore the evolution of plasmonic modes in two-dimensional nanocrystal oligomer clusters as the number of nanocrystals is systematically varied. Precise, hexagonally-ordered Au nanocrystal oligomers with 1–31 members are assembled via capillary forces into polygonal topographic templates defined using electron-beam lithography. The visible and near-infrared scattering response of individual clusters is determined with spatially resolved, polarized darkfield scattering spectroscopy. We observe a strong red-shift in plasmon resonance wavelength as the number of nanocrystals per cluster increases, in agreement with theoretical predictions. Simulations also elucidate the modes supported by the clusters, including electric

dipole and magnetic dipole responses, their coherent superposition, and the excitation of higher-order modes. The progression of structures studied here advances our understanding of fundamental plasmonic interactions in the transition regime between few-member plasmonic metamolecules and extended two-dimensional arrays.



**49. Jesse B. Gordon, Alison C. McQuilken, Maxime A. Siegler, Johns Hopkins University,
PI: David Goldberg**

Dioxygen Activation by Nonheme Thiolate-Ligated Mononuclear Iron Complexes

Mononuclear nonheme iron oxygenases are O_2 activating metalloenzymes that are implicated in a diverse array of critical metabolic pathways. One subclass of these oxygenases are thiol dioxygenases (e.g., cysteine dioxygenase), which catalyze the oxidation of thiols to sulfinic acids. Despite years of experimental and computational work on the native enzymes, explicit mechanistic details for sulfur oxygenation by thiol dioxygenases remains elusive. In order to better elucidate the key structural, spectroscopic, and mechanistic properties of these enzymes, a series thiolate-ligated mononuclear nonheme iron model complexes have been synthesized. The synthesis and O_2 reactivity of these complexes are presented here.

50. Natalie Gogotsi, University of Pennsylvania, PI: Christopher B. Murray

Analysis of structural and electronic properties of CdS/CdSe nano-heterostructures and their assemblies

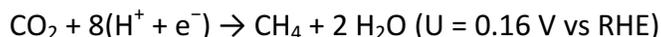
Heterostructured nanoparticles, including core-shell and dot-in-rod structures, have been garnering interest for their potential in applications including lighting/displays, solar concentration, photocatalysis, and photodetectors. One important aspect is that their structure and electronic properties can be synthetically tuned to control quantum yields, optical polarization, self-assembly, photocatalytic activity, etc. This work focuses on nanorod heterostructures containing a CdSe quantum dot core with surrounding CdS shell. It aims to elucidate various structural and electronic properties and their effects on assembly through a combination of nanoparticles and characterization techniques providing a more complete understanding of the materials.

Using ultrafast time-resolved photoluminescence spectroscopy, we studied the dynamics and efficiency of hole transfer to the core versus potential for trapping and have found efficient transfer of the photoexcited holes from the shell to the core, suggesting that non-ideal quantum yields result from parasitic trapping at longer time scales. Alongside electronic studies, we have conducted a variety of structural characterizations to clarify previously disputed properties of these heterostructures. These heterostructures have an overall polarity from the faceted rod structure and it's been suggested that there should be systematic alignment of the dipoles within a self-assembled structure. However, our studies of assembled monolayers have shown that there is random alignment with regards to the polarization. Without the presence of external stimuli, dipole forces do not direct the self-assembly of these nanorods. It is possible that with the addition of an electric field, such as through electrophoretic deposition, the polarity of the rods would have a role in the formation of assembled structures and this is currently being explored in greater detail, focusing on characterizing the effects of nanorod lengths, ligand chemistry, and polarity on the directed assembly.

51. Timothy A. Goetjen, Karin U. D. Calvino, Dr. Anders B. Laursen, Rutgers University, PI: G. Charles Dismukes

Tuning the Selectivity of a CO₂ Reduction Reaction Copper Catalyst

Finding effective catalysts to convert carbon dioxide to hydrocarbons and water using renewable electricity or solar energy can decrease our dependence on fossil fuels. Electrochemical CO₂ reduction has been demonstrated to form useful products such as alkanes on copper. The electroreduction half-reaction to methane is shown below.



This technology is still pre-commercial and limited from making significant impact by the low selectivity for a single hydrocarbon product, along with the high overpotential required to drive the reaction.

In the present work, we use the exposed surface facets and nanoscale architecture of copper to tune the product distribution of hydrocarbons (CH₄ and C₂H₄). Polydisperse crystalline copper nanowires were synthesized through a wet chemistry route and characterized through PXRD and SEM. The electrocatalytic activity of the copper nanowires was tested using an ink that was drop-casted on a glassy carbon electrode and used as the working electrode for carbon dioxide reduction. To determine the Faradaic yield of the reaction, the amount of charge used during the reaction was recorded, and gas chromatographs were taken both before and after the reaction to quantify the gas-phase reaction products. Higher selectivity for ethylene and lower methane production were seen with copper nanowires in comparison to copper foil. We hypothesize that two main factors influence selectivity of the reaction: roughness of the surface due to the nanowire morphology and the formation of a metastable copper(I) oxide layer on the catalyst due to air exposure that increases the binding energy of a carbon monoxide intermediate.

52. Douglas Gisewhite, Alexandra Nagelski, Nam Nguyen, Bryn Mawr College, PI: Sharon J. N. Burgmayer

The Investigation of Cyclization Dynamics in Molybdenum Cofactor Models

The pyranopterin dithiolene ligand is specific to mononuclear molybdenum (Mo) and tungsten (W) enzymes, and participates in global geochemical cycles and metabolism. The active site of mononuclear Mo and W enzymes, which is composed of one Mo or W ion and one or two pyranopterin dithiolenes, predominantly catalyzes oxygen atom transfers (OAT) and spans a reduction potential range of approximately one volt. Crystal structures of several bacterial molybdoenzymes suggest the pterin dithiolene can exist in both a tricyclic and bicyclic state.[1] Interconversion of the two states has been thought to play a role in the catalytic mechanism of the molybdenum cofactor (Moco). Recently, we reported the development of synthetic models incorporating a pterin dithiolene ligand with the ability to undergo a dynamic cyclization/scission process dependent on solvent dielectric.[2] Here, we present our recent results from a new model derivative, [TEA][Tp*Mo(O)(S2BDMPP)] where TEA is tetraethylammonium, Tp* is tris(3,5-dimethylpyrazolyl)hydroborate, and BDMPP is 6-(3-butynyl-2,2-dimethyl)-2-pivaloyl pterin. This model system was designed to prevent cyclization of the pyran ring. The electronic effects of pyran cyclization, and prevention, at Mo were compared through spectroscopic studies, electrochemical characterization, and theoretical methods on our newly synthesized Moco model, as well as that reported by Williams and coworkers in 2012.[3] Data from vibrational spectroscopy (FTIR) and electrochemistry (CV) provide experimental evidence of electronic structure variation controlled by pyran cyclization affecting pterin conformation relative to the dithiolene.

[1] Bertero, M.G.; Rothery, R.A.; Palak, M.; Hou, C.; Lim, D.; Blasco, F.; Weiner, J.H.; Strynadka, N.C.J.; *Nat. Struct. Bio.* 2003, 10, 9, 681-7.

[2] Williams, B. R.; Gisewhite, D.; Kalinsky, A.; Esmail, A.; Burgmayer, S. J. N.; *Inor. Chem.* 2015, 54, 8214-22.

[3] Williams, B.R.; Fu, Y.; Yap, G.P.A.; Burgmayer, S.J.N.; *J. Am. Chem. Soc.*, 2012, 134, 19584-7. NIH (GM081848) and NSF (CHE-0958996) are recognized for financial support.

53. Michael Gau, Temple University, PI: Michael Zdilla

Self-assembled, Labile, Multinuclear Manganese Clusters Inspired by the Oxygen-Evolving Complex

In nature, photosynthetic organisms utilize H₂O as a primary resource to produce O₂ and obtain e⁻ and H⁺, which are further used to build complex molecules. Biophysical analytical techniques have revealed the active site to be the oxygen-evolving complex or OEC. The structure of the OEC is identified as a Mn₄CaO_x distorted cubane metal cluster. Ever since its discovery, researchers have been synthesizing OEC models without the use of complex proteins in hopes of mimicking the structure and function of the OEC. These models aim to allow investigators to elucidate mechanisms, structures and test reactivity with fewer complications. Most OEC models to date

have been synthesized using chelating ligands that hinder the reactivity and flexibility of the Mn complexes due to full coordination on the metal center. A series of tri- and tetra- manganese clusters have been synthesized using substituted pyridines and polyoligomeric silsesquioxane (POSS) compounds as terminal ligands. These bi- and tri-dentate ligands provide an increase in stability, but maintain the reactivity of the clusters. More specifically, the manganese clusters are more robust to air exposure and do not decompose fully or as quickly as the unchelated complexes. Magnetic properties of the complexes and further characterization will be discussed.

54. Evan Gardner, Georgetown University, PI: Timothy H. Warren

Isolation of a Dinitrogen Dicopper(I) Complex via a Mixed-Valence Dicopper Hydride

Transition metal mediated reduction of dinitrogen (N_2) to ammonia (NH_3), a process that underpins the growth of modern society, relies on the coordination of dinitrogen to a transition metal preceding multi-electron and multi-proton transfer to dinitrogen. While most transition metal dinitrogen complexes employ early to mid-transition metals, we have recently isolated an unusual dicopper dinitrogen complex. The tris(pyrazolyl)borate copper(I) dinitrogen complex $[^{iPr_2}TpCu]_2(\mu-1,2-N_2)$ forms in the low temperature reaction of $[^{iPr_2}TpCu]_2(\mu-OH)_2$ with two equiv. triphenylsilane under a dinitrogen atmosphere. Only slight activation of N_2 ligand is evident by X-ray crystallography (N-N: 1.111(6) Å) and Raman spectroscopy ($\nu_{N_2} = 2130\text{ cm}^{-1}$). DFT studies of mono- and dinuclear copper dinitrogen complexes reveal a modest degree of cooperativity in the dinuclear $[Cu]-N_2-[Cu]$ interaction. Nonetheless, the N_2 is held weakly: addition of MeCN, $CNAr^{2,6-Me_2}$, and O_2 results in the formation of $^{iPr_2}TpCu-L$ ($L = MeCN, CNAr^{2,6-Me_2}$) or $[^{iPr_2}TpCu]_2(\mu-\eta^2:\eta^2-O_2)$. The addition of a single equivalent of triphenylsilane or triethylsilane in pentane at low-temperature to $[^{iPr_2}TpCu]_2(\mu-OH)_2$, allows for the isolation of the mixed valence intermediate $[^{iPr_2}TpCu]_2(\mu-H)$ that thermally decays to $[^{iPr_2}TpCu]_2(\mu-1,2-N_2)$. This dicopper hydride reduces unsaturated substrates such as CO and phenylacetylene to formaldehyde and styrene, respectively.

Interestingly, addition of hydrazine to $[^{iPr_2}TpCu]_2(\mu-1,2-N_2)$ gives the known diazene complex $[^{iPr_2}TpCu]_2(\mu-1,2-N_2H_2)$, illustrating the ability of the TpCu fragment to support both N_2 and as well as the highly reactive, $2 e^-$ reduced N_2H_2 species. Future efforts involve the incorporation hydrogen bond acceptors into the Tp scaffold to promote the reduction of bound N_2 ligands to N_2H_2 , N_2H_4 , and NH_3 via proton-coupled electron transfer reactions.

55. Anastassia D. Gallo, Temple University, PI: Ann M. Valentine

Improving the Efficiency of Nicatransferrin Expression

A monolobal transferrin, nicatorferrin, was identified in the primitive ascidian species *Ciona intestinalis*. Nicatransferrin helps in understanding how nature evolved to manage hydrolysis-prone metals in oxygen-containing environments. Previously, nicatorferrin was isolated from the native organism or was expressed in and purified from yeast. Protein expression in *E. coli*

provides a faster growth rate, less expensive media, and better understood genetics than expression in yeast. A codon optimized gene for nicastransferrin in *E. coli* was obtained, which improves the protein expression by increasing the translational efficiency of the gene. A disadvantage of the *E. coli* expression system is the formation of insoluble aggregates from protein misfolding, yielding inactive protein.

56. Birane Fall, Temple University, PI: Michael Zdilla

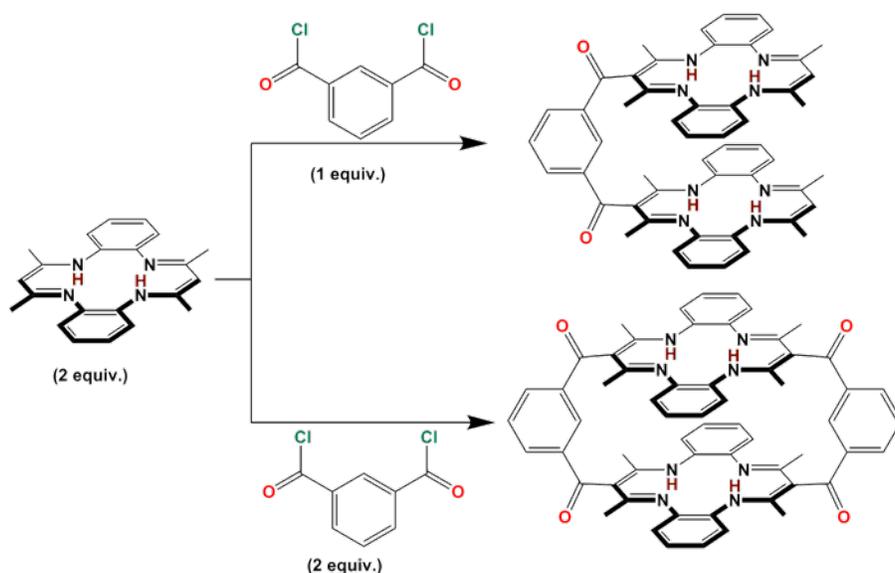
Sodium Ionic Conduction in Crystalline DMF₃NaClO₄

The energy density of lithium/sodium battery surpasses the other battery technology. There are safety issues associated with these batteries and limited use in high power applications because of flammable liquid electrolytes. There have been ongoing efforts to replace liquid electrolytes with solid electrolytes with desired properties. Solid electrolytes made with ceramic/glass has high ionic conductivity (10^{-2} - 10^{-3} S/cm) comparable to liquid electrolytes but they are brittle, poor adhesion to electrodes, difficult to process and also not stable with lithium/sodium metals. The most investigated solid electrolyte made with organic/soft polymer, polyethylene oxide/LiX suffers with low ionic conductivity which is because of high affinity of lithium to ether oxygen and also ion migration is coupled to slow back bone segmental motion of amorphous polymer network. The most viable approach for high conductivity soft solid electrolytes is the design low affinity channel walls for entrapped ions. The first such material, DMF/LiCl has the highest conductivity reported to date for a soft solid organic electrolyte. Here we report another sodium soft solid crystal DMF₃.NaClO₄ with highest room temperature ionic conductivity of 3×10^{-4} S cm⁻¹ reported to date.

57. Soumyajit Dey, Temple University, PI: Michael J. Zdilla and Bradford B. Wayland

Tethering Metal-Centered Radicals for Substrate Activations and Catalysis

Metal complexes of tetraaza-annulene (N₄²⁻) macrocyclic ligands are being evaluated as easily prepared and relatively inexpensive substitutes for porphyrin ligands in reactions of small molecule including H₂, CO, CO₂ and CH₄. Among these we target our focus towards the reduction and transformation of CO and CO₂ due to their significances in syngas chemistry as a possible means of biomass conversion to green chemicals. The expedition involves the evaluation of thermodynamic and mechanistic benchmark for reduction, coupling and hydrogenation of CO and CO₂, along with encompassing other demanding processes including C-H and O-H bond cleavage reactions of CH₄ and H₂O. Our group has got some initial results on reversible CO hydrogenation using smaller and more flexible Rh(TMTAA) as an alternative to porphyrins. Now, we seek to extend this work to tether two Rh(TMTAA) units to orient several carbon molecules and selectively couple them; which will ameliorate the benchmark of the investigation. The consequences of these comparative investigations will also be explored here.



58. Peng Cui, University of Pennsylvania, PI: Neil C. Tomson

Redox-Active Macrocycles for Base Metal Cluster Chemistry

Peng Cui, Samuel P. McCollom, Brian C. Manor, Patrick J. Carroll, Neil C. Tomson

The investigation of cluster-surface analogy using well-defined molecular catalysts are of vital importance in mimicking, understanding and modifying the activities of heterogeneous metallic surfaces. However, classical metal clusters are generally supported by strong-field ligands, which were poor mimics of the “sea-of-electrons” available on metal surfaces. It can be envisioned that redox-active macrocycles, due to their role as electron reservoirs when combined with first-row metals, are excellent candidates for studying the cluster-surface analogy. A series of macrocyclic di-nuclear complex featuring a $[(^3\text{PDI})_2\text{M}_2\text{Cl}_x\text{L}_y]^{m+}$ (PDI = pyridinediimine; for M = Cu (**1**): L = OTf, $x = 2$, $y = 2$, $m = 0$; for M = Co (**2**), Fe (**3**), Mn (**4**): L = CH₃CN, $x = y = m = 2$; for M = Cr (**5**), $x = 3$, $y = 0$, $m = 1$) core were synthesized via transmetalations with a macrocyclic precursor $[(^3\text{PDI})_2\text{Sr}(\text{OTf})_2]$. Reduction of the Fe(II) and Co(II) chloride complexes *in-situ* with KC₈ or Na(Hg) in the presence of PMe₃ led to the formation of $[(^3\text{PDI})_2\text{M}_2\text{Cl}(\text{PMe}_3)_2][\text{OTf}]$ (M = Fe (**6**), Co (**7**)), in which the $(^3\text{PDI})_2$ ligands are reduced to the dianion $[(^3\text{PDI})_2]^{2-}$ and the metal-metal bonding was observed. Reduction of the Co(II) chloride complex *in-situ* with KC₈ or Na(Hg) without PMe₃, however, generated a neutral bridging hydride complex $[(^3\text{PDI})_2\text{Co}_2\text{H}_2]$ (**8**), where the $(^3\text{PDI})_2$ ligand was also reduced as $[(^3\text{PDI})_2]^{2-}$. Interestingly, reaction of **6** with NaN₃ at room temperature directly formed a μ_2 -nitride complex $[(^3\text{PDI})_2\text{Fe}_2\text{N}(\text{PMe}_3)_2][\text{OTf}]$ (**9**) with two Fe(III) centers supported by a reduced $[(^3\text{PDI})_2]^{2-}$ macrocycle.

59. Lauren Cordeiro, University of Delaware, PI: Charles Riordan*Synthesis and Reactivity of Nickel Tetramethylcyclam Complexes with Organoselenium and Elemental Selenium*

A series of novel nickel-selenium complexes comprising of the $[\text{Ni}(\text{tmc})]^{2+}$ system with varying phenylselenolate ligands, X, where X = SeC_6H_5 , $\text{Sep-C}_6\text{H}_4\text{Cl}$, and SeC_6F_5 have been synthesized and characterized. Characterization of each complex was performed using NMR spectroscopy, Uv-vis spectroscopy, and electrospray ionization mass spectrometry (ESI-MS), as well as crystallographic structural determination by x-ray diffractometry of the $[\text{Ni}(\text{tmc})\text{SeC}_6\text{H}_5]^{2+}$ complex. Their reactions with alkyl halides, were monitored and are currently undergoing kinetic analysis. From these experiments it is evident that reaction of $[\text{Ni}(\text{tmc})\text{X}]^+$ complexes with alkyl halides gives rise to new C-Se bond formation. In addition, a bioinspired approach has been undertaken to investigate the $\text{Ni}(\text{tmc})\text{SeC}_6\text{H}_5]^{2+}$ complex and its analogous reactivity to the selenium containing enzyme glutathione peroxidase (GPx). The study thus far has shown that the $[\text{Ni}(\text{tmc})\text{SeC}_6\text{H}_5]^{2+}$ complex was successful in oxidizing the thiol cofactor to generate a disulfide bond. Further studies into nickel-selenium chemistry also indicate formation of a bridging diselenido dinickel(II) complex, $\{[\text{Ni}(\text{TMC})]_2(\text{Se}_2)\}^{2+}$ through addition of elemental selenium to the nickel(I) complex. Additional analysis of the complex seeks to provide insight into the structure of the complex, i.e. whether the diselenide adopts end-on or side-on geometry.

60. Alex M. Confer, Johns Hopkins University, PI: David Goldberg*Nitric Oxide Activation Mediated by a Thiolate-Ligated, Nonheme $\{\text{FeNO}\}^7$ Complex*

The diverse redox chemistry of a thiolate-ligated, nonheme $\{\text{FeNO}\}^7$ complex, $[\text{Fe}(\text{NO})(\text{N3PyS})]\text{BF}_4$, is presented. Aerobic photoillumination ($\lambda > 400$ nm) of this $\{\text{FeNO}\}^7$ complex in CH_3CN leads to the formation of an iron(III)-nitro complex, $[\text{Fe}^{\text{III}}(\text{NO}_2)(\text{N3PyS})]^+$, in which only one oxygen atom from O_2 is incorporated per $\{\text{FeNO}\}^7$ unit. The Fe^{III} -nitrite complex has limited stability at 23 °C and decays by oxygen atom transfer to a thiolate donor from the N3PyS supporting ligand, thus generating a mixture of $\{\text{FeNO}\}^7$ and S-oxygenated products. In methanol, by contrast, the photoinitiated reaction of $[\text{Fe}(\text{NO})(\text{N3PyS})]\text{BF}_4$ with O_2 leads exclusively to sulfur-based oxidation. This dramatic solvent dependence can be rationalized through a common $\text{Fe}^{\text{III}}\text{-O}_2^-$ intermediate that branches toward $\text{NO}\cdot$ or sulfur oxygenation depending upon its stability in protic vs. aprotic environments. The one-electron reduction of $[\text{Fe}(\text{NO})(\text{N3PyS})]\text{BF}_4$ ($E_{1/2} = -1.18$ V vs. Fc^+/Fc) with decamethylcobaltocene (CoCp^*_2) in CH_3CN to yield a rare nonheme $\{\text{FeNO}\}^8$ complex is also demonstrated and supported by UV-vis, EPR, NMR, and Resonance Raman spectroscopies. This $\{\text{FeNO}\}^8$ complex is extremely sensitive to O_2 , H_2O , $\text{NO}\cdot$, and reacts readily with weak acids (e.g., $[\text{Me}_3\text{NH}]^+[\text{BPh}_4]^-$) to afford putative $\{\text{FeN}(\text{H})\text{O}\}^8$ intermediates. Taken together, these results indicate that a mononuclear, thiolate-ligated nonheme iron center can facilitate both oxidative and reductive modes of nitric oxide activation, as well as exhibit nitrite reductase (NiR) activity using a coordinated thiolate as the reducing agent.

61. Bren E. Cole, University of Pennsylvania, PI: Eric Schelter

Rare Earth Separations: Investigation and Modification of the TriNOx ligand system

Bren E. Cole, Brian C. Manor, Patrick J. Carroll, Eric Schelter

Rare earth metals are used in many technologies, including electric vehicle batteries, wind turbines, and lighting phosphors.¹ In a 2011 criticality assessment, the U.S. Department of Energy determined that several rare earth elements are critical to the development of clean energy technologies.² Recently, attention has been focused to the recycling of products that use rare earths elements. Previous work by our group has shown that use of a tripodal hydroxylaminate ligand $[\{(2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2\}_3\text{N}]^{3-}$ (TriNOx³⁻) can result in metal complexes that exhibit a self-association process that is sensitive to small differences in the ionic radius of the coordinated rare earth cation.³ By exploiting the differences in solubility between the monomeric RE(TriNOx)(L) and dimeric species $[\text{RE}(\text{TriNOx})]_2$ in organic solvents, separations of early and late combinations can be accomplished by simple leaching. In this work, further investigation and development of the RE(TriNOx) system has resulted in an optimized separation of europium and yttrium, the two rare earths present in red phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. Isolation of the triply-oxidized $[\{(2\text{-}^t\text{BuNO})\text{C}_6\text{H}_4\text{CH}_2\}_3\text{N}]$ (TriNOx^{•••}) tri-radical species was accomplished to investigate alternative routes to RE(TriNOx) complexes. Complexes of the formula RE(TriNOx)(L) L = 1,1,3,3-tetramethylguanidine, triphenylphosphine oxide, pyridine, H₂O were synthesized and characterized by single crystal X-ray diffraction. These compounds, with variable donor groups in the axial position, exhibit different solubilities in organic solvents, and are promising to affect more efficient separations.

(1) Humphries, M. *Rare Earth Elements: The Global Supply Chain*, Congressional Research Service, CRS Report R41347, Washington DC, **2013**, pp. 1-26.

(2) U.S. Department of Energy, *Critical Materials Strategy*, Washington, DC, **2011**, pp.1-191.

(3) Bogart, J. A.; Lippincott, C. A.; Carroll, P. J.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 8222-8225.

62. Thibault Cheisson, University of Pennsylvania, PI: Eric Schelter

Synthesis, Characterization and Coordination of a Nitroxyl Triradical Ligand

Bren E. Cole, Thibault Cheisson, Patrick J. Carroll, Eric Schelter

Among stable radicals, nitroxyl-based radicals are ubiquitous and have found applications ranging from industrial oxidations to *in-vivo* noninvasive medical imaging.¹ In recent years, our group has developed a new C₃-symetric ligand bearing three hydroxylamine moieties known as **H₃TriNOx** (Figure 1).^{2a} This ligand was found to exhibit unprecedented properties for the separation of rare-earth metals, as well as a rich redox chemistry.^{2b}

In this poster, we present the synthesis of the parent triradical **TriNOx^{•••}** by reaction of **H₃TriNOx** with silver oxide. The radical species was characterized by high-resolution mass spectroscopy, X-ray diffraction, IR, EPR and magnetometry indicating the formation of a triradical.

Finally, the reactivity of **TriNOx^{•••}** with organolanthanides precursors *via* a sterically-induced reduction mechanism³ to yield monomeric or dimeric complexes will be presented (Figure 1).

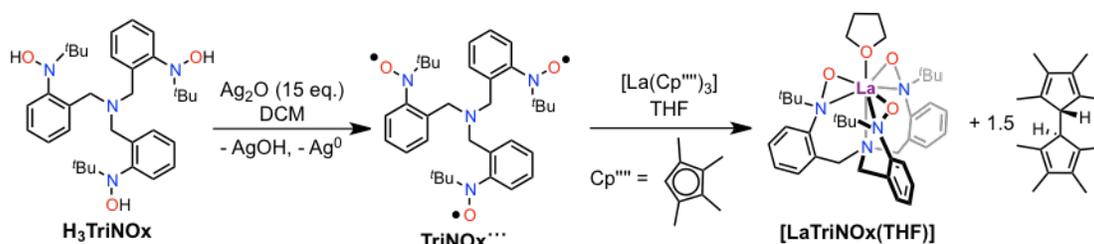


Figure 1 - Synthesis of **TriNOx^{•••}** and subsequent coordination to lanthanum

References:

1. a) R. Ciriminna, M. Pagliaro, *Org. Process Res. Dev.* **2010**, *14*, 245-251; b) P. Kuppusamy, H. Li, G. Ilangoan, A. J. Cardounel, J. L. Zweier, K. Yamada, M. C. Krishna, J. B. Mitchell, *Cancer Res.* **2002**, *62*, 307-312.
2. a) J. A. Bogart, C. A. Lippincott, P. J. Carroll, E. J. Schelter, *Angew. Chem. Int. Ed.* **2015**, *54*, 8222-8225; b) J. A. Bogart, B. E. Cole, M. A. Boreen, D. Weinberger, B. C. Manor, P. J. Carroll, E. J. Schelter, *submitted*.
3. R. R. Langeslay, J. R. Walensky, J. W. Ziller, W. J. Evans, *Inorg. Chem.* **2014**, *53*, 8455-8463

63. Ravneet Kaur Bhullar, Ian Mc Kendry, Rick Remsing, Temple University, PI: Michael Zdilla

Frustrated solvation structures can enhance electron transfer rate in layered Manganese oxide materials

One of the major hurdles in the production of solar hydrogen is the development of an effective catalyst for water oxidation. Metal oxides are a promising class of catalytic materials because they are robust, cheap and environmentally friendly. Birnessite is layered metal oxide containing mixed Mn(III/IV) oxide layers with an interlayer of water molecules and cations (K^+ , Ca^{2+} , etc.). The polar MnO_2 materials interact with interlayer H_2O molecules producing highly ordered interfacial structure. This ordering leads to increase in the frustration of hydrogen bonding within the water molecules. Buserite is also layered MnO_2 material with two interlayers of water molecules. We have synthesized these layered materials and verified by XRD. We are currently working on experimental determination and comparison of catalytic activity of Birnessite and Buserite in OER (oxygen evolution reaction). The experimental results suggest that Birnessite has enhanced catalytic activity for OER as compared to buserite due to the increased manganese content.

64. Mayukh Bhadra, Johns Hopkins University, PI: Kenneth D Karlin

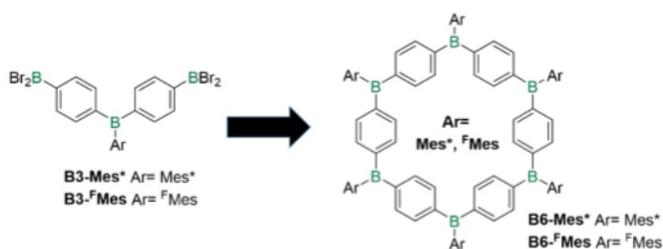
Hydrogen Bonding and Structural Variations Direct Reactivity of Mononuclear Cupric Superoxide Complexes

Mononuclear copper-dioxygen adducts of synthetic model complexes are of prime importance in gaining mechanistic insights into reductive activation of dioxygen by biological enzymes such as PHM & D β M (neurohormone monooxygenases), and LPMOs (polysaccharide monooxygenases), which insert an oxygen atom from dioxygen into substrates. A copper(II)-superoxide intermediate, generated from a Cu(I) precursor and O₂, is thought to be the reactive species in oxidative transformations of C–H bonds of biological substrates. Hydrogen bonding interactions have been postulated to be an essential factor for promoting increased affinity of O₂ binding to copper and stabilization of those product species possessing a Cu(II)- η^1 -O₂^{•-} moiety. Considering that there is literature on structurally-chemically related Cu(II)-hydroperoxo complexes, shown to be affected by the presence of H-bonding groups in the secondary coordination sphere, we studied a series of copper compounds possessing substituted TMPA (tris(2-pyridylmethyl)amine) derivatives containing benzyl amine moieties on one pyridyl donor arm. New cupric superoxide complexes have been synthesized and their reactivity toward substituted phenols with varying O–H bond strengths are compared with those of two previously published superoxide complexes, [((PV)TMPA)Cu(II)(O₂^{•-})]⁺ (with H-bonding pivalamido substituent on a pyridyl arm) and [(TMPA)Cu(II)(O₂^{•-})]⁺. The differences in pseudo first-order rate constants of O-H bond oxidation (in 2-MeTHF at -135 °C) monitored by UV-Vis spectroscopy, crystal structures of analogous azide (Cu^{II}-N₃) complexes and cupric-superoxo resonance Raman spectroscopic shifts (i.e., ν (Cu–O) and ν (O–O)), along with LCu(II)/Cu(I) reduction potentials suggest the existence of possible H-bonding interactions from secondary coordination sphere in modulating reactivity.

65. Nurcan Baser-Kirazli, Rutgers University-Newark, PI: Frieder Jäkle

Enhancement of Electron-Deficient Character of Organoboron Macrocycles

Conjugated macrocycles have attracted interest not only because of their cyclic structures without any end group, but also the potential for use in catalysis, material science, chiral sensing, supramolecular chemistry, self-assembly, and nanotechnology.^{1,2} In recent years, the functionalization of conjugated systems with main group elements has been appealing amongst scientists. Particularly, the incorporation of tricoordinate organoborane groups into conjugated systems has attracted considerable attention due to the interaction between the vacant p-orbital of boron and π -conjugated systems.^{3,4}



Previously, our group introduced the first example of electron-deficient conjugated organoboron macrocycles with fluorene bridges.⁵ The objective of the current work is to enhance the electron-deficient character of the prospective macrocycles and to further explore their redox and

optoelectronic properties. We have successfully prepared the triboron building blocks **B3-Mes*** and **B3-FMes** with bulky supermesityl (Mes*) and electron withdrawing fluoromesityl (FMe) groups attached to the central boron atom (Figure 1). These compounds were fully characterized and an X-ray crystal structure of B3-Mes* was acquired. Their utility as a building block for the preparation of macrocycles was investigated.

Bibliography:

- [1] Kitsiou, C.; Hindes, J.J.; Unsworth, W.P. *Angew. Chem. Int. Ed.* **2015**, 54, 15794-15798.
- [2] Iyoda, M.; Rahman, M. *Angew. Chem. Int. Ed.* **2011**, 50, 10522–10553.
- [3] Yin, X.; Guo, F.; Lalancette, R.; Jäkle, F. *Macromolecules* **2016**, 49, 537-546.
- [4] Chen, P.; Yin, X.; Baser-Kirazli, N.; Jäkle, F. *Angew. Chem. Int. Ed.* **2015**, 54, 1-6.
- [5] Chen, P.; Jäkle, F. *J. Am. Chem. Soc.* **2011**, 133, 20142.

66. Suzanne Adam, Johns Hopkins University, PI: Kenneth D. Karlin

Structure and Acid Dependence of (H^+/e^-) O–O vs. M–O Cleavage in Low-Spin Heme-Peroxo-Cu Complexes: Towards understanding the mechanism of O_2 -activation and reductive cleavage in CcO

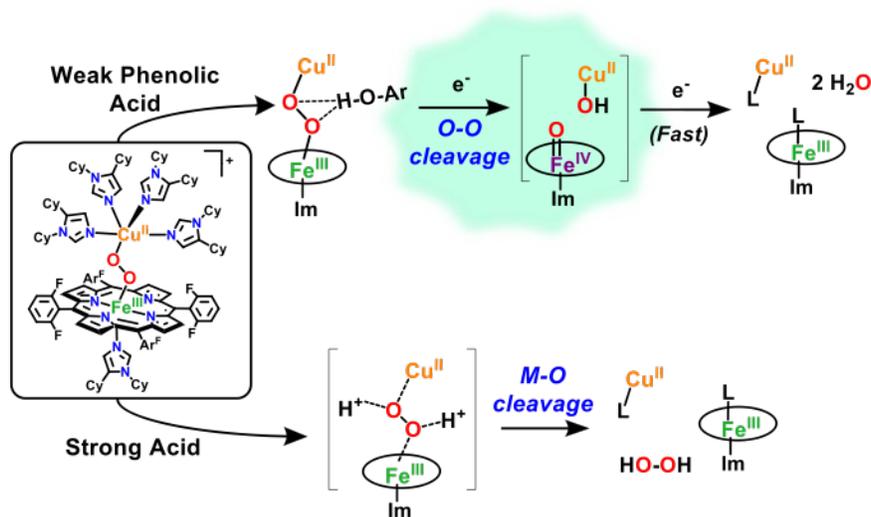
Suzanne M. Adam,[†] Isaac Garcia-Bosch,[†] Andrew W. Schaefer,[‡] Savita K. Sharma,[†] Edward I. Solomon^{*,‡}, and Kenneth D. Karlin^{*,†}

[†]Johns Hopkins University, Baltimore, Maryland 21218, United States

[‡]Department of Chemistry, Stanford University, Stanford, California 94305, United States

The hetero-binuclear active site of Cytochrome c Oxidase (CcO) catalyzes the 4-proton/4-electron reduction of O_2 to water; a reaction which is accompanied by the pumping of four additional protons across the mitochondrial membrane creating a pH gradient subsequently utilized to form ATP. This process involves efficient transformations of fundamentally interesting intermediates including high-valent metal-oxo species where release of partially reduced, reactive oxygen species (i.e. H_2O_2 , $\cdot OH$) is prevented. CcO's involvement in these important chemical processes has led to extensive research efforts aimed at investigating the details of the enzymatic mechanism, including protonation and/or H-bonding aspects, as it is widely accepted that a conserved Tyrosine residue near the active site plays a critical role in the O–O cleavage event. In this work, we describe the nature and comparative reactivity of two novel low-spin heme-peroxo-copper model complexes, (**LS-4DCHIm**), $[(DCHIm)F_8Fe^{III}-(O_2^{2-})-Cu^{II}(DCHIm)_4]^+$, and **LS-3DCHIm**, $[(DCHIm)F_8Fe^{III}-(O_2^{2-})-Cu^{II}(DCHIm)_3]^+$ (DCHIm = 1,5-dicyclohexylimidazole; F_8 = tetrakis(2,6-difluorophenyl)porphyrinate) toward different proton (4-nitrophenol and $[DMF \cdot H^+](CF_3SO_3^-)$,

DMF = dimethylformamide) and/or electron (decamethylferrocene (Fc*)) sources. Spectroscopic and reactivity studies along with density functional theory calculations show that both the structure of the bridging peroxy-complex and the nature of the proton source play a role in determining whether the mechanism proceeds via acid/base chemistry, or substrate-mediated redox chemistry. Specifically, in the presence of reductant, heterolytic O–O cleavage, rather than M–O cleavage and release of H₂O₂, is favored when an appropriate phenolic weak acid is able to first create an “activating” H-bonding interaction with the peroxy core.



67. Corey Herbst-Gervasoni, Temple University, PI: Ann Valentine

Spectropotentiometric Analysis of Titanium Tristiron

Enterobactin (ent) is a siderophore with the strongest affinity to ferric iron ($K_d = 10^{-49}$ M). Ent is shown to also have interactions with titanic titanium. Following the synthetic route of Baramov as a guide, the synthesis of ent will be outlined. As a model system, titanium tristiron was spectrophotometrically analyzed using varying ligand to metal ratios. Changes in absorbance of the $\pi \rightarrow \pi^*$ and LMCT of the titanium tristiron complex were used to observe changes in the complex while varying the pH. Ongoing work involving ent and titanium(IV) will also be described.

68. Samuel P. McCollom, University of Pennsylvania, PI: Neil Tomson

Dioxygen Activation on Copper Through Molecular-Scale Electrostatic Fields

Enzymes containing Cu(I) can form Cu_nO₂ complexes that catalyze the oxidations of small molecules, which range in reactivity from catechol to methane. CuO₂ and Cu₂O₂ synthetic analogues have been made to probe possible intermediates in the enzymatic pathway. The 2:1 Cu:O₂ complexes have been extremely well characterized in a plethora of geometries and are known to show highly characteristic UV/vis and resonance raman spectra. Many of these complexes can catalyze oxidations as well, including aerobic oxidation with no additives. Fewer

CuO₂ analogues have been made, and do not share as distinct characteristic identification features. Most notably, low temperature stable copper superoxos have been fully characterized with minor reactivity explored. This present study uses tetradentate ligands with phosphinimine arms that have formal cationic charges on phosphine, bound to copper to explore their reactivity with dioxygen. The first is a tris(2-aminoethyl)amine (tren) based ligand with a phenyldimethyl substituted phosphine. Preliminary investigations into treating this copper complex with dioxygen yields a green compound with spectroscopic evidence suggesting a room temperature stable end-on superoxo. This copper complex can also moderately catalyze benzylic alcohol oxidation to aldehydes. The second is a tris(2-aminophenyl)amine based ligand, which has a phenylene backbone instead of the ethylene backbone of tren, with a diphenylmethyl substituted phosphine. Treating this copper complex with O₂ gives a purple-brown diamagnetic compound but shows less catalytic reactivity than the tren based system.

69. Lukman Solola, University of Pennsylvania, PI: Eric Schelter

Alkali-Metal Capped Cerium(IV)-Imido Complexes

Terminal transition metal-ligand multiple bond complexes abound in the literature.¹ Interest in these complexes is driven by their synthetic applications such as in group transfer.² However, there is a paucity of complexes exhibiting lanthanide-ligand multiple bonds³ presumably due to the energy mismatch that exists between the lanthanide and ligand orbitals,⁴ and the propensity of these moieties to oligomerize upon formation. In a bid to isolate a cerium(IV)-imido complex, our previously reported tripodal nitroxide ligand framework [{{(2-^tBuNOH)C₆H₄CH₂}₃] (H₃TriNOx) was employed.⁵ The first examples of Ce^{IV}(TriNOx) anilide and alkali-metal capped imido complexes⁶ have been synthesized and characterized. The structure, bonding and reactivity of these complexes will be presented.

- 1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-interscience: New York, 1988.
- 2) Mindiola D. J.; *Acc. Chem. Res.* 2006, 39, 813
- 3) (a) So, Y-M.; Wang, G-C.; Li, Y.; Sung; H. H-Y.; Williams, I. D.; Lin Z.; Leung, W-H. *Angew. Chem. Int. Ed.* 2014, 53, 1626-1629. (b) Schadle, D.; Meerman-Zimmerman, M.; Schadle, C.; Maichle-Massmer C.; Anwander R. *Eur. J. Inorg. Chem.* 2015, 1334-1339.
- 4) Summerscales, O. T.; Gordon, J. C. *RSC Adv.* 2013, 3, 6717-6727.
- 5) (a) Bogart, J. A.; Lippincott C. A.; Carroll P. J.; Schelter E. J. *Angew. Chem. Int. Ed.* 2015, 54, 8222-8225. (b) Bogart, J. A.; Lippincott C. A.; Carroll P. J.; Booth C. H.; Schelter E. J. *Chem. Eur. J.* 2015, 21, 17850-17859
- 6) Solola, L. A.; Zabula, A. V.; Dorfner, W. L.; Manor, B. C.; Carroll, P. J.; Schelter, E. J. *J. Am. Chem. Soc.* 2016, 138, 6928-6931

70. David Watts, University of Maryland – College Park, PI: Andrei Vedernikov

C-H and O₂ Activation at a Pt(II) Center Enabled by a Novel Sulfonated Pincer Ligand

The oxidative functionalization of inert C-H bonds, such as those in benzene or methane, has been a long standing challenge in both academic and industrial laboratories. The use of homogenous Pt(II) complexes as catalysts, originally demonstrated by Shilov et al., has aided in this pursuit. However, the need for expensive and/or impractical oxidants (H₂PtCl₆, SO₃, CuCl₂) has prevented scalability. A more economically viable and green alternative would be the use of O₂ as the terminal oxidant. Some mediator-containing systems that use heteropolyacid/O₂ or CuCl₂/O₂ mixtures have achieved this at the cost of selectivity and compatibility. A more elegant solution is to design ligands that allow one to tune the reactivity of the metal center for both C-H and O₂ activation. Here we present a new class of sulfonated CNN pincer ligands that meet the above requirement, along with results of some model studies.

71. Tian Qiu, University of Delaware, PI: Joel Rosenthal

Developing cobalt tetrapyrrole catalysts that display multielectron redox property for oxygen reduction reaction (ORR)

The oxygen reduction reaction (ORR) is the most essential process in nature. It is also the cathode reaction of a hydrogen fuel cell which couples the oxidation of H₂ to O₂ reduction. This reaction can proceed through two pathways which are the O₂ to H₂O₂ two electron reduction and the O₂ to H₂O four electron reduction. The four electron reduction pathway is more attractive as it releases more energy than the two electron reduction. Current fuel cells utilize platinum based catalysts to achieve four electron reduction of oxygen. It is very important to develop inexpensive catalysts that can selectively and efficiently facilitate four electron ORR. Cobalt porphyrins can activate O₂. Monomeric cobalt porphyrins are limited to the two electron ORR. Co-facial cobalt porphyrins and cobalt haptophane porphyrins that perform four electron ORR require laborious synthetic routes and are inconvenient to prepare on large scales. In confronting this limitation, we have developed a series of novel cobalt tetrapyrrole catalysts for ORR. By incorporating sp³ hybridized carbon centers, a rich multielectron redox chemistry is enabled for the new complexes, which is important for four electron ORR catalysis.