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Professor Daniel Mindiola
Scott Wallace

Schedule of Events

Welcome reception (NSH 132) & poster hanging (NSH 1 st floor).....	8:30 – 9:30 a.m.
Opening remarks (NSH 123).....	9:30 – 9:40 a.m.
Oral presentations: session 1 (NSH 123)	
Talk 1.....	9:40 – 10:00 a.m.
Talk 2.....	10:00 – 10:20 a.m.
Talk 3.....	10:20 – 10:40 a.m.
Poster session (NSH 1 st floor), posters 1 – 20.....	10:40 – 11:40 a.m.
Lunch (NSH 132).....	11:40 – 12:40 p.m.
Oral presentations: session 2 (NSH 123)	
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Talk 5.....	1:00 – 1:20 p.m.
Talk 6.....	1:20 – 1:40 p.m.
Poster session (NSH 1 st floor), posters 21 – 38.....	1:40 – 2:40 p.m.
Oral presentations: session 3 (NSH 123)	
Talk 7.....	2:40 – 3:00 p.m.
Talk 8.....	3:00 – 3:20 p.m.
Talk 9.....	3:20 – 3:40 p.m.
Concluding remarks/awards (NSH 123).....	3:40 – 4:00 p.m.

Detailed Presentation Schedule

- Oral presentations: session 1 (NSH 123)
- Talk 1: Two-dimensional electronic conjugation: cooperative molecular motions for sensing and switching**
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Indiana University.....9:40 – 10:00 a.m.
- Talk 2: Cloning, expression and characterization of chlorite dismutase from *Dechloromonas aromatica***
Bennett Streit page 7
University of Notre Dame.....10:00 – 10:20 a.m.
- Talk 3: Structural characterization and dynamic solution behavior of *gem*-dimetallic complexes**
Katherine L. Hull page 8
University of Notre Dame.....10:20 – 10:40 a.m.
- Poster session (NSH 1st floor),
posters 1 – 20.....10:40 – 11:40 a.m.
- Oral presentations: session 2 (NSH 123)
- Talk 4: Toward photo-therapeutic agents for hypoxic environments: unusual periphery modified chlorin molecules.**
Tillmann Köpke page 9
Indiana University.....12:40 – 1:00 p.m.
- Talk 5: Towards molecular wire conductivity tuned by transition metal binucleation**
Kumar Parimal page 10
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- Talk 6: Mechanism of catalytic aziridination with manganese corrole: the often postulated high-valent Mn(V) imido is not the group transfer reagent**
Michael J. Zdilla page 11
Purdue University.....1:20 – 1:40 p.m.
- Poster session (NSH 1st floor),
posters 21 – 38.....1:40 – 2:40 p.m.
- Oral presentations: session 3 (NSH 123)
- Talk 7: Ligand-based DNA backbone modifications**
Megan M. Knagge page 12
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- Talk 8: Various organic reactions on inorganic building blocks lead to metallo-superamolecular**
Weizhong Chen page 13
Purdue University.....3:00 – 3:20 p.m.
- Talk 9: Bismuth-based intermetallic clusters**
Michael W. Hull page 14
University of Notre Dame.....3:20 – 3:40 p.m.

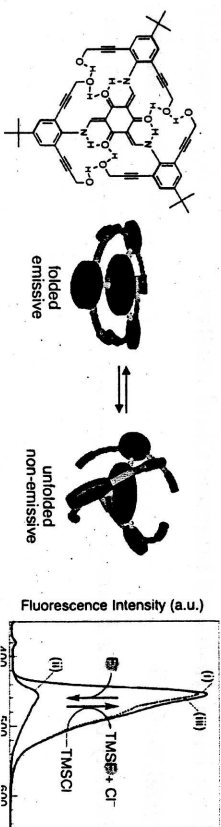
Oral presentations

Talk 1: Two-dimensional electronic conjugation: cooperative molecular motions for sensing and switching

Xuan Jiang, John C. Bollinger, and Dongwhan Lee*

Indiana University

Fast and reversible interconversion between two stable states of a molecule is a topic of fundamental and practical importance. Current efforts in many research groups focus on chemical systems displaying predictable structural changes upon irradiation, changes in oxidation states, or interaction with externally added guest species. Undoubtedly, such bistability has immediate technological implications in molecular-level devices for sensing, switching, memory, transport, and actuation. We have designed and synthesized dynamic 2-D conjugated systems, the structural and emission properties of which change reversibly in response to external stimuli. Specifically, the symmetrically disposed hydrogen bonding networks in these tris(*N*-salicylideneamine) derivatives render significant structural rigidity, which directly translates to enhancement in fluorescence efficiency. Manipulation of this intricate array of non-covalent bonds has proven to be a powerful mechanism to achieve reversible fluorescence sensing and switching. In this presentation will be discussed our recent efforts to integrate cooperative dynamic properties into "readable" 2-D electronic conjugation for applications in molecular devices and materials.



Talk 2: Cloning, expression and characterization of chlorite dismutase from *Dechloromonas aromatica*

Bennett Streit and Jennifer DuBois*

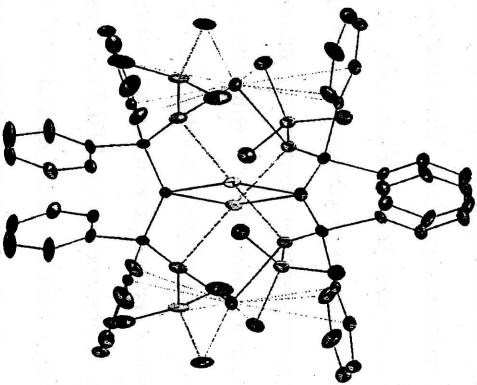
University of Notre Dame

The chlorooxides are primarily anthropogenic substances that have only recently become widespread environmental contaminants. Chlorite (ClO_2^-) is widely used in pulp and paper bleaching plants and has recently been sited as a top 10 EPA chemical in drinking water due to it being a possible agent of anemia. Chlorite dismutase (Cld) is a unique bacterial heme enzyme that catalyzes the disproportionation of chlorite (ClO_2^-) into a chloride ion (Cl^-) and molecular oxygen (O_2). This reaction detoxifies ClO_2^- for the organism, and could be used to remediate ClO_2^- in drinking water. The Cld enzyme from *Dechloromonas aromatica* has been cloned and expressed in high yields. Via the pyridine hemochrome assay the homotetrameric enzyme was determined to contain a heme b cofactor with nearly stoichiometric heme:monomer binding of 3.6 and 3.7 by ionically coupled plasma optical emission spectroscopy and the pyridine hemochrome assay respectively. The molecular weight of the monomer was determined by MALDI-TOF mass spectrometry to be 28.39 ± 0.03 kDa giving a tetrameric MW of 113.56 kDa, in agreement with other Cld enzymes. The chlorite dismutase activity was measured via iodometric titration of unreacted chlorite and found to be robust: $22000 \mu\text{mol chlorite mg}^{-1} \text{min}^{-1}$ at 4°C in a 100 mM phosphate buffered solution. The enzyme was shown concomitantly to undergo relatively rapid, ClO_2^- dependent deactivation. Preliminary spectroscopic evidence is suggestive of formation of a Compound I or Compound II-like intermediate. We hypothesize that self-inactivation occurs via covalent functionalization of an active site amino acid side chain.

Talk 3: Structural characterization and dynamic solution behavior of gem-dimetallic complexes

Katherine L. Hull, Bruce C. Noll, Kenneth W. Henderson*
University of Notre Dame

Gem-dimetallic complexes derived from bis-diphenyl-*N*-trimethylsilylphosphiniminomethane have been prepared by double deprotonation of this ligand using organometallic bases. Applying two equivalents of the strong base *n*-BuNa to the ligand yields a new disodio complex whereas controlled sequential deprotonation, transmetalation, or mixing of the disodio and dilithio analogues yields a mixed metal Li/Na derivative. Other heterometallic compounds consisting of Li/K and Na/K have also been synthesized and structurally characterized. Each metalated compound forms a dimer in solution and in the solid state. These compounds are the first examples of R_2C^2- dianions containing a heavy alkali metal to



be structurally characterized. The dynamic solution behavior of the Li/Na system has been investigated by *in situ* 1H NMR experiments. DFT calculations have also been conducted to probe the electronic structure of these dianions.

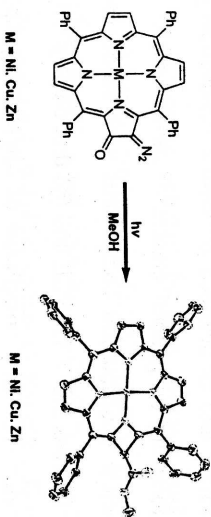
Talk 4: Toward photo-therapeutic agents for hypoxic environments: unusual periphery modified chlorin molecules.

Tillmann Köpke, Maren Pink, and Jeffrey M. Zaleski
Indiana University

Aromatic tetrapyrroles can roughly be divided into two classes. The first class of molecules are fully oxidized, the most common of which are the 22 π -electron porphyrins. The second class of molecules that include chlorins (dihydro-porphyrins) and bacteriochlorins (tetrahydroporphyrins) are partially reduced but still contain the 18 π -electrons required for aromaticity.

Porphyrins and chlorins serve as a primary pigment for light harvesting applications such as photomedicine and solar materials due to their intense absorption bands between 400-500 nm with $\epsilon \sim 80,000 M^{-1}cm^{-1}$ and Q-bands in the region of 650-900 nm with $\epsilon \sim 20,000 M^{-1}cm^{-1}$. Synthetic advances have led to the development of unusual porphyrinoids with modulated optical and electronic properties. Introducing a photo-labile unit on the periphery the macrocycle can lead to generation of highly reactive radical intermediates that may have potential as phototherapeutic agents for photodynamic therapy (PDT).

In addition to rearrangements, radical species can either abstract H-atoms from DNA or protein backbones or insert into chemical bonds. Both reactions can potentially have significant biological impact since application of these intermediates to DNA cleavage demonstrates the fundamental utility of radical reagents. The synthesis and photochemistry of photo-labile chlorins and a original approach to atypical chlorin molecules will be presented.



Talk 5: Towards molecular wire conductivity tuned by transition metal binucleation

Parimal, K.; Shansky, E. S.; Nygaard, S.; McNitt, K. A.; Bruick, N. A.; Barry, K. P.; Flood, A. H. *

Indiana University

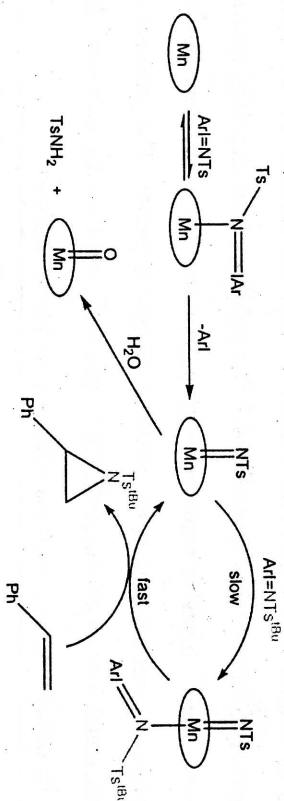
The need to create molecular electronics components for complementing and accessorizing solid-state devices has emerged with the miniaturization of computer circuitry. To address this need a series of potential molecular wires have been designed for investigation in which two key parameters are considered important: molecule-electrode energy level alignment and delocalized molecular conduction pathways. Consequently we are focusing on general classes of ruthenium(II), iridium(III) and rhenium(I) binuclear coordination compounds with redox energy levels that can be (a) tuned across 0.0 V vs. SCE and (b) that display delocalized mixed-valent (MV) behavior. The MV complexes of interest rely upon bridging ligands bearing sulfur end groups to facilitate the formation of self-assembled monolayers (SAMs) onto gold electrodes. To measure the electrical properties we intend to use conducting atomic force microscopy (AFM) and as a means to characterize the electronic properties and structural features of the SAMs we are using surface-enhanced Raman spectroscopy (SERS). This talk will outline the synthesis of tetrazine-based bridging ligands that have necessitated modifications of previous methods to incorporate the sulfur functionality. Progress towards MV transition metal complexes will be addressed. Finally, preliminary SERS and AFM data will be shown in order to highlight the pathway forward to electrical device measurements.

Talk 6: Mechanism of catalytic aziridination with manganese corrole: the often postulated high-valent Mn(V) imido is not the group transfer reagent

Michael J. Zdilla and Mahdi M. Abu-Omar

Purdue University

The reaction of ArI=NTs (Ar = 2-(*tert*-butylsulfonyl)benzene and Ts = *p*-toluenesulfonyl) and (tpfc)Mn (tpfc = 5,10,15-tris(pentafluorophenyl)corrole) affords the high-valent (tpfc)MnV=NTs on stopped-flow timescale. The reaction proceeds via the adduct [(tpfc)MnIII(ArINTs)]. The complex (tpfc)Mn catalyzes [NTs] group transfer from ArINTs to styrene substrates with low catalyst loading and without requirement of excess olefin. The catalytic aziridination reaction is most efficient in benzene because solvents such as toluene undergo a competing hydrogen atom transfer (HAT) reaction resulting in H2NTs and lowered aziridine yields. The high-valent manganese imido complex (tpfc)Mn=NTs does not transfer its [NTs] group to styrene. Double labeling experiments with ArINTs and ArINTs^{tBu} establish the source of [NR] transfer as a "third oxidant," which is an adduct of Mn(V) imido, [(tpfc)Mn(NTs)(ArINTs^{tBu})].



Talk 7: Ligand-based DNA backbone modifications

Megan M. Knagge, Mildred Rodriguez, and Jonathan J. Wilker
Purdue University

High target fidelity and almost limitless adaptability have made antisense oligonucleotides an attractive option in the continuing pursuit of rationally designed pharmaceuticals. Their utility as therapeutics, however, has been limited by high charge and nuclease susceptibility.¹ A variety of nucleic acid derivatives have been developed to address these limitations, including organically modified species, such as peptide nucleic acids and phosphorothioate DNA,² and inorganic derivatives, such as nucleic acids containing metal-chelating bases and oligonucleotides with 5'-or 3'-pendant metal complexes.³ These modifications have addressed many of the disadvantages of oligonucleotides with respect to antisense therapy; however, significant obstacles remain. We have designed a new class of nucleic acids in which ligands are incorporated into the DNA backbone as nucleotide-replacements. This strategy could offer enhanced binding strength, control over charge, and improved nuclease resistance. We have synthesized three ligands, bipyridine, dithioether, and piperazine, appropriately protected for incorporation into oligonucleotides via standard automated techniques. A series of nucleic acid derivatives containing variable numbers of the ligand nucleotide-substitutes was synthesized. The stability of the duplexes formed between these ligand-containing oligonucleotides and their unmodified complements was assessed in the presence of various metals. The presence of certain metal ions, including Pt^{2+} , Cu^{2+} , and Os^{4+} , significantly enhanced the stability of the modified duplexes relative to unaltered duplexes.

1. Alama, A.; Barbieri, F.; Cagnoli, M.; Schetini, G. *Pharmacol. Res.* 1997, 30, 171-178.

2. Kurreck, J. *Eur. J. Biochem.* 2003, 270, 1628-1644.

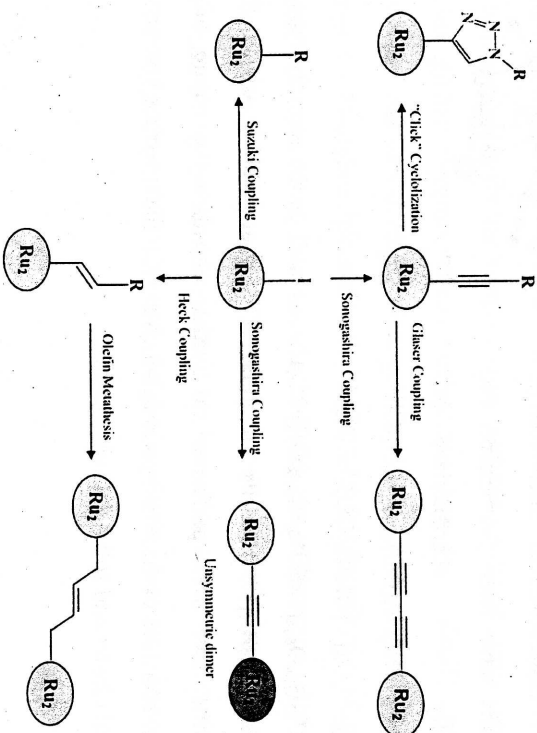
3. (a) Meggers, E.; Holland, P.L.; Tolman, W.B.; Romesberg, F.E.; Schultz, P.G. 2000, 122, 10714-

10715. (b) Frank, N.L.; Meade, T.J. *Inorg. Chem.* 2003, 42, 1039-1044.

Talk 8: Various organic reactions on inorganic building blocks lead to metallo-supramolecular

Weizhong Chen, Guolin Xu and Tong Ren*
Purdue University

A series of Ru_2 compounds bearing peripheral iodo/ethynyl functionalities have been synthesized and structurally characterized. The peripheral iodo/ethynyl groups enables the Ru_2 compounds to undergo various Pd-catalyzed coupling reactions such as Sonogashira, Heck, Suzuki reactions with terminal alkynes/olefins/boronic acids under mild reaction conditions (see scheme). Moreover, the peripheral cross/homo coupling reactions on Ru_2 units lead to a number of symmetric/unsymmetric supramolecular dimers. In addition, several photoactive organic dendrons including poly(benzyl ether) dendrons, poly(benzyl ester) dendrons, and poly(phenylvinylene) dendrons have been covalently attached at the periphery of Ru units.



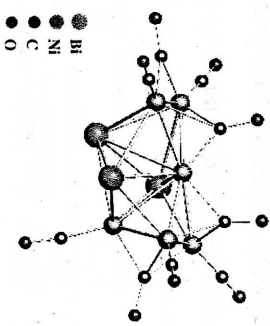
Schematic diagram of various organic reactions on Ru_2 building blocks

Talk 9: Bismuth-based intermetalloid clusters

Michael W. Hull, Jose. M. Goicoechea, Slavi C. Sevov*

University of Notre Dame

Main-group metal cluster chemistry has been an intensely researched field for a number of years, effectively applying many of the insights of carborene chemistry. It has recently experienced a renaissance as witnessed to by the variety of Zintl clusters primarily composed of Group 14 metals. The aim of our group has been to extend this work to other metals, which has resulted in a new set of heterometallic bismuth clusters. Some of these clusters approach the size and packing arrangement of metalloid clusters. Given the heterometallic nature of these clusters, they contribute to the new sub-field of "intermetalloid" chemistry. For example, pictured to the right is a cluster consisting of both a main group metal and a transition metal, $[\text{Bi}_3\text{Ni}_6(\text{CO})_9]$. A series of bismuth-based intermetalloid compounds have been synthesized and structurally characterized— $[\text{K}-\text{C}_{18}\text{H}_6\text{N}_2\text{O}_6]_3[\text{Bi}_3\text{Ni}_4(\text{CO})_6] \cdot \text{C}_2\text{H}_8\text{N}_2 \cdot \text{C}_7\text{H}_8$, $[\text{K}-\text{C}_{18}\text{H}_6\text{N}_2\text{O}_6] [\text{Bi}_4\text{Ni}_4(\text{CO})_6] \cdot \text{C}_7\text{H}_8$, and $[\text{K}-\text{C}_{12}\text{H}_2\text{O}_6]_4[\text{Ni}@\text{Bi}_6\text{Ni}_6(\text{CO})_8] \cdot 3\text{C}_7\text{H}_8$ —as well as the recently reported ligand-free $[\text{Zn}_9\text{Bi}_{11}]^5$. Density Functional Theory and Self-Consistent Field calculations have been performed to further elucidate the nature of the electronic structure of these compounds which exist at the interface between the traditional cluster and solid-state chemistries.



Poster Presentations

Poster 1: Synthesis of an extended structure porphyrin via Bergman cyclization

Leigh J.K. Boerner, Mahendra Nath, Maren Pink, and Jeffrey M. Zaleski

Indiana University

Porphyrins are a class of conjugated systems that have an abundance of applications from dye and inks to uses in optical materials. Modification of the porphyrin chromophore has many potential applications, primarily when this results in the presence of strong absorption bands in the red and near infrared regions. These extended structure porphyrins are potentially useful in biological systems because human tissue is largely transparent to both red and near infrared wavelengths. Presented here is ongoing work toward the synthesis and Bergman cyclization of porphyrinic enediyne which are capable of photoactivated diradical formation as potential phototherapeutic agents in hypoxic environments. Synthesis of the 2,3,12,13-tetra(ethynyl)-5,10,15,20-tetraphenyl porphyrins has been accomplished and produced target compounds in high yields. Bergman cyclization of the free base, Zn(II) and Ni(II) derivatives has produced a mixture of products. The mono-cyclized 2,3-dihynyl-5,20-diphenylpiceno[10,11,12,13,14,15-fghj]porphyrin has been isolated and crystallized, and shows several degrees of distortion relative to the starting material. The presence of side products indicates that the barriers to these reaction lay below that required for formation of the fully cyclized bis-piceno[20,1,2,3,4,5,10,11,12,13,14,15-fghj]porphyrin due to internal ring strain.

Poster 2: Mechanistic investigations of ketone enolization mediated by magnesium bis(hexamethyldisilazide)

Xuyang He, J. Jacob Morris, Bruce C. Noll, Seth N. Brown,* and Kenneth W. Henderson*

University of Notre Dame

Mechanistic investigations of the enolization of propiophenone mediated by magnesium bis(hexamethyldisilazide, $\text{Mg}(\text{HMDS})_2$, in toluene will be presented. Low temperature NMR, IR and UV-Vis spectroscopic studies have revealed the formation of the intermediate $[\text{Mg}(\text{HMDS})_2 \cdot \text{OC}(\text{Ph})\text{Me}]$ prior to enolization. The monomeric structure of this complex was confirmed by DOSY NMR spectroscopy, computational methods and also through the crystallographic characterization of closely related two model complexes. Under pseudo-first order conditions enolization is first order in ketone, zero order in base, with a large primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 18.9$). Also, the activation parameters of the reaction have been derived from the Eyring plot and all the cumulative data is consistent with enolization occurring through a single intermediate by an intramolecular mechanism.

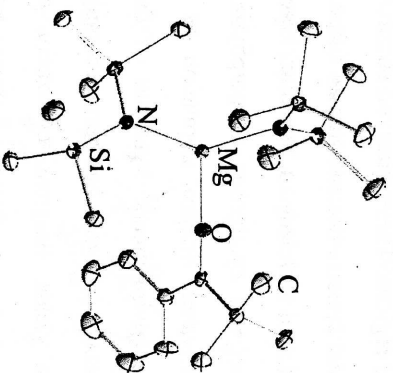


Figure 1. Molecular structure of $[\text{Mg}(\text{HMDS})_2 \cdot \text{OC}(\text{Ph})\text{Me}]$, a model pre-enolization complex.

Poster 3: B-form DNA binding and solution physical properties of $\text{Pt}(4\text{'-X-try})\text{CN}^+$ compounds

Meaghan L. Clark, Michael H. Wilson, Robert L. Green, Olivia E. Johnson, and David R. McMillin.

Purdue University

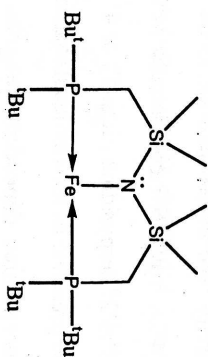
The DNA binding interactions of $\text{Pt}(\text{II})$ terpyridines are of interest because they are useful probes of DNA structure because they exhibit antitumor activity. We report here the DNA binding and solution physical properties of $\text{Pt}(4\text{'-X-try})\text{CN}^+$ compounds where 4'-X-try denotes 4'-dimethylamino-2,2':6,2''-terpyridine (dma-T) or 4'-pyrroliidinyl-2,2':6,2''-terpyridine (pyrr-T). The presence of intermolecular association in aqueous solutions is evidenced by concentration dependent titrations of the complexes yielding ϵ values lower than the ϵ value of the monomer in methanol. As previously reported the photophysics of these types compounds is interesting because the electron-rich 4' substituents create a strongly emissive complex that arises from a mostly ligand-based charge-transfer state. The easily detected emission makes them excellent probes of DNA.¹ The binding behavior of $[\text{Pt}(\text{dma-T})\text{CN}]^+$ and $[\text{Pt}(\text{pyrr-T})\text{CN}]^+$ indicate that the primary mode of binding is intercalation.

1. Wilson, M.H.; Ledwaba, P.L.; Field, J.S.; McMillin, D.R. *Dalton Trans.* 2005, 2754-2759.

Poster 4: Synthesis of a monomeric highly reactive tricoordinate iron(II) complex

Drew Buschhorn, Benji Fullmer, Michael Ingleson, Kenneth G. Caulton
Indiana University

Using the bulky pincer ligand PNP (see graphic) iron complexes of the type $(PNP)FeCl_n$ ($n=0,1$) were formed from the reaction of anhydrous $FeCl_2$ with the magnesium chloride PNP salt, followed by reduction. The syntheses are shown in detail for both the 14 e⁻, four coordinate, distorted tetrahedral $(PNP)FeCl$ complex as well as the highly unsaturated 13 e⁻, three coordinate, planar $(PNP)Fe$. The novel reactivity of these complexes including formation of $FePNP(CO)_2$ and $FePNP(PhN_3)$ from the $n=0$ species is shown along with evidence in the form of $^1H/^{31}P$ NMR, IR and crystal structure data.

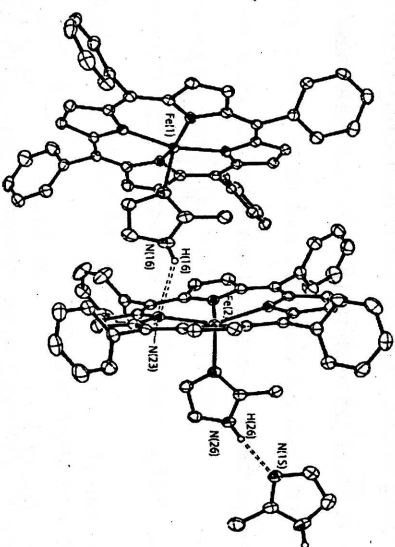


Poster 5: Influence of hydrogen bonding on electron configuration of high-spin imidazole iron(II) porphyrinates

Chuanjiang Hu, Bruce C. Noll, Charles E. Schulz, and W. Robert Scheidt*

University of Notre Dame

As models of five-coordinate high-spin ferrous heme proteins, both imidazole- and imidazole-ligated high-spin $Fe(II)$ porphyrinates have been studied in our previous work. These species show different structural and Mössbauer properties which indicate that they have different electron configurations. In order to study the influence of hydrogen bonding, we synthesized an interesting complex, $[Fe(TPP)(2-MeHIm)]_2 \cdot (2-MeHIm)$. In the crystal structure, there are two independent iron porphyrinates in an asymmetric unit. Both of them are five-coordinate high-spin iron(II) species. They have different environments. Molecule 1 is similar to that in previous

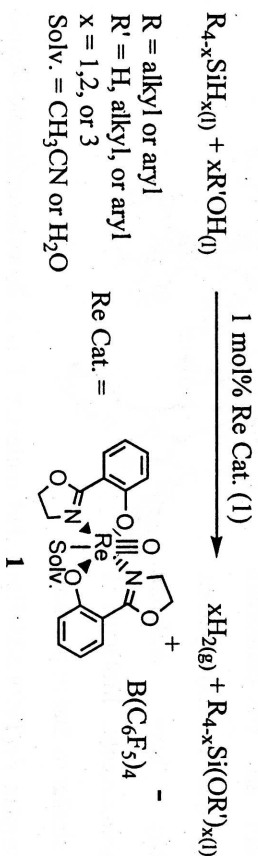


complex $Fe(TPP)(2-MeHIm)$, but molecule 2 is a 2-methylimidazole-ligated porphyrinate hydrogen bonded with a 2-methylimidazole solvate. (right figure) The average Fe-Np bond lengths and the iron displacements out of the porphyrin plane in molecule 2 are both larger than those in molecule 1, 0.019 and 0.13 Å, respectively. Their Mössbauer data show that both quadrupole splitting (ΔE_Q) are temperature dependent. ΔE_Q for molecule 2 is 3.17 mm/s at 4.2 K which is between those values for imidazole- and imidazole-ligated species.

Poster 6: Hydrolysis and alcoholysis of silanes catalyzed by oxorhenium (V) oxazoline

Rex A. Corbin, Elon A. Ison, and Mahdi M. Abu-Omar
Purdue University

A series of primary, secondary, and tertiary alkyl/aryl silanes undergo rapid hydrolysis and alcoholysis to yield dihydrogen and silanols or silyl ethers in the presence of catalytic amounts of rhenium complex 1 (see equation). These reactions were conducted under ambient temperature and pressure. Spectroscopic and kinetic characterizations in conjunction with isotope labeling experiments have revealed the most viable reaction pathway for activation of silane (Si-H) by oxorhenium (V) complexes. Kinetic investigations and isotope labeling studies employed direct monitoring in real time of H₂ or H-D evolution via residual gas analysis (RGA) quadrupole mass spectrometry. Furthermore, substrate induced electronic and steric effects upon the organosilicon center were probed and correlated using the Taft linear free energy relationship.



Poster 7: Reductive cleavage of H-X bonds by a Ni₂N₂ diamond core
Debashis Adhikari, Falguni Basuli, John C. Huffman and Daniel J. Mindiola*

Indiana University

Pincer ligands represent a robust scaffold for the stabilization of reactive complexes in the context of synthetic inorganic and organometallic chemistry. For example, Pincer ligands are often sought as ancillary ligands in catalysis. Herein we report a Ni(II) complex supported by the pincer PNP [PNP = Ni₂-P(CHMe₂)₂-4-Me-C₆H₃]₂ scaffold whose single electron reduction gives a Ni₂N₂ diamond core structure resulting from significant rearrangement of the tridentate ligand framework. This reduced product shows interesting redox chemistry and magnetic properties. We will present structural elucidation of the Ni(I) dimer species and its ability to cleave H-X (H or a heteroatom) bonds.

Poster 8: Mechanistic studies of catalytic hydrosilylation of carbonyls with Re≡X (X = O, NAr, N) multiple bonds

Guodong Du, Philip E. Fanwick and Mahdi M. Abu-Omar
Purdue University

Recently, application of high valent transition metal oxo complexes in catalytic hydrosilylation has attracted considerable attention. One of the issues arises from these studies concerning the role of the terminal metal oxo bond. Here we present our investigation of the catalytic reactivity of a series of rhenium(V) complexes differing by the presence of multiply bonded terminal groups (Re=X, where X = O, NAr, N). Mechanistic implications of our findings in catalytic silane activation are discussed.

Poster 9: Development and application of homo-chiral magnesium amide bases

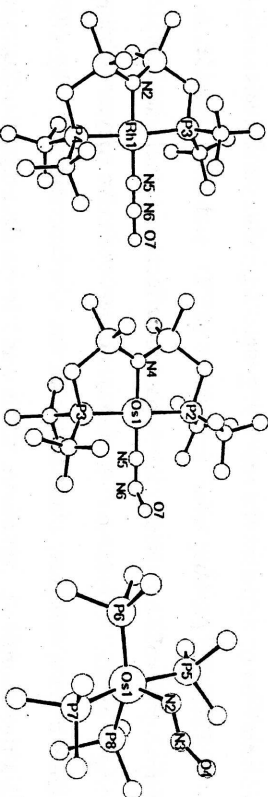
Erin Hurley, John F. Allan, Kenneth W. Henderson, * William J. Kerr,
Jennifer H. Moir
University of Notre Dame

Chiral organometallic reagents for use in asymmetric transformations have been of considerable interest in recent years. There are many known lithium reagents for this purpose, however magnesium reagents are much less common. We have previously created novel group 1 and 2 chiral amide bases and studied the structure and reactivity of these species. Homo-chiral magnesium amides have been shown to possess advantages over their lithium counterparts, such as more simple and predictable solution aggregation. We have explored the use of homo-chiral magnesium bisamides in asymmetric deprotonation of ketones and now are looking at the reactivity of the magnesium trisamide anion.

Poster 10: 2-Electron reduction of N₂O yield a new ligand binding mode: N-nitrosoimide

Hongjun Fan and Kenneth Caulton*
Indiana University

A new mode of bonding of the traditionally weak ligand N₂O to highly reducing transition metal complexes is described based on DFT calculations for a variety of late transition metals. As shown below, the η^1 -NNO can be singly bent (at the central nitrogen) or doubly bent (at both N), and thus involve a double or triple M-N bond, respectively. The bend ligand is therefore properly termed as N-nitrosoimide, N₂O⁻.



Poster 11: Unusual reactivity of a three-coordinate Ni(I) d⁹ system

Benji Fullmer
Indiana University

Using 1,3[bis-(di-tert-butyl)-phosphino]-methyl]-tetramethyldisilazane ("PNP"), a tri-coordinate hard/soft donor ligand, a unique d⁹ Ni system was synthesized. This molecule ((PNP)Ni) reacts with CO to reversibly form a pseudo tetrahedral 17 electron complex. (PNP)Ni also reacts with NO to form a pseudo tetrahedral complex but it was found that this reaction is not reversible. Also of much interest is the fact that (PNP)Ni reacts with CO₂ to form a complex where an oxygen from the CO₂ group replaces the N in the (PNP) backbone and forms an isocyanate complex that is still Ni(I).

Poster 12: Investigations on the catalytic and folding mechanisms of phenylalanine hydroxylase from *Chromobacterium violaceum*

Amanda Lee, Aristobulo Loaiza and Mahdi AbuOmar
Purdue University

Chromobacterium violaceum (cPAH) is the bacterial form of mammalian phenylalanine hydroxylase, a non-heme iron-dependent enzyme that catalyzes the hydroxylation of phenylalanine to tyrosine using oxygen and tetrahydrobiopterin. Defects in mammalian PAH lead to the metabolic disorder phenylketonuria (PKU). Previous structural studies on this enzyme conflict about whether oxygen binds to the open coordination site resulting in a six-coordinate iron or displaces the remaining water ligand to yield five-coordinate iron. Electron paramagnetic resonance (EPR) and nitric oxide as a spectroscopic probe are used to investigate the effects of cofactor and substrate binding to cPAH. A rhombic distortion was observed for the enzyme-substrate-cofactor ternary complex, consistent with the displacement water by NO to yield a five-coordinate iron center. This was also confirmed by the observance of hyperfine broadening of the EPR resonance of the iron-nitrotyl enzyme complex by ^{17}O -enriched water, indicating that water is bound directly to Fe^{2+} and is displaced when the substrate and cofactor binds to the enzyme.

Mapping the series of events that a nascent polypeptide chain must undergo in order to obtain its biologically active structure, and being able to predict the rates of folding or unfolding are arguably two of the most difficult tasks in biology. Our lab also investigates the effects that different metals have on the folding kinetics of cPAH. Here we present preliminary data used to determine the mechanism of unfolding. We use stopped flow circular dichroism to follow the chemical-induced unfolding reactions and to obtain rate constants for the dilution-induced refolding reactions for apo and holo cPAH.

Poster 13: Toxin interception with selenium and vanadium: a possible mechanism of cancer prevention

Elizabeth E. Hamilton, Sarah M. Gentry, Jessica M. Fautch and Jonathan J. Wilker*
Purdue University

The cancer preventing properties of selenium and vanadium have been demonstrated in a number of studies with common environmental carcinogens such as nitrosamines and polycyclic aromatic hydrocarbons. These carcinogens derive their toxicity from metabolism into potent alkylating agents, which can then damage DNA. Human trials involving selenium show the efficacy of this inorganic element as a chemopreventive agent. Despite such exciting findings, the mechanism of cancer prevention remains unknown. Selenium and vanadium are present in the human diet. In aqueous environments, these elements equilibrate to oxo species. We propose these inorganic oxo species may be nucleophilic and, therefore, can react directly with the electrophilic alkylating toxins before they alkylate DNA. Small molecule studies were used to investigate the reaction between inorganic oxo species (e.g., $[(\text{C}_4\text{H}_9)_4\text{N}]_3(\text{V}_3\text{O}_9)$) and alkylating agents. We show that inorganic oxo compounds convert alkylating agents into alcohols. Additionally, an enzyme assay was developed to investigate the ability of inorganic oxo compounds to protect plasmid DNA from an alkylating agent assault. Analysis of the DNA product by the enzyme assay demonstrated that inorganic oxo compounds such as Na_2SeO_4 and Na_3VO_4 were able to prevent DNA alkylation. Together, these results show inorganic compounds react with carcinogens, transforming them into alcohols, thereby preventing DNA damage. This detoxification reaction may have implications for preventing cancer.

Poster 14: Denitrogenation of pyridines and trapping of the titanium alkylidyne moiety

Allison Fout
Indiana University

Given the complexity of the hydrodenitrogenation process, further insight into the mechanism is vital in creating a superior catalyst which can perform such a reaction under milder conditions. Development of a more cost effective catalyst that is able to denitrogenate N-heterocycles without an obscene pressure of H₂, which is expensive and can be a potentially hazardous reagent, is critical.¹ Our goal is to gain a better understanding of the HDN mechanism utilizing a [PNP] pincer-type ligand with a titanium metal center having a highly reactive Ti-C multiply bonded ligand. We report the room temperature ring-opening of pyridine, which involves a unique ring-opening metathesis (ROM) step via a [2+2] cycloaddition of the aromatic C=N bond across a reactive Ti≡C^tBu linkage.² Further reaction of the ring-opened pyridine product with chlorotrimethylsilane resulted in the complete denitrogenation of pyridine. We were also able to isolate kinetic products which are key intermediates along the denitrogenation pathway. These reactions offer new insights into the HDN process, and particularly into how C-N bond cleavage occurs under mild conditions, and without a reductant such as H₂. Other reactivity pertinent to the Ti≡C^tBu linkage will be presented and discussed.

1. Weller, K. J.; Fox, P. A.; Gray, S. D.; Wigley, D. E. *Polyhedron* 1997, 16, 3139-3163.
2. Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* 2006, 128, 6798-6799.

Poster 15: Two-dot molecular quantum cellular automata

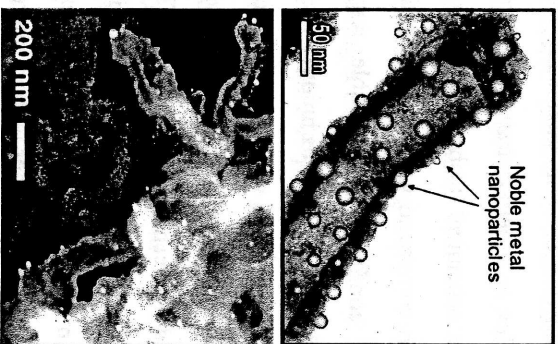
Hua Qi, Anuraha Gupta, Thomas P. Fehlner, Gregory L. Snider and Craig S. Lent[†]
University of Notre Dame

$\text{Trans}[(\text{H}_2\text{NCH}_2\text{CH}_2\text{C}(\text{N})(\text{dppe})_2\text{Ru}(\text{C}=\text{C}))_6\text{Ru}(\text{dppe})_2(\text{N}=\text{CCH}_2\text{CH}_2\text{NH}_2)]\text{[PF}_6\text{]}_2$, a derivative of trans-[Cl(dppe)₂Ru(C=C)₆Ru(dppe)₂Cl] functionalized for binding to a highly B doped Si (111) substrate, has been synthesized and characterized spectroscopically, electrochemically and crystallographically. The presence of the silicon surface bound complex was demonstrated by X-ray photoelectron spectroscopy (XPS) and electrochemical techniques. Nearly perpendicular orientation of the surface bound compound was assured by the length of the surface binding linker and confirmed by variable angle ellipsometric film thickness measurement. Electro-chemical techniques were used to generate the active Ru^{III}-Ru^{II} mixed valence state with three identical counter ions. The differential capacitance of oxidized and unoxidized films was measured as a function of applied electric field between Hg and Si plates. The difference between the measurements establishes a maximum associated with the flipping dipole created by the electron moving between the two metal centers at an electric field strength that permits electron transfer without energy change. This is equivalent to switching of a two dot QCA cell. In comparison with the unsymmetrical Fe^{III}-Ru^{II} centers in *trans*-[Ru(dpmp)₂(C=CFc)-[N(CCH₂CH₂NH₂)]][PF₆][X], Fe = (η⁵-C₅H₅)Fe(η⁵-C₃H₄), X=[SO₃CF₃], [PF₆], [Cl], the RuIII-RuII system gives a stronger single signal per molecule in accord with the longer distance between metal centers. These results are now being used as the basis for fabrication of a small device by nano-and micro-fabrication in order to measure single molecule switching in an array of a few hundred molecules on a silicon surface. Progress of this research is reported.

Poster 16: Synthesis of noble metal/semiconductor composite electrodes based on fibrous architectures

Carmen M López and Kyoung-Shin Choi*
Purdue University

Recently we have produced high surface area ZnO electrodes with fibrous morphology that demonstrated enhanced photoelectrochemical performance when compared to other nanocrystalline ZnO electrodes of



comparable surface areas. This enhancement is due to the superior physical and electrical connectivity of the particles that compose the fiber walls, which provide a continuous pathway for transport of charge carriers generated by light. Additionally, the intrinsic porosity of fibrous films increases interfacial areas, which can improve the kinetics of reactions occurring at the interface. Fibrous films can be used, as well, as support to deposit noble metal nanoparticles and create

semiconductor/noble metal composite electrodes with enormous junction areas. These nanoparticles may, in turn, enhance the photocatalytic activity of the semiconducting film by facilitating separation and interfacial transfer of photogenerated electrons and holes, which may then be used to drive solution redox processes. In this poster we present the electrochemical synthesis of semiconductor/noble metal composite electrodes and discuss the effect of the synergistic interactions between components in the photoelectrochemical properties observed.

Poster 17: Beyond molecular wires: planar conjugated discotic molecules for fluorescence switching and excited-State energy transfer

Young-Kwan Lim, Justin A. Riddle, Xuan Jiang, John C. Bollinger, and Dongwhan Lee*
Indiana University

Signal amplification in “molecular wire” sensors exploit binding-induced local perturbations in the extended electronic structures. Implementation of conceptually parallel processes in 2-D conjugated systems should further benefit from the additional dimensionality of the space sampled by electrons and excitons. Unlike 1-D systems, however, conjugation and deconjugation of 2-D systems require simultaneous manipulation of multiple nonproximate bonds in order to maximize the effects of electronic perturbation. We have recently demonstrated one practical solution to meet this synthetic challenge by installing a cyclic array of hydrogen bonding networks around dynamic conjugated systems. The making and breaking of these mutually reinforcing non-covalent bonding interactions nicely correlated with the concerted tilting motions of multiple aromatic groups sharing a common $[\pi, \pi]/[n, \pi]$ -conjugated molecular core. In this presentation, we will describe our modular approaches to construct an extended family of planar conjugated discotic molecules having (a) large 2-D conjugation areas for low energy excitation and (b) FRET donor-acceptor pairs for large *pseudo* Stokes shifts in dual fluorophore systems.

Poster 18: Photophysics of new platinum(II) complexes of a tridentate heteroaromatic ligand

McGuire, Robert; Wilson, Michael H.; McMillin, David R.
Purdue University

We report studies of the new ligand, 6'-(2"-pyridyl)-dipyrido[3,2-a:2',3'-c]phenazine (dppzp) complexed to platinum(II). This work is an outgrowth of investigations focusing on the mol. and electronic structures of d8 platinum(II) complexes of the 2,2':6',2"-terpyridine (trpy) ligand or an analogous heteroarom. chelator. The complexes are of interest because the photophys. properties vary widely depending on the system and the environment. Thus, adding ring substituents, introducing a fused-ligand framework, varying the counterligand, and/or incorporating the trpy complex into a DNA host can have a drastic impact on the emission. For many reasons, the dppzp ligand promises to be equally intriguing as a ligand platform: 1. Because of the extended fused-ring structure, there will be low-lying intraligand (IL) electronic excited states in addn. to classic metal-to-ligand (MLCT) excited states. 2. Many complexes based on the related bidentate dppz ligand bind avidly to B-form DNA hosts. 3. Finally, the dppzp ligand presents potentially reactive nitrogen centers while the platinum center has open coordination sites, hence the excited state(s) properties may be very sensitive to the environment because more than one quenching mechanism may be available.

Poster 19: Activation of Small Molecules by a Transient Niobium (III) Species

Uriah Kilgore and Dan Mindiola*

The reaction of Li(PNP) and (DME)NbCl₃ generates a transient Nb(III) "(PNP)NbCl₂" (PNP⁻ = Ni₂-P(CHMe₂)₂-4-methylphenyl]₂) species, which is capable of activating a variety of substrates including N₂, P₄, and azobenzene. In the presence of N₂, the transient Nb(III) intermediate activates N₂ to form the bridging diimido [(PNP)NbCl₂]₂(m-N₂), which can also be independently synthesized from Nb(IV) and Nb(V) precursors via a one-electron and transmetalation reactions, respectively. In the presence of azobenzene, transient "(PNP)NbCl₂" cleaves the N=N bond via a metal-ligand cooperative four-electron reduction to form niobium imide and phosphoramidine functionalities. "(PNP)NbCl₂", when treated with white phosphorus, P₄, forms the first crystallographically characterized niobium species bearing the cyclo-P₃ ligand, (PNP)NbCl(η³-P₃). Structural studies are presented and discussed for various niobium systems bearing the pincer-type framework PNP as well as the N₂ and azobenzene activated products.

Poster 20: A new class of metal-chelating nucleic acids

Mildred Rodriguez, Megan M. Knagge, Jonathan J. Wilker
Purdue University

Antisense oligonucleotides are emerging as an intriguing class of rationally designed therapeutics. Binding of nucleic acid-based drugs to the mRNA of a disease-causing gene can halt expression of a deleterious protein. Given the high fidelity of base-base interactions, these nucleic acid drugs have great potential for having a high degree of target specificity.^{1,2} However, several obstacles must be overcome for antisense oligonucleotides to function as effective therapeutic agents: stability to degrading enzymes, capacity to effectively bind m-RNA, and ability to enter the cell.³ To address these challenges, synthetic efforts have often focused on the development of oligonucleotides with modifications to the phosphate backbone, the site of degradation by nucleases.⁴ The major categories of these molecules include phosphorothioate oligodeoxynucleotides, methylphosphonate oligodeoxynucleotides, and peptide nucleic acids.⁵ We are developing a new class of metal-chelating nucleic acids in which phosphodiester linkages or an entire nucleoside have been replaced by metal ligand complexes. A diverse group of ligands have been selected to afford many metal-ligand combinations. Appropriately protected ligands will be synthesized and incorporated in short oligonucleotide strands via standard automated synthesis. Complementary oligonucleotide strands via standard automated synthesis. Complementary strands will be combined with the antisense oligonucleotides and stability of these duplexes will be studied in the presence and absence of metal ions.

1. Kurreck, J. *Eur. J. Biochem.* 2003, 270, 1628-1644.

2. De Mesmacker, A., Häner, R., Martin, P., and Moser, H.E. *Acc. Chem. Res.* 1995, 28, 366-374.

3. Alama, A. *Pharmacol. Res.* 1997, 36, 171-178.

4. Brasch, D.A. and Corey, D. R. *Biochemistry.* 2002, 41, 4503-4510.

5. Milligan, J.F., Matteucci, M.D., and Martin, J.C. *J. Med. Chem.* 1993, 36, 1923-1937.

Poster 21: Construction of chiral frameworks from carboxylates and divalent metals

Jeffrey A. Rood, Bruce C. Noll, Kenneth W. Henderson*
University of Notre Dame

The development of well-defined network assemblies is an area of intense research interest due to the potential of these materials for applications in catalysis, chemical separation, and small molecule storage. Much of the attention in this area has been directed toward the synthesis of highly stable metal carboxylate frameworks. We recently reported that lightweight magnesium-carboxylates can form robust frameworks capable of small molecule exchange. We are interested in extending this work towards the synthesis of chiral frameworks, which have promising utility in enantioselective processes. Herein, we report on synthetic pathways to the preparation of chiral frameworks based on carboxylates and divalent metals.

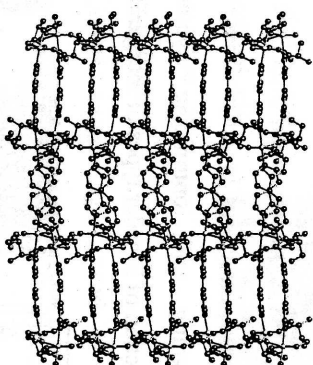


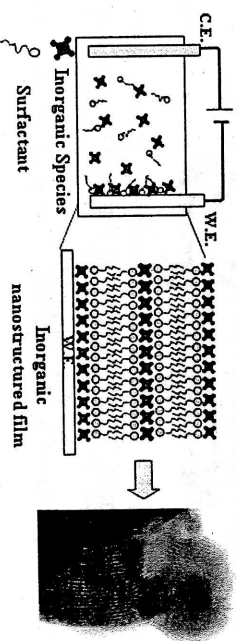
Figure 1. Chiral 6³ nets connected through Cu centers by 4,4'-bipyridine.

Poster 22: Electrochemical deposition of zinc oxide with ordered nanoporous structures

Ellen Steimmiller, Yiwei Tan, and Kyoung-Shin Choi

Purdue University

Nanoporous electrodes are of interest because they increase surface areas and show great promise for use in energy production devices, catalysis, and sensing applications. When the size and connectivity of nanopores can be homogeneously controlled, nanoporous electrodes also allow us to study the effect of specific nanostructural details on the physical and chemical properties of electrodes. In this poster, we present an electrochemical method to prepare inorganic films with high quality ordered nanoporous structures. This was achieved by utilizing self-assembled amphiphiles on the working electrode as templates for the electrodeposition of inorganic materials. We will discuss in detail how deposition parameters (e.g. potential, temperature) and compositions of plating solutions (e.g. pH and surfactants) affect the size, orientation, and homogeneity of nanoporous structures in ZnO. These results will provide a foundation for designing and optimizing synthetic conditions for electrochemical construction of broader types of inorganic nanostructures.



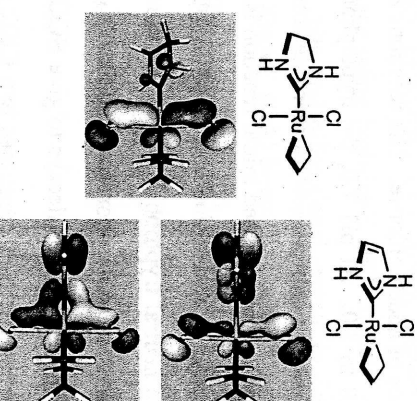
Schematic representation of an electrochemical interfacial surfactant templating method. A lamellar packing structure with characteristic TEM image is shown.

Poster 23: What difference one double bond makes: electronic structure of saturated and unsaturated N-heterocyclic carbene ligands in Grubbs 2nd generation-type catalysts

Richard Lord, Huijun Wang, Mario Vieweger, and Mu-Hyun Baik

Indiana University

N-heterocyclic carbene (NHC) ligands are a versatile and useful class of ligands that have enjoyed much success over the past few decades in organometallic chemistry. This fact is exemplified most convincingly in Grubbs 2nd generation olefin metathesis catalysts. We explore the electronic impact of the NHC-ligand by decoupling electronic and steric effects through simplified model N-heterocyclic carbenes. Saturated and unsaturated N-heterocyclic carbene ligands give rise to fundamentally different frontier orbitals in these catalysts, suggesting a need to classify them as two electronically distinctive ligand classes.



Poster 24: Kinetics and mechanisms of chlorine dioxide oxidation of tryptophan

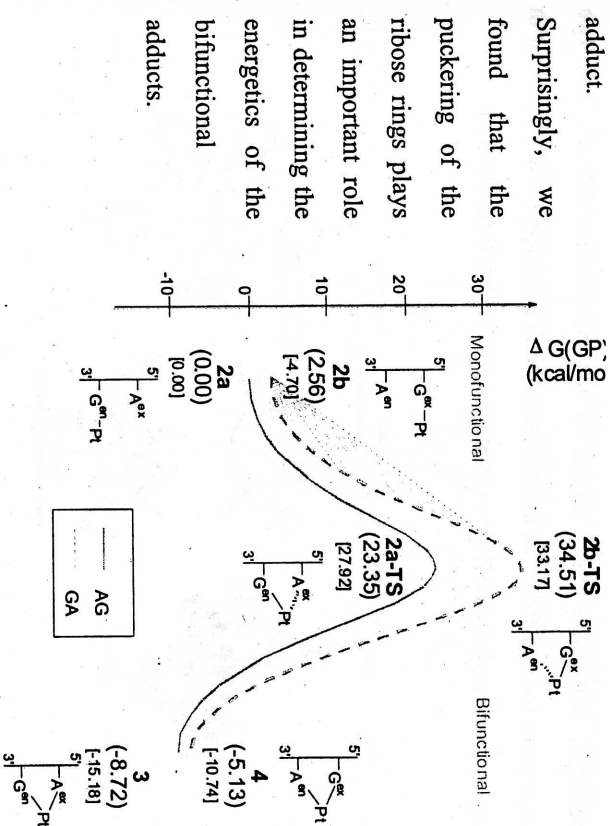
David J. Stewart, Michael J. Napolitano, and Dale W. Margerum*
Purdue University

The reactions of aqueous ClO_2 and tryptophan are investigated by stopped-flow spectrophotometry from pH 3 to 10. The reaction rates increase from pH 3 to 4, are essentially constant from pH 5 to 7, and increase from pH 7 to 10. The reactions are first-order in tryptophan with variable order in ClO_2 that depends on the conditions. Below they are first-order in $[\text{ClO}_2]$ in the absence of added chlorite. The reactions are mixed first and second-order from pH 4.0 to 5.0. At pH 7.0, the tryptophan reaction with ClO_2 is first order in each reactant with a second-order rate constant of $3.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (25.0 °C, $\mu = 1.0 \text{ M}$). The proposed initial reaction is a one-electron oxidation that forms a tryptophyl radical cation and chlorite ion. The radical cation deprotonates to form a neutral tryptophyl radical that combines rapidly with a second ClO_2 to give an observable, short-lived adduct ($k_{\text{obs}} = 48 \text{ s}^{-1}$) with proposed C(H)-OClO bonding. The adduct decays to give HOCl in a three-electron oxidation. Thus, the overall reaction consumes two ClO_2 per tryptophan and corresponds to a four-electron oxidation. Decay of the tryptophyl- ClO_2 adduct gives three initial products that are separated by HPLC and characterized by mass spectrometry and UV-vis spectroscopy. These products in turn undergo rearrangement to form N-formylkynurenine (NFK) and other products.

Poster 25: Sugar puckering controls formation of the intrastrand crosslinks in DNA by cisplatin

Yogita Mantri, Mu-Hyun Baik
Indiana University

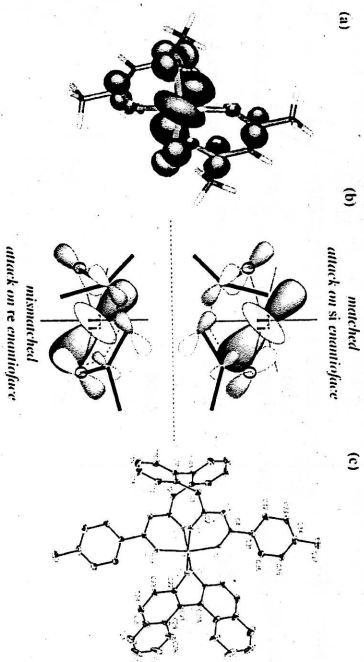
Cisplatin is one of the most widely used anti-cancer drugs. Its primary cellular target is genomic DNA to which it binds predominantly by forming an *intra*-strand crosslink between two adjacent purine bases. This bifunctional binding is thought to occur *via* initial formation of a monofunctional adduct followed by closure in the 5' or 3' direction. Experimental evidence suggests that the 5' direction is exclusively preferred. This study focuses on understanding this directional preference using high-level DFT models. Fully optimized monofunctional, transition state and bifunctional structures for the dinucleotides 5'dApG3' (AG) and 5'dGpA3' (GA) bound to cisplatin reveal a significant kinetic preference for formation of the AG adduct over the GA adduct.



Poster 26: Toward using electronic dissymmetry for stereocontrol of the aldol condensation

Julian P. Bigi, Liam Zakko, Bruce C. Noll and Seth N. Brown*
University of Notre Dame

The present study attempts to extend the ability of titanium(IV) bis(diketonates) to achieve chiral recognition on the basis of *electronic* (rather than steric) dissymmetry to reaction chemistry, specifically the aldol condensation. A series of bis(β -diketonato)titanium(IV) enolates are formed *in situ* from titanium triflates and aromatic and aliphatic ketones in dichloromethane. Enolate formation exhibited high *E/Z* selectivity as well as regioselectivity. The enolate formed from 2',4',6'-trimethylacetophenone was reacted with aldehydes to form the aldol product. While *para*-chlorobenzaldehyde reacts to give the thermodynamic ratio of two diastereomers, pivaldehyde yields two diastereomers in a 4:1 ratio at room temperature, with slow equilibration to the equilibrium 1:1 *dr*. The two diastereomers formed from the condensation with pivaldehyde were present in both open chain and chelated forms, with the open-chain form favored.

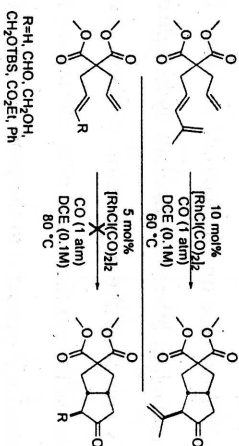


Poster 27: The mechanism of the rhodium(I) catalyzed [2+2+1] catalyst scope and requirements

William Pitcock and Mu-Hyun Baik*
Indiana University

Rhodium(I) catalyzed carbocyclizations are becoming a dominating way to effect complex transformations while concomitantly setting multiple stereocenters in a stereoselective fashion. In this regard, a rhodium(I) catalyzed [2+2+1] carbocyclization of a variety of tethered ene-dienes to afford substituted hexahydropentalenones in excellent yields and diastereoselectivities has been reported recently. Formally a Pauson-Khand reaction, it was found that the corresponding transformation does not work for the analogous *bis*-enes.

In order to understand this stark contrast in reactivity, we modeled the kinetics and thermodynamics of the two parent systems using high level density functional theory. The goal is to understand why the diene moiety is needed and also to determine what conditions or catalyst modifications may be necessary to effect the transformation in the *bis*-ene system.

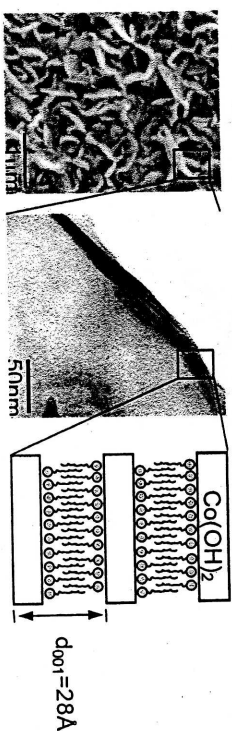


Poster 28: Electrochemical method for preparing layered single and double hydroxide plated Electrodes with tunable interlayer spacings

Matthew Yarger and Kyoung-Shin Choi*

Purdue University

Layered hydroxide materials have been studied for the construction of 3-D catalysts, stacked single layer magnets, and sensing devices. The materials that interest us consist of positively charged host layers with intercalated anions stabilized between the layers to maintain charge neutrality, providing unique synthetic flexibility incorporating an indefinite amount of species within the interlayer region through anion exchange reactions. In this presentation, we report an electrochemical method for synthesizing cobalt hydroxide materials with tunable interlayer spacings, using anionic surfactants as molecular spacers during the electrodeposition process. The surfactants are added to a plating solution containing cobalt and nitrate ions. The generation of OH⁻ at the working electrode, through the reduction of nitrate ions (NO₃⁻ + H₂O + 2e⁻ → NO₂⁻ + 2OH⁻ E₀ = 0.01V vs. NHE), increases the local pH and provides for the precipitation of cobalt hydroxide on an electrode surface. This method allows for the synthesis of surfactant intercalated cobalt hydroxide as thin films, rather than powders, which enhances the application of these materials in electrode devices. We will discuss the synthesis and characterization of cobalt hydroxide prepared by this method and extend it to the production of Zn/Al layered double hydroxide materials to investigate optimum structures in assembling (electro)chemical sensors.



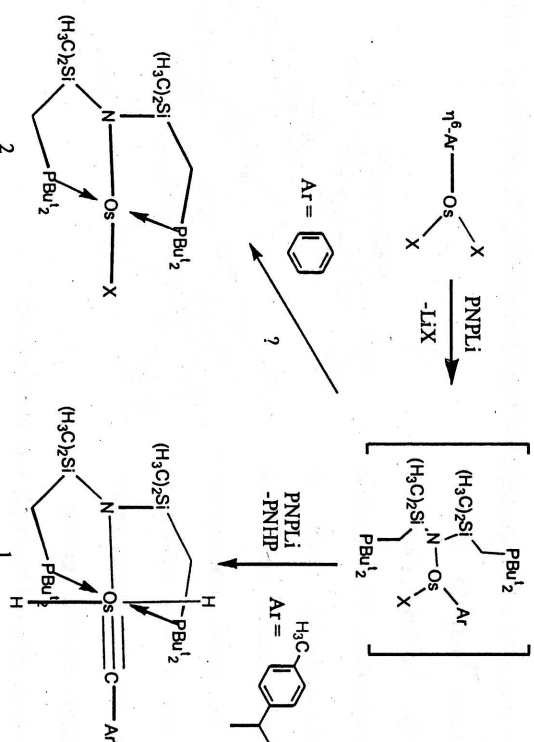
Poster 29: New advances in chemistry of unsaturated osmium compounds

Nikolay P. Tsvetkov, Joo-Ho Lee, Kenneth G. Caulton

Indiana University

Chemistry of transition Me - Osmium - is of great interest because of the predicted properties and finally great reactivity unsaturated Os(II). We continue to develop chemistry of unsaturated compounds with the well-known PNP "Fryzuk ligand". Recently we showed that (cym)OsCl₂ gave carbene complexes **1** of Os when treated with PNPLi-4-crown-12 as a source of PNP ligand. This confirms that Os prefers to be more saturated and have higher coordination number.

To avoid the formation of the **1** as a result of C-H activation of benzylic proton and to make four-coordinated complex **2** we tried to find another source of "starting" Os (II). All our attempts to accomplish our ideas and also reactivity of the resulting compounds will be discussed.



Poster 32: Hydrogen atom transfer to high valent manganese(V) imido corrole

Jennifer Dexheimer, Michael Zilla, Mahdi and Abu-Omar
Purdue University

We have prepared (tpfc)Mn^V(NTs) (1), (tpfc) = 5,10,15-tris(pentafluorophenyl)corrole and Ts = *p*-toluenesulfonyl) and investigated its reactivity with hydrogen atom donor substrates. Complex 1 oxidizes several phenols (4-X-2,6-*t*-Bu₂C₆H₂OH, where X = OCH₃, C(CH₃), CH₃, H, CHO, CN) to give the phenoxyl radical, TsNH₂, and (tpfc)Mn^{III}. The experimental rate law for this reaction is $d[\text{Mn}^{\text{III}}]/dt = 2k[(\text{tpfc})\text{Mn}^{\text{V}}(\text{NTs})][\text{Phenol}]$. The second-order rate constants correlate well with O-H bond dissociation energies (BDE) of the phenols, and display a primary kinetic isotope effect (KIE), $k_H/k_D = 4.6 (\pm 1.1)$. These results are consistent with hydrogen atom transfer from phenol to the imido ligand. However, the rate constants do not show linearity with respect to the Hammett constant σ . Mechanistic implications of this reaction will be discussed.

Poster 33: Network control using lithiated mixed-anion aggregates

J. Jacob Morris, Bruce C. Noll, Kenneth W. Henderson*
University of Notre Dame

The synthesis and characterization of well-defined network assemblies continues to be an area of intense interest due to the potential applications of these materials in areas as diverse as catalysis, chemical separation, optics, and electronics. The controlled formation of crystal and network structures remains problematic due to the delicate balance between weak bonding interactions and packing forces. Our approach centers on the use of structurally well-defined organolithium aggregates to control network assembly. We have recently demonstrated that tetrameric lithium aryloxides can be linked through linear ditopic Lewis bases to create a series of one, two, and three-dimensional polymers. Upon gaining a firm understanding of the design principles involved with the simple lithium aryloxide systems we wished to add another level of sophistication by controlling the number of lithium atoms within each aggregate that would act as points of network extension. Theoretically, this would give greater control over the dimensionality of the resulting framework. To achieve this aim we targeted the preparation of heteroleptic aggregates containing chelating sidearms to block one or more of the lithium sites.

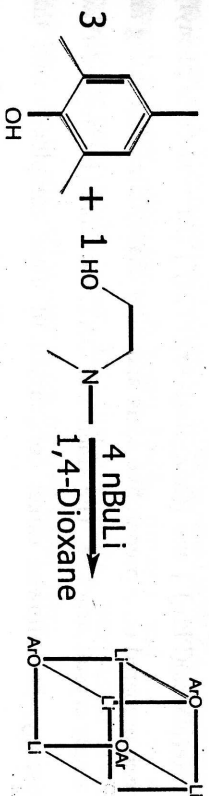


Figure 1. Synthesis of a tetrameric mixed-anion aggregate

Poster 34: Synthesis of cationic rhenium(VII) oxo imido complexes and their tunability towards oxygen atom transfer

Jeanette E. Cessarich, Elton A. Ison, Nicholas E. Travia, Phillip E.

Fanwick, Mahdi M. Abu-Omar

Purdue University

A facile method has been developed for the synthesis of cationic Re(VII) *cis* oxo imido complexes of the form [(salpd)Re(O)(NAr)⁺] (salpd = N,N'-propane-1,3 -diylbis(salicylideneimine)), [(saldach)Re(O)(NAr)⁺] (saldach = N,N'-cyclohexane-1,3-diybis(salicylideneimine)), and [(hoz)₂Re(O)(NAr)⁺] (hoz = 2,(-2')-hydroxyphenyl)-2-oxazoline), (Ar = 2,4,6-(Me)₃C₆H₂, 4(OMe)C₆H₄, 4-(Me)C₆H₄, 4-(CF₃)C₆H₄, 4-(Me)C₆H₄SO₂), from the reaction of oxorhenium(V) [(L)Re(O)(SolV)⁺] and aryl azides under ambient conditions. Unlike previously reported cationic Re(VII) dioxo complexes, these cationic oxo imido complexes can be obtained on a preparative scale and an X-ray single crystal structure of [(saldach)Re(O)(NMe₃)⁺] has been solved. Mechanistic insight suggests the reactions of oxo Re(V) with aryl azides proceed through an azido adduct. Treatment of the cationic oxo imido complexes with a reductant (PR₃, PhSM₂, or PhSH) results in oxygen atom transfer (OAT) and the formation of cationic Re(V) imido complexes. [(salpd)Re(NMe₃)(PPh₃)⁺] and [(hoz)₂Re(NAr)(PPh₃)⁺] (Ar = *m*-OMe phenyl) have been prepared on a preparative scale and fully characterized including an X-ray single crystal structure. The kinetics of OAT, monitored by stopped-flow spectroscopy, has allowed direct comparison of these complexes with the known cationic dioxo Re(VII) [(hoz)₂Re(O)₂]⁺. The rates of OAT are significantly affected by the electronics of the imido ancillary ligand with electron-withdrawing imidos being most reactive.

Poster 35: Trans effected shift in NO stretching frequency observed

in iron(II) tetraarylporphyrinato nitrosyls with 1-methylimidazole

Jeffrey W. Pavlik, Nathan J. Silvernail, Bruce C. Noll and W. Robert

Scheidt

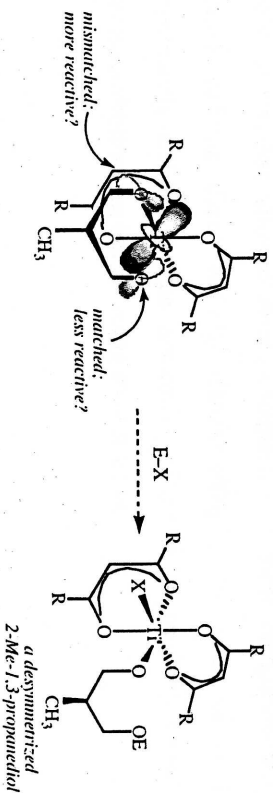
University of Notre Dame

Nitrosyl stretching frequency variation with temperature was determined by multi-temperature infrared spectroscopy. Vibrational spectra of four six-coordinate and one five-coordinate iron(II) tetraaryl porphyrin derivatives were recorded over a temperature range of 107 K to 348 K at 20 K intervals for each compound. The six-coordinate compounds analyzed were [Fe^{II}(porph)(NO)(1-Melm)] where porph = tetraphenyl porphyrin (TPP), tetrapara-fluorophenyl porphyrin (Tp-FPP), and tetrapara-methoxyphenyl porphyrin (Tp-MeOPP). For [Fe^{II}(Tp-FPP)(NO)(1-Melm)], two crystalline forms were tested, monoclinic and triclinic. The five-coordinate compound was [Fe^{II}(TPP)(NO)]. Both the monoclinic and triclinic forms of [Fe^{II}(Tp-FPP)(NO)(1-Melm)], as well as [Fe^{II}(Tp-MeOPP)(NO)(1-Melm)], displayed positive, linear ν_{NO} temperature dependencies of 0.031, 0.020 and 0.018 cm⁻¹/K respectively. A linear temperature dependency of -0.011 cm⁻¹/K was recorded for [Fe^{II}(TPP)(NO)(1-Melm)]. In the case of [Fe^{II}(TPP)(NO)], this trend was not observed. The observed frequency shifts, coupled with X-ray structural data reveal a linear relationship between Fe-N_{im} distance and ν_{NO} for all six-coordinate compounds studied. This change in Fe-N_{im} bond length is believed to be a result of unit cell volume variation with temperature.

Poster 36: Electronic dissymmetry in 1,3-propanediolate complexes of (dike)₂Ti^{IV}

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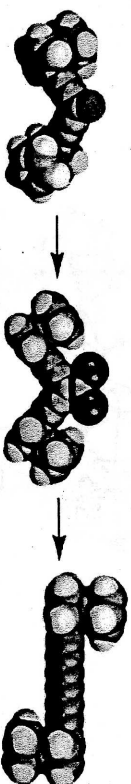
Electronic dissymmetry due to π bonding in C_2 -symmetric (dike)₂Ti₂ complexes has been demonstrated to promote chiral recognition of BINOL enantiomers (Brown, S. N.; Chu, E. T.; Hull, M. W.; Noll, B. C. J. Am. Chem. Soc. 2005, 127, 16010-16011). This dissymmetry could also be expressed in the desymmetrization of a meso substrate. To explore this idea, a 2-methyl-1,3-propanediolate complex of titanium(IV) containing a linked bis(β -diketonate), (Tol₂Bob)Ti(OCH₂CH(CH₃)CH₂O), was synthesized, and its structure and reactivity analyzed. Coupling patterns in the ¹H NMR demonstrate that the propanediolate ring is not in a symmetrical conformation. Density functional theory calculations, as well as NOESY and crystallographic studies, of it and other propanediolate complexes reveal a consistent structural distortion indicative of a stereoelectronic bias. In solution and in the solid, however, multiple conformations appear to be accessible. This flexibility allows both oxygens to move between "matched" and "mismatched" positions in relation to the LUMO, and this may explain the lack of stereoselectivity in reactions of (Tol₂Bob)Ti(OCH₂CH(CH₃)CH₂O) with electrophiles such as chlorotrimethylsilane.



Poster 37: Novel preparation and structural study of 1, 6-bis(ferrocenyl)-1, 3, 5-hexatriyne and its precursors

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This poster describes the novel preparation and structural study of 1, 6-bis(ferrocenyl)-1, 3, 5-hexatriyne (Fc(C \equiv C)₃Fc, **3**). The title compound, a member of α, ω -diferoceanyl polyynes (Fc(C \equiv C)_{*m*}Fc) with $m = 3$, was prepared from a reaction involving alkynyl migration in vinylidene carbenoid, between 3-(dibromomethylidene)-1,5-bis(ferrocenyl)pent-1,4-diyne (FcC₂C(CBr₂)C₂Fc) and BuLi. The crystal structures of both the title compound (Fc(C \equiv C)₃Fc, **3**) and its precursors (FcC₂C(=O)C₂Fc, **1** and FcC₂C(CBr₂)C₂Fc, **2**) are shown below. The voltammetric study of compounds **1**, **2** and **3** revealed pseudo-two-electron oxidations attributed to two ferrocenyl units. This behavior is in stark contrast with the previously studied Fc(C \equiv C)Fc and Fc(C \equiv C)₂Fc (stepwise one-electron oxidation, efficient electron coupling), and Fc(C \equiv C)₄Fc and Fc(C \equiv C)₆Fc (true two-electron oxidation, absence of electron coupling). The same synthetic route was also successfully applied to the preparation of 1, 6-bis(trimethylsilyl)-1,3,5-hexatriyne (TMS(C \equiv C)₃TMS), which is a structural analog to the title compound and is an useful bridging ligand to prepare Ru₂-alkynyl compounds.



Poster 38: Metal-metal interactions in ferrocenyldiketonate titanium complexes

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Several ferrocenyldiketonate titanium complexes, $(\text{Fc}_2\text{BOB})\text{TiX}_2$, were synthesized and characterized by NMR, IR, MS, X-ray crystallography, and elemental analysis. Electrochemistry and electronic spectra provide interesting information on the interactions between the $\text{Ti}(\text{IV})$ metal center and the $\text{Fe}(\text{II})$ centers of the ligand ferrocenyl groups. In particular, distinct color changes and a progressive shift in the ferrocene absorption bands in the UV-Vis spectra was observed as a function of the ancillary X groups, while the cyclic voltammograms demonstrate that most of the complexes synthesized exhibit single reversible or quasi-reversible oxidation curves for the ferrocenyl groups. These results imply that changing the ancillary ligands X tune the electron density around titanium and enhance the Fe-Ti electronic communication rather than the Fe-Fe communication. Transient absorption spectra of some of the complexes provide a glimpse into the potential of these compounds as sensitizers for solar energy conversion.

