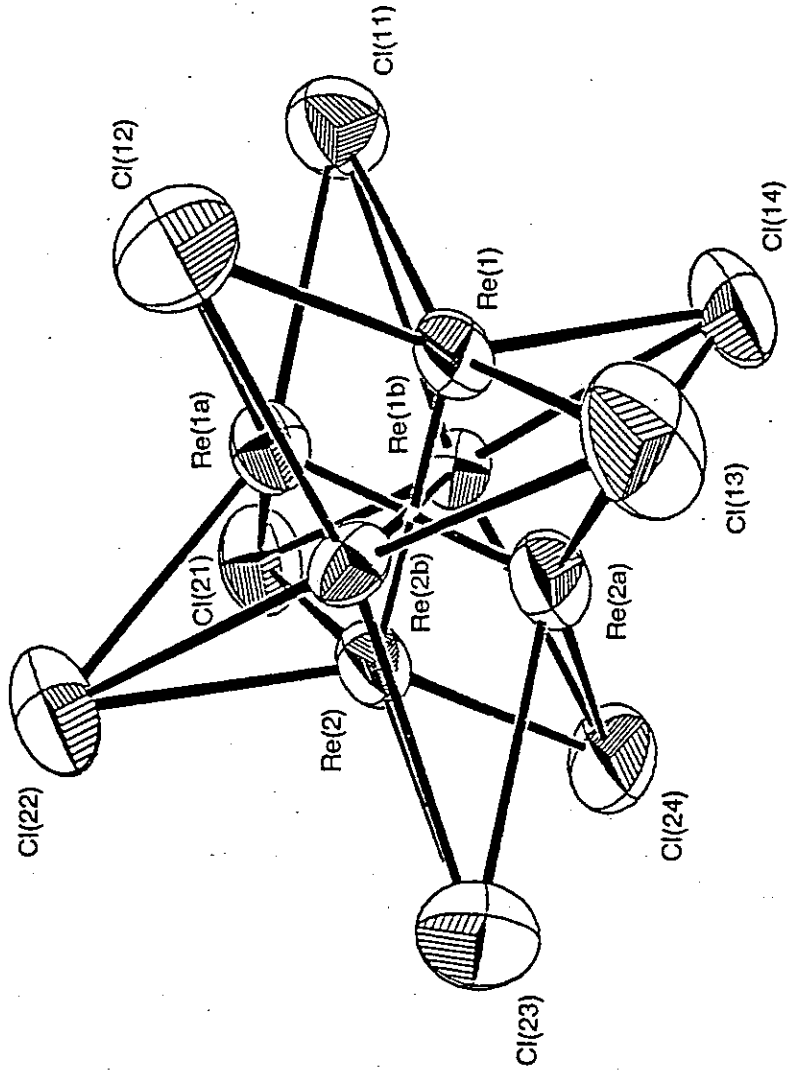


Saturday, October 17,
Purdue University
West Lafayette, IN



PINDU



PINDU

October 17, 1998

Morning Session

- 8:30 - 8:55 Welcome Breakfast in WTHR 172
Set-up posters in front of WTHR 201
- 8:55 - 9:00 Opening Remarks, WTHR 172: Jillian Buriak
- 9:00-10:00 Talks, WTHR 172
Jason Klein, Purdue
Session Chair:
- 10:00-11:15 Posters, in front of WTHR 201
- 11:30-12:30 Talks, WTHR 172
Teresa Neil, Notre Dame
Session Chair:
- 12:30-2:00 Lunch

Afternoon Session:

- 2:00 - 3:15 Poster Session, in front of WTHR 201
- 3:30-5:00 Talks, WTHR 172
Brian Pate, Indiana
Session Chair:
- 5:00 Closing Remarks, WTHR 172

Morning Session

- 8:30 - 8:55 Welcome Breakfast in WTHR 172
Set-up posters in front of WTHR 201
- 8:55 - 9:00 Opening Remarks: Jillian Buriak, Purdue
- 9:00-10:00 Talks, WTHR 172
Session Chair: Jason Klein, Purdue
- 9:00 Charge Effects on Oxygen Atom Transfer
Sean B. Seymore
Notre Dame
- 9:30 Photopatterning and Lithography on Porous Silicon Surfaces.
Michael Stewart and Jillian Buriak.
Purdue University

A method is described that enables high levels of alkyl and alkenyl passivation of porous silicon (por-Si). An ordinary tungsten light source is used to activate the surface of n-type por-Si towards nucleophilic attack. Terminal alkenes and alkynes are hydroxylated by the activated surface. The hydrophobic surface is resistant to attack by boiling aerated acidic and alkaline solutions and preserves 97% of the photoluminescence. Regiospecific hydroxylation is possible using focused patterns of light on the por-Si surface. The photopatterned regions are able to survive alkaline treatment while the unfunctionalized regions are dissolved.

10:00-11:15 Posters in front of WTHR 201

Posters:

Purdue University

2. Mixed Carbonyl-Nitrile Complexes Containing the Electron-Rich Triply Bonded $\text{Re}(\text{PP})$, Unit. $\text{PP} = \text{dppm}, \text{dppa}$.
James Chantler, Phillip E. Fanwick and Richard A. Walton.

Many complexes have been synthesized which contain the $\text{Re}_3(\text{dppm})$ unit attached to nitrile and/or carbonyl ligands. Further investigation has shown that the presence of the carbonyl ligand has a stabilizing effect on additional nitrile ligands. During the synthesis of these species, the $\text{Re}_3(\text{dppm})$ unit remains intact. Similar compounds containing the $\text{Re}_3(\text{dppa})$ core have been prepared in efforts to establish the effect of the bisphosphine ligands on the stability of the dirhenium core

4. Group(IV) And Group (V) Metal Alkylidene And Alkylidyne Derivatives Supported By Carbazole Ligation.
Patrick N. Riley, Phillip E. Fanwick and Ian P. Rothwell.

The alkylidyne bridged dimers $[(\text{R})_2\text{M}(\mu\text{-CSiMe}_2)_2\text{M}(\text{R})_2]$ ($\text{M} = \text{Nb}, \text{Ta}, \text{R} = \text{CH}_2\text{SiMe}_3$), react with an excess of carbazole reagents to produce the tetra-substituted derivatives $[(\text{N}')_2\text{M}(\mu\text{-CSiMe}_2)_2(\text{N}')_2]$ ($\text{N}' = \text{cb}$ (1), thcb (2), cbh-3Bu (3)). Reaction of (1) with various substituted alkynes produces novel 1,3-dimetalbenzenes. Reaction of organic isocyanides with (1) leads to insertion of the isocyanide into the bridging alkylidyne unit. The *bis*(benzyl)[(cb)₂Ti(CH₂Ph)₂] (4) and alkylidene bridged dimer [(cb)₂Ti(μ-CHSiMe₃)₂Ti(cb)₂] (5) are formed by adding carbazole to the tetra(alkyl)s [TiR₄] (R = CH₂Ph, CHSiMe₃). The reaction of (4) and (5) with 2,6-dimethylphenylisocyanide leads to organometallic products

containing new carbon-carbon bonds. The structures and spectroscopic properties of these new compounds will be discussed.

8. **Synthesis And Catalytic Reactivity Of Cationic Titanium Compounds Supported By Aryloxy Ligands.**

Matthew G. Thorn, Phillip E. Fanwick and I. P. Rothwell.

The great success of group 4 metallocene olefin polymerization catalysts has stimulated interest in the development of related homogeneous catalysts supported by non-Cp ancillary ligation. The synthesis and polymerization reactivity of cationic alkyl derivatives of Ti that contain *ortho*-phenyloxy and chiral *ortho*-(1-naphyl)phenyl phenoxy ligation will be presented.

10. **Cyclodimerization And Polymerization Of Dirhenium(III) Units.**

Sophia S. Lau, Phillip E. Fanwick and Richard A. Walton,

The reaction of $\text{ReCl}(\text{OAc}) \cdot 2\text{H}_2\text{O}$ with various monodentate tertiary phosphine ligands has been investigated. Depending on the basicity and the cone angle of the phosphine ligands, reduction, alkoxide incorporation, and cyclodimerization of the dirhenium unit can occur. The aforementioned dirhenium(III) complex can also react with linker ligands such as pyrazine and 4,4' bipyridine to form polymeric chains of dirhenium units.

14. **Synthesis And Reactivity Of Group IV And V Metal Derivatives With η^2 -Aryloxy Ligation.**

Douglas R. Mulford, Phillip E. Fanwick and Ian P. Rothwell

A novel set of Group IV and V metal derivative compounds which have η^2 -aryloxy ligands have been synthesized. The reactivity of these compounds and the influence of the forced *cis* arrangement of the aryloxides will be presented.

16.

Arene And Aryl Phosphine Hydrogenation Using Early d-Block Metal Aryloxides.

M. M. Salberg, P. E. Fanwick and I. P. Rothwell,

Previous work has shown that niobium aryloxy compounds can catalytically hydrogenate aryl phosphines and aromatic hydrocarbons into their saturated counterparts. These reactions are carried out using catalyst precursors $[\text{Nb}(\text{OAr})_2\text{Cl}_2]$ ($\alpha = 2,3$; $\text{OAr} = 2,3,5,6$ -tetraphenyloxy) activated with Bu^tLi , followed by heating with the substrate under hydrogen pressure. Pressure dependence studies have been carried out on the aryl phosphine systems in order to elucidate a viable mechanism for the hydrogenation process. Studies are currently being performed to determine possible intermediates involved in the reaction.

19.

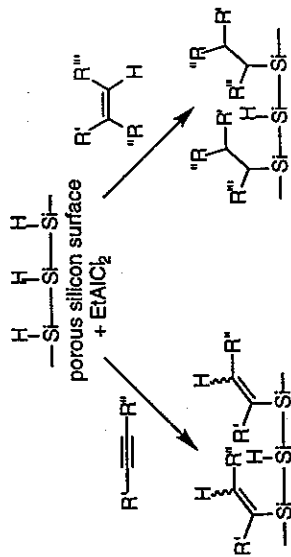
Rhenium Heptahydride Complexes With Alkyl Phosphines: Synthesis And Reactivity.

Kimberly J. Smith, Andrea L. Ondracek and Richard A. Walton.

Rhenium heptahydride complexes with aryl phosphines have been studied extensively since 1969 when Chatt and Coffey reported the synthesis of $\text{ReH}_7(\text{PPh}_3)_2$. However, little work has been reported on similar compounds using alkyl phosphines. The *cis* and *trans* isomers of $\text{ReOCl}_2(\text{PMe}_3)_2$ and $\text{ReOCl}_2(\text{PEt}_3)_2$ have been synthesized in good yield and fully characterized including crystal structures. These isomers are the precursors for the heptahydrides $\text{ReH}_7(\text{PMe}_3)_2$ and $\text{ReH}_7(\text{PEt}_3)_2$. The synthesis, characterization, and thermal stability of these unusual heptahydrides will be presented, as well as the new pentahydrides $\text{ReH}_5(\text{PMe}_3)_2$ and $\text{ReH}_5(\text{PEt}_3)_2$.

20. **Catalytic Hydrosilylation Of Photoluminescent Porous Silicon Surfaces.**

Matthew J. Allen, Jillian M. Buriak



Since its discovery in 1990, photoluminescent porous silicon has been the subject of intense interest. Potential applications for porous silicon include use as chemical sensors, optoelectronic devices such as electroluminescent displays, photodetectors, and as a matrix for photopumped tunable lasers. We have found that Lewis acid mediated hydrosilylation of the surface is a mild and general approach for covalent modification of the surface. This functionalization of the surface has great effects on the surface stability and photoluminescence which will be described in detail.

University of Notre Dame

6. **2,6-Bis(Acidphosphate)Anthracene: Synthesis and Photodimerization In Solution And Layered Structures.**

Wensheng Yang and Marya Lieberman

It has been well known that anthracene derivatives can undergo photodimerization under irradiation and produce [2+2] photodimers. Here we synthesized a new anthracene derivative, 2,6-Bis(acid phosphate) anthracene 1, which could be expected to be assembled into layered materials when exposed to metal ions such

as copper, zirconium etc. It was found that for 1, photodimerization can only be carried out in solution. In layered zirconium anthracene-2,6-bisphosphate, however, no photodimerization occurred. The powder X-ray diffraction pattern showed in the layered materials, the arrangement of the anthracene rings was in a head-to-tail manner, which is not the demanded configuration for a dimerization to go.

12. **New Fe(III)-NO Porphyrins. Elusive Six-Coordinate Intermediates.**
Mary K. Ellison and W. Robert Scheidt*

18. **Synthesis, Structural Characterization, and Magnetic Properties of Neutral and -Cation Radical Derivatives of Copper(II) Mono-, Oxoporphyrin.**
Teresa L. Neal, Seong-Joo Kang, Charles E. Schulz, and W. Robert Scheidt*

University of Indiana

1. **Dehydrohalogenation as a Source of OsH₂Cl(PPPh)₃ (n=1,3)**
German Ferrando and Kenneth G. Caulton

Reaction of OsCl₂(PPPh)₃ and equimolar NEt₃ with excess H₂ in benzene at 20 °C gives OsH₂Cl(PPPh)₃, which can be dehydrogenated to OsHCl(PPPh)₃ either physically (repeated vacuum treatment in solution) or chemically (hydrogenation of equimolar styrene). Both hydride complexes are fluxional but show AM. ³¹P{¹H} NMR patterns at low temperature, and the T₁ value of OsH₂Cl(PPPh)₃ is consistent with it containing one H₂ ligand. Ethylene reacts rapidly with OsH(H₂)Cl(PPPh)₃ to give OsHCl(CH₂)₂(PPPh)₃.

3. **Use Of β -Diketone Ligands For The Synthesis Of New Manganese Carboxylate Clusters.**

Cristina Cañada, John C. Huffman, George Christou.

We have long been investigating the chemistry of manganese-carboxylate clusters with oxide bridges and chelating ligands. Many structures of various nuclearities (up to 18) have been obtained using the chelating ligand dbm (dbmH = dibenzoylmethane).

We have recently begun to investigate the use of other β -diketonates to assess their influence on the product identity. These ligands are dpm (dpmH = dipivaloylmethane) and hfac (hfacH = hexafluoroacetylacetonate). Reactions between these chelates and $\text{NMe}_4[\text{Mn}_2\text{O}_2(\text{O}_2\text{CPh})_2(\text{H}_2\text{O})]$ have been investigated and the products characterized by several physical and spectroscopic techniques such as IR, NMR, EA, CV and DPV. The product of the reaction with dpm, $\text{NMe}_4[\text{Mn}_2\text{O}_2(\text{O}_2\text{CPh})_2(\text{dpm})_2]$, has been oxidized by controlled potential electrolysis to give a new cluster whose properties will be described.

5. **High-spin Molecules: Magnetic Properties Of Tetranuclear And Hexanuclear Manganese Oxo-aggregates..**

Guillem Aromi, Juan-Pablo Claude, John C. Huffman, Michael J. Knapp, David N. Hendrickson, and George Christou.

An important aspect of transition-metal cluster chemistry is that it provides access to molecules with unusually high spin ground states that exhibit, in some cases, the new magnetic phenomenon of single-molecule magnetism. Intense research efforts are being devoted to develop methods capable of yielding new examples of high-spin molecules. Synthetic pathways to a new family of hexanuclear manganese clusters with a Mn_6 octahedral core, a S-12 spin ground state and formula $[\text{Mn}_6\text{O}_8\text{X}_2(\text{R}_2\text{dbm})_4]$ have been developed (R=dbmH - 4,4'-R-dibenzoylmethane, R = Me, Et, and X = Cl, Br). The magnetic properties and the characterization of these complexes by ^1H NMR and EPR spectroscopies, and cyclic voltammetry will be presented. These results will be compared with

the physicochemical behavior of the related tetranuclear clusters of the type $[\text{Mn}_4\text{O}_4(\text{OAc})_4(\text{dbm})_4]$ (X = Cl, Br), which have a S=7/2 spin ground state and show single-molecule magnetism behavior.

7. **Investigation of the Substitution Reactions of $\text{M}_4(\text{O}^i\text{Bu})_4$ (M = Mo, W) with Thiolate Ligands.**

Malcolm H. Chisholm and Kristine B. Quinlan.

While the reactivities of compounds $\text{M}_4(\text{OR})_4$ (M = Mo, R = Bu, Pr, CH₂Bu, CH(Me)Ph, SiMe₃, M = W, R = OⁱBu, Pr, CH₂Bu) have been thoroughly investigated, relatively few corresponding thiolate complexes are known. The reactivity of these thiolate complexes could shed light on the energetic differences between alkoxide and thiolate ligands, which has been the subject of ongoing debate. The mixed alkoxide-thiolate complexes $\text{M}_4(\text{O}^i\text{Bu})_2(\text{S}^i\text{Bu})_2$ (M = Mo, W) have been synthesized and characterized. These substitution reactions have been studied by nmr to identify the mono-, di- and tri-substituted products. The equilibrium constants for the reactions have also been determined. The reactivity of $\text{W}_4(\text{O}^i\text{Bu})_2(\text{S}^i\text{Bu})_2$ with small unsaturated molecules has been investigated.

9. **Synthesis and Characterization of Paramagnetic Polyoxovanadates and Vanadium Carboxylate Clusters.**

Ming-Hsi Chiang, J. C. Huffman, W. Streib, J. Bollinger, G. Christou.

Reactions of orthovanadate and vanadyl in an aqueous solution in the presence of sodium acetate acting as a proton acceptor give different paramagnetic polyoxovanadates. On the other hand, reactions in MeCN produce paramagnetic vanadium carboxylate clusters.

is believed to be responsible for the Single Molecule Magnet behavior. The temperature at which this behavior is observed (2.8K) is a limitation for potential technological applications, but it can be modified by changing the carboxylate ligands that stabilize the cluster. We present spectroscopical and physico-chemical evidence for two new groups of Mn_n derivatives obtained by the replacement of organic carboxylate groups with nitrate ligands and ferrocene carboxylate derivatives, respectively.

Some C-F Bond Cleavage Reactions Mediated by Unsaturated Os and Ru Complexes.

Dejian Huang, Kenneth G. Caulton*

We demonstrated here three C-F bond cleavage reactions mediated by 16-electron Ru and Os complexes supported by two sterically demanding phosphine ligands, L (L = PBu₃Me). First, in the presence of a catalytic amount of CsF, MHF(CO)₂L (M = Ru, Os) reacts with Me₃SiCF₃ to give difluorocarbenes, MHF(CF₂)(CO)₂L, which undergoes rearrangements to Ru(CF₂H)F(CO)₂L or OsF₂(CFH)(CO)₂L. Second, RuH(X)(CO)₂L (X = Ph, F) reacts with vinyl fluoride at room temperature to form Ru(CH₂-CH₂)F(CO)₂L and eliminates HX. Third, fluorobenzene and RuH(NO)₂L undergo C-F/Ru-H exchange reaction to form RuF(NO)₂L and benzene. The mechanisms of these reactions will also be discussed.

17.

A New Oxidation State for the Family of $[Mn_nO_n(RCOO)_n(H_2O)]_x$ Compound, Examples of Single Molecular Magnets.

Monica Soler, Swapan K. Chandra, Daniel Ruiz, David N. Hendrickson, George Christou.

Neutral and monoanionic Mn_n complexes $[Mn_nO_n(RCOO)_n(H_2O)]_x$ (R = Et, Ph, ...etc., x = 3 or 4) and $(Pr^+N)[Mn_nO_n(EtCOO)_n(H_2O)]_x$ have been reported to display both large ground spin state of S = 10 (or 9) and S = 19/2 respectively, and high anisotropy with negative zero field splitting which are characteristics for single-molecule magnets (SMM).

We have recently attempted to synthesize two-electron reduced species of Mn_n complexes. An example which will be presented is the dianion $(Pr^+N)_2[Mn_nO_n(2,4-(NO_2)_2C_6H_3COO)_n(H_2O)]_x$ which has been synthesized and characterized. Magnetic studies show both a high spin ground state and SMM behaviour for this complex.

Modeling the Photosynthetic Water Oxidation Center: Crystal Structure and Properties of a New Tetranuclear $[Mn_4O_4]$.

Nuria Aliaga, Sheyi Wang, Kirsten Folling, and George Christou.

Controlled Potential Electrolysis (CPE) procedures are described that allow access to $[Mn_4O_4(O_2CC_6H_4-p-Me)_4(dbm)]_2$ (dbmH-dibenzoylmethane) from $[Mn_4O_4(O_2CC_6H_4-p-Me)_4(dbm)]_1$ via coupled oxidation/oxide incorporation. CPE at 1.2 V vs SCE in MeCN leads to conversion of 1 to 2 in 30-40% yield (based on dbm). The crystal structure and properties of 2 will be described.

New derivatives of $[Mn_nO_n(RCOO)_n(H_2O)]_x$ Single Molecule Magnet.

Pau Artus, Daniel Ruiz, David N. Hendrickson, George Christou.

The family of compounds $[Mn_nO_n(RCOO)_n(H_2O)]_x$ (R = various) has been found to show an unusually large spin relaxation time that

11:30-12:30

Talks

Session Chair:

Teresa Neil, Notre Dame

Afternoon Session

2:00 - 3:15

Poster Session

Purdue

11:30 What Metal-Metal Bonds Are Up To These Days: From Selective Hydrogenation Chemistry To The Electrochemical Determination Of Oxidation Kinetics. Some Old Tricks With New Twists.

Katherine C. Glasgow, Malcolm H. Chisholm, and Ann M. Macintosh.
Indiana University

Metal-metal bonds typically provide a reservoir of electrons that can be tapped for such reactions as reductive coupling and olefin hydrogenation. Two current research topics in the Chisholm group include mechanistic studies of a selective hydrogenation catalyst $W_2(OCH_2Bu)_4(py)_2$ (W-W) and the electrochemical investigations of the electronic structure and oxidation of $M_2(O_2CR)_4$ -type complexes. Both studies probe the role of the metal-metal multiple bonding in terms of its effects on the reactivity of the complexes.

12:00

Synthesis And Catalytic Epoxidation Activity Of A Substituted Iron Cyclam Complex. April Pulvirenti, Phillip E. Fanwick, and Thomas Bein.
Purdue University

The complex $[FeL(CH_3CN)_4](PF_6)_2$ (L = 3,14-dimethyl-2,6,13,17-tetraazacyclo[14,4,0,0,0]docosane) has been synthesized and characterized by infrared, visible, and single crystal X-ray diffraction methods. The complex is an effective and selective catalyst for epoxidation of small olefins with several oxidants. Hydrogen peroxide oxidant and ambient temperatures tend to give the highest yield in epoxide.

12:30-2:00

Lunch

2. Epoxidation Catalysis With Manganese-1,4,7-Triazacyclononane Derivatives Included In Mesoporous Hosts. Jake M. Reder, Steve Jurgens and Thomas Bein.

Manganese complexes of N-substituted 1,4,7-triazacyclononane (TACN) were anchored to the walls of siliceous mesoporous hosts. These systems are selective epoxidation catalysts with the oxidant H_2O_2 .

The effect of catalyst structure, the nature of the support and the anchoring method on the catalytic activity are examined.

4. Synthesis Of Aluminophosphate Phases Using Ferrocenium Salt As Templating Agent.

Kwangwook Choi, Svetlana Mintova and Thomas Bein,

An aluminophosphate molecular sieve with AFT structure was synthesized hydrothermally using bis(cyclopentadienyl) iron(III) ion, Cp_2Fe , as templating agent. A dense aluminophosphate having the α -quartz structure is obtained when the template concentration falls below a critical threshold. Additionally, an as yet unidentified porous phase was obtained with the same preaged gel using a microwave field and much shorter synthesis times. Thermal analysis and UV-VIS spectra show the iron complex to be included in these aluminophosphate molecular sieves.

8.

Catalytic Zeotype Films For Gas Sensing On Calorimetric Sensors.
Ken E. Yasuda, Svetlana Mintova, Jaco Visser and Thomas Bein,

Films of transition metal-containing microporous materials were deposited on micromachined calorimeters. Thermal responses to trace hydrocarbons in air were measured. Enhanced levels of chemical selectivity were observed with zeotype-modified sensors, while openly-exposed catalyst films showed no selectivity.

10.

Encapsulation Of The Solvatochromic Dye Nile Red In Zeolites: *In Situ* Synthesis Vs. Adsorption Method.
Julia L. Meinershagen and Thomas Bein

The intrazeolite synthesis of the highly fluorescent dye Nile Red for use as an optical sensor has been studied. The solvatochromic nature of Nile Red allows for large changes in wavelength in different environments, making it an excellent candidate for optical sensing. Several synthetic pathways in various zeolites have been explored in order to optimize yields of the encapsulated dye and reduce side products. The stable, hydrophobic dye/zeolite SiY ensemble prepared by inclusion synthesis shows dramatic, reversible shifts in the reflectance spectra in the presence of low pressure ethanol and acetone vapors. The color of the zeolite ensemble changes nearly instantaneously from blue to pink, similar to effects in solution, while no response to hexane was detected. The dye/zeolite ensembles show chemical and size selectivity in their optical responses that can be applied in chemical sensing.

14.

Metal And Ligand Centered Emission From Substituted Platinum Terpyridine Complexes
Joseph F. Michalec, Stephanie A. Bejune and David R. McMillin

The electronic excited states of the late transition metals are of great interest in the area of molecular sensors. Because late transition metal systems typically have vacant coordination sites, exciplex

(excited state complex) formation is an important process, and the excited states are quite sensitive to the local environment. In our quest to develop platinum terpyridine complexes that have longer lived excited states, we have developed substituted terpyridines that show not only rather long lived excited states, but also unexpected oxygen sensitivity.

[Pt(terpy)Cl]⁺ is known to interact with DNA in many ways. However, it shows no emission in solution due to the existence of a d-d deactivating state, and therefore is not a good molecular probe. In our previous work, we have shown how substitution at the 4' position of terpyridine can lead to complexes that have long lived excited states due to a lowering of the energy of metal to ligand charge transfer state. In this work substitution at the 4' position with aryl substituents should help delocalize the charge developed in the excited state. This delocalization should decrease the energy of the excited state and allow for a longer lived excited state. With this work we hope to gain better insight into the dynamics of the excited states of these complexes and in turn develop complexes that can be better luminescent probes of their local environment.

16.

Study Of The Polyhydrido Trimethylphosphine Rhenium Complex ReH₃(Pme)₃ By Using Ftir.

Ruomei Li, Kimberly Smith, Richard A. Walton and Ben S. Freiser

The electron impact and chemical ionization mass spectra, the reactivity of fragment and dimer ions from polyhydrido trimethylphosphine rhenium, ReH₃(PMe₃)₃, were studied in the gas-phase using Fourier transform ion cyclotron resonance mass spectrometry. The synthesis of ReH₃(PMe₃)₃ was initially reported in 1985, but the gas-phase reactivity of this complex has not yet been explored. In this project, the positive and negative ions ReH₃(PMe₃)₂⁺ (X = 1 to 7) were generated by standard electron impact in the cell of the FTICR. The dimer complex ion, Re₂H₆(PMe₃)₄⁺, was produced as the major product from the self chemical ionization reaction of ReH₃(PMe₃)₃ with ReH₃(PMe₃)₃. Collision-induced dissociation of Re₂H₆(PMe₃)₄⁺ yields fragments at m/z 344 and 346,

which is in good agreement with the results of the self chemical ionization reaction of $\text{ReH}_2(\text{PMe}_3)_2$. Dissociative charge exchange was observed with the radical cation CS_2^+ to generate $\text{ReH}(\text{PMe}_3)_2$ and $\text{Re}_2\text{H}_2(\text{PMe}_3)_4$. The cation $(\text{PMe}_3)_2\text{ReCH}_2\text{S}^+$ was produced from the reaction of dimer complex ion $\text{Re}_2\text{H}_2(\text{PMe}_3)_4$ with neutral CH_3SCH_3 . Selected reagents, like pyrrole, *tert*-butyl isocyanide, allyl iodide, benzeneselenol, and carbon tetrachloride were allowed to react with $\text{ReH}(\text{PMe}_3)_2$ and $\text{Re}_2\text{H}_2(\text{PMe}_3)_4$. Comparison of the reactivities between $\text{ReH}(\text{PMe}_3)_2$ and $\text{Re}_2\text{H}_2(\text{PPh}_3)_4$ is also an interesting issue we are planning to study. Finally, investigation of H/D exchange reaction for the ions $\text{ReH}(\text{PMe}_3)_2$ and $\text{Re}_2\text{H}_2(\text{PMe}_3)_4$ will yield information on the type and number of unique exchangeable hydrogens.

19. **Kinetics And Mechanism Of The Hydroxylamine/Hypobromous Acid Reaction.**

Brent J. Giles and Dale W. Margerum

Hydroxylamine (NH_2OH) is widely used as a reducing agent and intermediate in industrial processes. Its one-electron oxidation has been extensively studied. Research in the Margerum laboratory has examined the two-electron oxidation of hydroxylamine by halogen species Cl_2 , Br_2 , I_2 , HOCl , ClNH_2 , and BrNH_2 . Although they differ in subsequent details, all of these reactions proceed by a rate-determining addition step of a halogen cation X^+ to hydroxylamine.

The reaction of hydroxylamine with hypobromite (OBr^-) was studied between pH 9-13. The initial reaction is too fast for conventional stopped-flow kinetic techniques, and was studied using a pulsed-accelerated flow (PAF) apparatus. The major species in this pH range, NH_2OH and OBr^- , are not the reactive species. Instead, the reaction proceeds between NH_2OH and HOBr ($\text{pK}_a = 8.8$). A separate, unexpected reaction occurs above pH 12, and is due to the reaction of OBr^- with the strong nucleophile NHO^- (NH_2OH , $\text{pK}_a = 13.74$). This effect was subsequently also found in the reactions of hydroxylamine with OCl^- and NH_2Cl .

Both reactions yield the same intermediate, believed to be BrNH_2OH . Although this intermediate decomposes with a half-life of less than four milliseconds, stopped-flow techniques allowed a spectrum ($\lambda_{\text{max}} = 380 \text{ nm}$) to be reconstructed. The initial decomposition yields the nitroxyl anion (NO^-). Further reactions give the products NO , ONOO^- in the presence of dissolved oxygen, and N_2O and/or N_2 .

Comparisons of the reactions of hydroxylamine with the halogen species studied show that these reactions vary across the range of measurable rate constants. A deciding factor in the observed rate constant is the quality of the leaving group in the halogen-containing species with respect to the halogen cation X^+ .

Notre Dame

6. **Molecular Structure of Fe(IV) Species: - Nitrido-bis(5,10,15,20-tetra-p-tolylporphyrinato)iron Hexachloroantimonate.**
Li Ming and W. Robert Scheidt*

12. **Functionalization of Soluble Silicon Phthalocyanines for Formation of Self-Assembled Monolayers**
Zhiyong Li and Marya Lieberman*

18. **Mechanistic Studies of Oxidations Catalyzed by O-Ir(Mes)₃**
John Muldoon, Michael Wargoeki, Bridley R. Grant, and Seth N. Brown.

The cheapest, most plentiful oxidant available is molecular oxygen, but O_2 does not react readily with organic compounds. We have found that Wilkinson's unique iridium oxo complex $\text{O-Ir}(\text{mes})_3$ ($\text{mes} = 2,4,6\text{-trimethylphenyl}$, mesityl) is an effective catalyst for the air oxidation of phosphines and arsines. It also acts as a cocatalyst,

with osmium tetroxide, to allow the dihydroxylation of alkenes with only air and water as stoichiometric reagents. Mechanistic studies of both elementary reactions and full catalytic cycles will be presented.

Indiana University

1. **New Synthetic Strategies for Manganese Carboxylate Clusters. Crystal Structure and Properties of a New [Mn₄O₄] Butterfly Core: Potential Precursors for PSII Models.**

Sumit Bhaduri , Guillem Aromi, John C. Huffmann, George Christou.

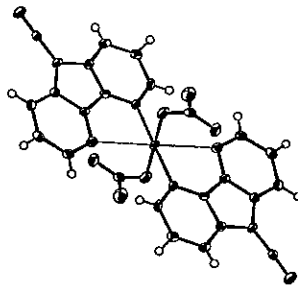
Our group has been synthesizing carboxylate-oxo aggregates with [Mn^{IV},^{III}Mn^{IV}] cubane like cores, as they have been proven to be useful models for the S₁ state of the water oxidation center in photosystem II. In our efforts to improve the properties of the model complexes and diversify the structural repertoire of these clusters we have attempted to introduce propionate as a new bridging carboxylate ligand.

In this paper, a new synthetic strategy is reported whereby the new complex, Mn₄O₄(CH₃CH₂CO₂)₆(dbm)₄(dbmH- dibenzoyl methane) with a butterfly like core has been synthesized. The complex has been crystallographically characterized and its physical properties investigated.

Present efforts are aimed at the use of this compound as the starting point for new clusters, a method that has been successfully used in our group to produce a diverse number of structural types from similar butterfly-like complexes.

3. **Photoactivated Cu(II) Complex of 9-diazo-4,5-diazafluorene: From Solid State Reactivity to DNA Cleavage**

Hilary J. Eppley, Victoria J. Isada, Susan M. Lato, John C. Huffmann, Andrew D. Ellington, Jeffrey M. Zaleski



Photodynamic therapy (PDT) utilizes photoexcitation of porphyrins and related compounds to generate singlet oxygen from oxygen found in the cells. Singlet oxygen undergoes a wide variety of reactions with cell components, and ultimately leads to the destruction of some types of cancer cells. An attractive alternative strategy to the design of traditional PDT agents is to devise compounds that may be activated even in the absence of oxygen, and hence could be effective even in hypoxic environments such as solid tumors. Terminal diazo compounds are known to release nitrogen upon photoactivation, producing highly reactive carbene and cation radical intermediates. Several synthetic organic and natural products containing terminal diazo groups have been shown to cleave DNA thermally and/or photochemically, and effects on the diazo group's photoreactivity upon binding a metal to such a compound was unknown. The synthesis of a thermally and photochemically active Cu(II) complex of 9-diazo-4,5-diazafluorene and its subsequent structural and spectroscopic characterization will be presented. In addition to ground state studies, the solid and solution state photoreactivity will be discussed. Effects of wavelength, temperature, concentration, and oxygen on plasmid DNA cleavage by the complex will be shown and compared to the results obtained using only the free ligand.

5. **The Self-Assembly of Dinuclear and Hexanuclear Iron(III) Oxide Complexes.**
Elisa I. Seddon, Craig Grant, Kirsten Folling, John C. Huffman and George Christou

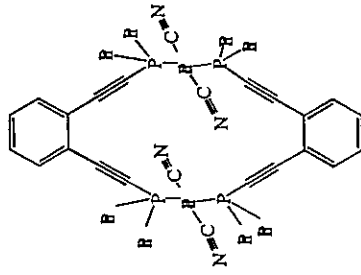
Polynucleating ligands such as the *bis*-bipyridine ligand **L** (1,2-*bis*(2,2'-bipyridyl-6-yl)ethane) have been regularly used in supramolecular chemistry with transition metals to access interesting self-assembled structures. Recently we have incorporated carboxylates into these metal-ligand systems and have obtained unique metal oxide complexes. Slightly perturbing a single reaction system affords the isolation of three different complexes: $[\text{Fe}_2\text{O}(\text{O}_2\text{CPh})_2(\text{L})_2]_n$, $[\text{Fe}_2\text{O}(\text{O}_2\text{CPh})(\text{L})(\text{C})(\text{H}_2\text{O})]_n$, and $[\text{Fe}_6\text{O}_4(\text{O}_2\text{CPh})_2(\text{L})_2(\text{H}_2\text{O})_4]_n$. The syntheses and characterization of these complexes will be presented.

7. **Thermal and Photochemical Activation of Novel Transition Metal Eneidyne Compounds.**
Pedro Benites¹, Aleyamma Abraham¹, Susan M. Lato¹, Andrew D. Ellington² and Jeffrey M. Zaleski

The natural product eneidyne is anti-tumor agents that cleave DNA through Bergman cyclization of the eneidyne unit, forming a 1,4-benzenoid biradical intermediate. The ability to effectively control biradical formation is an important requirement for the development of synthetic eneidyne based anti-tumor agents. Our work has focused on preparing complexes of metal-chelating eneidyne ligands in an effort to modulate the reactivity of the eneidyne unit. To this end, we have synthesized the 1,8-*bis*(pyridineoxy) eneidyne that binds Cu^+ and Cu^{II} . The resulting complexes can be activated thermally, at dramatically reduced temperatures relative to the free ligand. The Cu^+ complex of the 1,8-*bis*(pyridineoxy) eneidyne can also be photochemically activated ($\lambda = 400\text{nm}$) to promote DNA strand scission. The preparation, activation, and DNA cleavage reactivities of these complexes will be discussed.

9. **Synthesis and Characterization of Palladium and Rhodium Complexes with the 1,2-Bis[(diphenylphosphino)ethynyl]benzene Eneidyne Ligand.**

Aleyamma Abraham, Pedro Benites, Nicole Coalter, Brian Kraft, Chris Hughes and Jeffrey M. Zaleski



The eneidyne unit is known to undergo Bergman Cyclization in the presence of a hydrogen donor, forming a 1,4-benzenoid biradical intermediate. The possibility of synthesizing d^{10} and d^8 -metal dimers provides a way to control the formation of the biradical photochemically. $\text{Pd}(0)$, $\text{Pd}(II)$, and $\text{Rh}(I)$ dimers with bridging ligands such as DPPE (diphenyl phosphinoethane) form a metal-metal bond upon photochemical excitation. This is due to the excitation of an electron from an antibonding to a bonding orbital upon $h\nu$ photolysis. In the case of the 1,2-[(diphenylphosphino)ethynyl]benzene bridging ligand the formation of a bond between the metals will form a strained molecule which would favor cyclization of the eneidyne unit at $\lambda > 400\text{nm}$. The preparation, activation and reactivities of these complexes will be discussed.

11. Transition Metal Triazines as Photocatalyzed DNA Cleavers
Tucker D. Maurer, Susan M. Lato, Andrew D. Ellington, and Jeffrey M. Zaleski

Photodynamic therapy (PDT) is an area of anti-cancer research that involves *in-vivo* photoactivation of compounds that perform cell damage through production of 1O_2 . However, the freely diffusing nature of this mechanism precludes tissue specificity. In contrast, the ene-diyne class of natural product anti-cancer therapeutics are thermally activated, producing transient biradicals that are capable of performing DNA cleavage. Unfortunately, their function is limited due to dependence on bimolecular reducing equivalents. We have attempted to combine controlled, unimolecular photoactivation with the high reactivity of excited-state biradicals in the design of new PDT agents. Transition metal triazine compounds have been prepared that demonstrate photoactivation via low energy CT bands, producing biradicals capable of cleaving DNA. Synthesis, characterization, photophysical and DNA cleavage studies will be discussed.

13. Molecular Design of Single-Site Metal Alkoxide Catalyst Precursors for ROP of Cyclic Ethers and Esters.
Bjorn Antelmann, Malcolm H. Chisholm, John C. Huffman, Suri S. Iyer, Diana Navarro and William Simonsick

The reaction between methylenedioxy- and ethylenedioxy-bis(2,4-di-*tert*-butylphenoxide) and Et_2AlCl yields the corresponding biphenolates $[ClAl(L)_2]^-$, P^+O^- CHMe $^-O^-$. These compounds initiate the polymerization of propyleneoxide in bulk or in solvents such as toluene or benzene. They do not initiate the polymerization of L-lactide, but in the presence of PO, a random copolymer of L-lactide and PO is formed. These polymers have been studied by 1H and ^{13}C -NMR and by electrospray mass spectroscopy and also compared with the polymer formed by S-PO.

15. 1,1- and 1,2-Disubstituted Dimolybdenum Compounds of Formula $Mo_2X_4(CH_3SiMe_3)_n$. A Continued Investigation of the Pattern of Substitution Depending Upon the Preparative Route and the Nature of X.
M. H. Chisholm, D. R. Click.

The preparation of a series of compounds of general formula $Mo_2X_4(R)_n$, where X=Br, NMe₂, and Ph are reported. The substitution pattern may yield either 1,1- or 1,2- $Mo_2X_4(R)_n$ compounds depending on the preparative route and nature of X. The 1,1- and 1,2- $Mo_2X_4(R)_n$ compounds do not isomerize readily indicating a high kinetic barrier to R and X group transfer between molybdenum atoms. However, pyridine-d₄ may assist the isomerization of the disubstituted species. These new observations are discussed in light of previous work.

17. Preparation of Lanthanide Bisporphyrin Derivatives
Malcolm H. Chisholm, Brian D. Pate, Jeffrey M. Zaleski*

Systems of self-assembled aromatic chromophores are of interest as molecular semiconductors and photoconductors. Investigation of the phase characteristics of such systems may facilitate description of intermolecular interactions and emergent materials properties. In particular, arrays of *stacked* porphyrinic compounds display ordering of chromophores over both the molecular and materials regimes. In this context we will describe preparations of the lanthanide bisporphyrin complexes $LaH((C_{60}H_{18})Por)_2$ and $EuH((C_{60}H_{18})Por)_2$. Syntheses of porphyrin ligands which are expected to display thermotropic discotic mesophases will be elaborated.

3:30-5:00
Session Chair:

Talks
Brian Pate

3:30 **Synthesis, Characterization And Reactivity Of Co^{III}. And Co^{III}Co^{IV} Carboxylate Complexes**

Angelica D. Brown, Katerina Dimitroul', William Streib', George Christou'

Cubane-type complexes have been of interest because of their potential for multielectron transfer, and their often interesting magnetic and optical properties. The synthesis and characterization of new cobalt carboxylate complexes with a [Co(μ₃-O₄)(O₂CR)₂(bpy)₂(ClO₄)₂] have been prepared with a variety of carboxylate groups (R-alkyl, aryl), and characterized by elemental analysis, electronic spectra, cyclic voltammetry, EPR and NMR spectroscopies. The Co^{III} carboxylate complexes exhibit an irreversible reduction and a reversible oxidation at a chemically accessible potential, allowing the bulk preparation and isolation of the one-electron oxidized species [Co^{III}Co^{IV}O₄(O₂CR)₂(bpy)₂][Ce(NO₃)₆]. The electrochemical potential for the Co^{III/IV} redox couple depends on the electronic nature of the carboxylate group, ranging from 0.77 V for R = *p*-CH₃NO₂ to 0.70 V for R = *p*-C₆H₄CH₃ and *p*-C₆H₄OCH₃ vs. Fe/Fe in acetonitrile.

1. Zanello, P. *Coord. Chem. Rev.* 1988, 83, 199.
2. Bottomley, F.; Chen MacIntosh, S.M.; Thompson, R.C. *Organometallics* 1991, 10, 906; and references therein.
3. Ryu, C.K.; Kyle, K.R.; Ford, P.C. *Inorg. Chem.* 1991, 30, 3982.

4:00

Sequence Dependent Binding Of Porphyrins To DNA Hairpins.
Keith E. Thomas, Denise K. Crites and David R. McMillin.
Purdue University

Since the discovery that 5,10,15,20-tetra(N-methyl-4-pyridinium)porphyrin binds to DNA, there has been some question as to the specificity and type of binding. Intercalation and groove binding are the two major modes in which the porphyrin can bind to DNA. The type of binding appears to be sequence dependent with GC rich sequences favoring intercalation and AT rich sequences favoring groove binding. It has been proposed that a GC step is necessary for intercalation. Our results show that the robustness of the hydrogen bonding actually determines the nature of the binding. Our current research uses DNA hairpins to examine these interactions. By varying the composition of the hairpin stem, the specificity can be explored via spectroscopic techniques. Along with the specificity studies, competitive binding studies are being performed to reveal the quantitative differences in the sequence dependent binding. The results indicate that the binding constants for groove binding and intercalation are about the same.

4:30

A Comprehensive View of M-H Addition Across the RCCH Triple Bond. Evidence for a Non-Least Motion.
Alexei V. Marchenko and Kenneth G. Caulton.

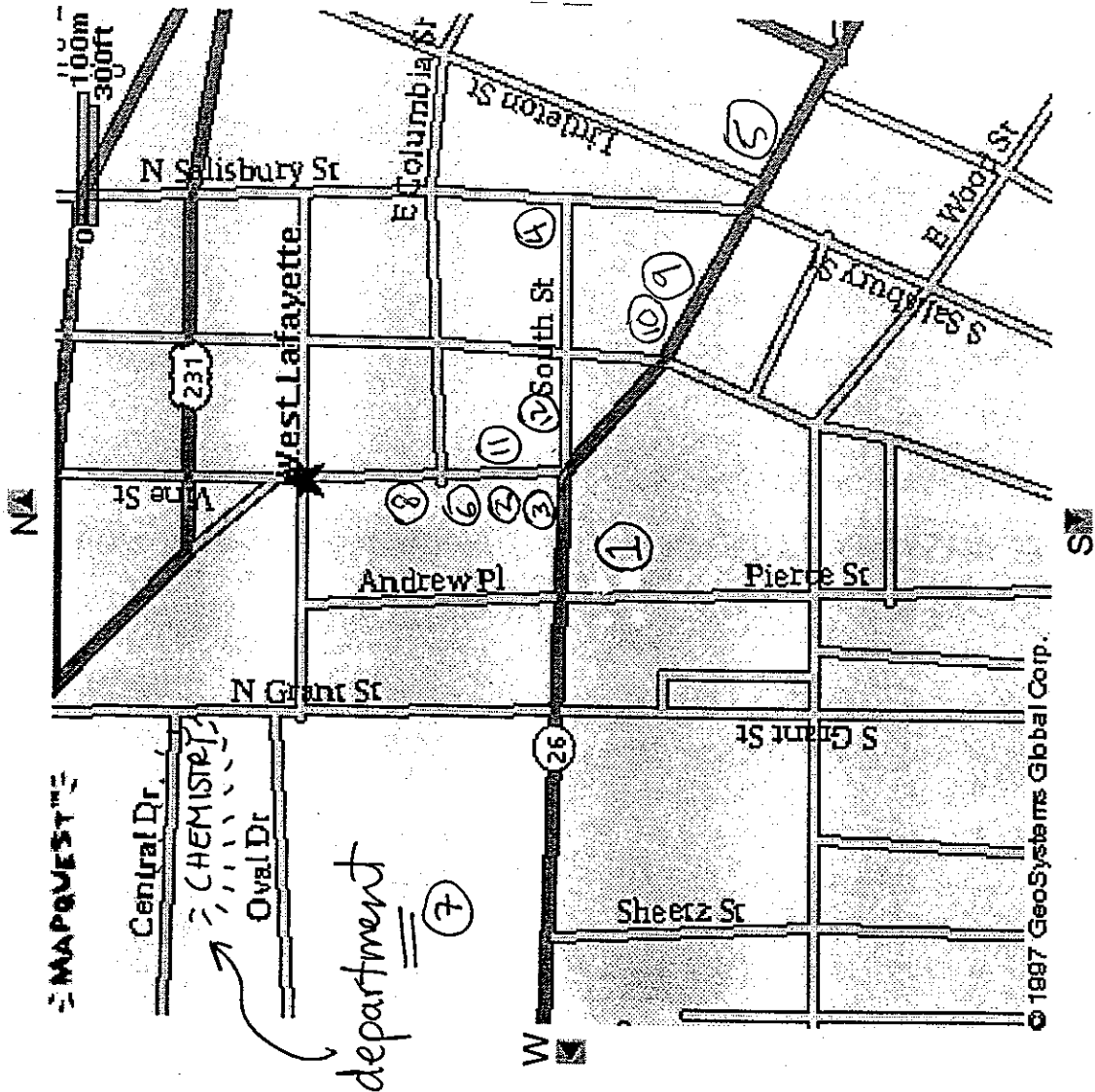
A variable temperature NMR study of reactivity of OsHCl(CO)(PPr₃)₂ toward a variety of terminal alkynes revealed OsHCl(η¹-RCCH)(CO)(PPr₃)₂ and OsH(=C-CHR)Cl(CO)(PPr₃)₂ to be the intermediates preceding the formation of Os(CH-CHR)Cl(CO)(PPr₃)₂, the final product for this type of reactions. Testing of mechanistic hypotheses, structure of intermediates, and influence of substituents at the RCCH triple bond will be discussed.

5:00

Closing Remarks

Local Restaurants

1. Chauncy Hill Mall:
 Utopia Diner
 Fazoli's (fast food Italian)
 Egg Roll Express (fast food Chinese)
 Arby's
 Taco Bell
 Parthenon (Greek)
 Jakes (bar, pizza, etc.)
 Wabash Yacht Club (bar, lunches etc.)
 Garcia's Pan Pizza (by the slice or on demand)
2. ThatsaWrap (good place for wraps)
3. Ben and Jerry's
4. South Street Grill (slightly more upscale)
5. Triple XXX (greasy spoon)
6. Subway
7. Union Market (Purdue cafeteria dining)
8. Einstein's Bagels
9. LaBamba's (burritos as big as your head)
10. Jimmy John's (gourmet (?) subs)
11. A. J. Wingers (chicken everything)
12. Vienna Cafe



McDonalds and Burger King are also in the area just north of campus