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2005

An Indiana Inorganic Chemistry Conference
Saturday, December 3, 2005

Indiana University
Bloomington, Indiana

Schedule of Events:

8:30 – 9:15 am

Welcome reception (C033) & Poster Hanging •

9:15 – 9:30 am

Opening Remarks (C033)

Oral Presentations: 1st Morning Session

9:30 – 9:50 am

Synthesis and reactivity of (PNP)Os complexes:

Reaction with CO, MeI, H₂, or HC≡CH

(PNP = N(SiMe₃(CH₂P^tBu₂))₂).

Jooh-Ho Lee, Maren Pink, Kenneth G. Caulton.

9:50 – 10:10 am

Control of Lithium Aggregate Assemblies Through Solvent

Effects

I. Jacob Morris, Bruce C. Noll, Kenneth W. Henderson.

10:10 – 10:30 am

Synthesis of high surface area micro-crystalline zinc electrodes by stabilizing fern-shaped dendritic growth.

Carmen M. López and Kyoung-Shin Choi.

10:30 – 11:30 am

Posters session, Posters Numbered 1-21

- All posters are to be hung in Chemistry Atrium.
- Adhesive will be provided

Oral Presentations: 2nd Morning Session

11:30 – 11:50 am

Catalytic reductions and hydrogen production using high-valent oxo-rhenium complexes. Elon A. Ison, Rex A. Corbin, Evan R. Trivedi, Jeanette E., Cessarich, Mahdi M. Abu-Omar.

11:50 – 12:10 pm

Recycling Story: Isocyanates and Carbodiimides Derived from Carbon Dioxide. Uriah J. Kilgore, Falguni Basuli, John C. Huffman, and Daniel J. Mindiola*.

12:10 – 12:30 pm

Structural and Vibrational Study of Heme Carbonyls With Solid-State Interactions. Nathan J. Silvermail, Arne Roth, Bruce C. Noll and W. Robert Scheidt

12:30 – 2:00 pm

Lunch Break (see inside back of program)

2:00 – 3:00 pm

Poster Session, Posters numbered 22 – 42

Oral Presentations: Afternoon Session

3:00 – 3:20 pm

Cationic porphyrins: synthesis, structure and interaction with DNA. Kim Andrews, Alexander H. Shelton and David R. McMillin*

3:20 – 3:40 pm

Why Cyanide Pretends to be a Weak Field Ligand in [Cr(CN)₆]⁴⁻
Richard L. Lord and Mu-Hyun Baik*

4:00 pm

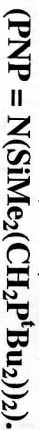
Concluding remarks and awards

Oral Presentation Abstracts

First Morning Session:

Synthesis and reactivity of (PNP)Os complexes:

Reaction with CO, MeI, H₂ or HC≡CH



Joo-Ho Lee, Maren Pink, Kenneth G. Caulton.

Indiana University

Recently, (PNP)RuX (X = halides...) complexes were introduced and extensively studied. For the comparison of 4d metal (Ru) with 5d metal (Os) which likes to have higher coordination number and oxidation state, synthesis of (PNP)Os complex was tried through the reaction of [cymeneOsCl₂]₂ and [LiPNP]₂LiCl (cymene = *p*-*i*-Pr-toluene) which gave (PNP)Os(H)₂(≡CAr) (Ar = C(*p*-*i*-Pr-phenyl) (figure 1), I, by triple dehydrogenation of the methyl group on cymene instead of (PNP)OsCl. Here, we introduce the reactivity of this carbene with small molecules (CO, MeI, or H₂).

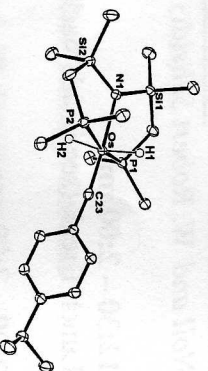


Figure 1. (I)

The CO insertion to Os promoted hydride migrations from Os to carbene carbon. At room temperature, only one hydride migration is observed by NMR spectra. However, if this carbene complex was heated at 65 °C over 4 hours, it induced the second hydride migration in order to produce a benzyl complex. Adding H₂ to I generated (PNP)OsH(CO) through liberation of free cymene.

In addition, MeI converted I to (PNP)Os(H)(I)(CAr). In this molecule, iodide and hydride can be removed by LDA, which gave (PNP)Os(≡CAr).

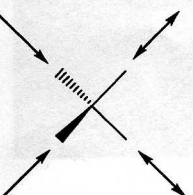
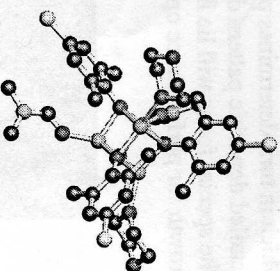
Addition of H₂ to I liberated free cymene to form (PNP)Os(H)₃. Reaction of (PNP)Os(H)₃ with CO generated (PNP)OsH(CO)₂ and H₂ which could be also produced by addition of CO to (PNP)OsH(CO). Mixing (PNP)Os(H)₃ with HC≡CH gave the vinylidene complex (PNP)OsH(=CCH₂) and ethylene.

Control of Lithium Aggregate Assemblies Through Solvent Effects

J. Jacob Morris, Bruce C. Noll, Kenneth W. Henderson

Notre Dame University

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 organyloxides can be linked through the linear ditopic Lewis base 1,4-dioxane to create a series of one, two, and three dimensional polymers. Herein, we present an extension to this work in which the solvent dimethylformamide (DMF) is used to further control network assembly. By altering the crystallization conditions, we have been able to synthesize two distinct structural phases from the same lithium aryloxyde building unit, as well as use DMF to rationally break the network down in dimensionality.



V-Shaped Node

Synthesis of high surface area micro-crystalline zinc electrodes by stabilizing fern-shaped dendritic growth.

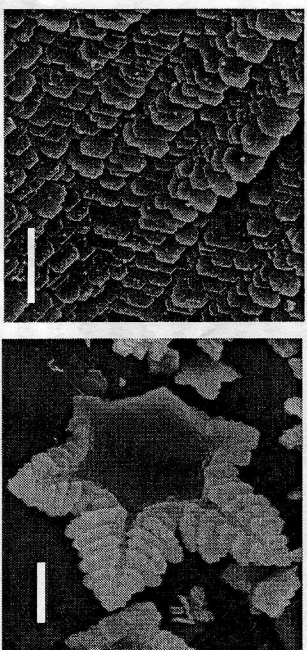
Carmen M. López and Kyoung-Shin Choi

Purdue University

The shape of crystals grown under or near equilibrium conditions is mainly governed by surface free energies. As a result crystal shapes obtained under these conditions are generally simple with well-developed facets that can achieve the minimum surface energy (i.e. faceted polyhedra). As the system is driven farther from equilibrium, surface kinetics and bulk transport of material and heat play a major role to determine crystal shapes. This often results in complicated growth patterns, which are not necessarily the most stable in terms of surface energy (i.e. dendrite or branching formation).

Achieving a good understanding and control of such crystallization processes is essential to produce efficient polycrystalline-based electrode materials in that the overall efficiency of these electrodes are critically determined by the shape, size, and interconnections of individual particles that compose electrodes.

In this talk, we present a systematic control of faceting and dendritic growth of zinc metals during the electrodeposition process. We will discuss key synthetic conditions (deposition potential, temperature, and Zn^{2+} concentration) that affect the electron transfer and mass transport processes, which in turn determines preferences for faceting and branching as well as detailed dendritic pattern development (i.e. individual motif and connections). The special focus will lie in probing a possibility of exploiting dendritic growth for performance optimization of inorganic electrode materials.



Scanning electron micrographs of crystal growth patterns that can be obtained under diffusion-controlled conditions. The scale bar represents 1 μm .

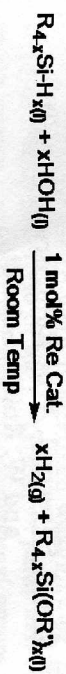
Second Morning Session:

Catalytic reductions and hydrogen production using high-valent oxo-rhenium complexes.

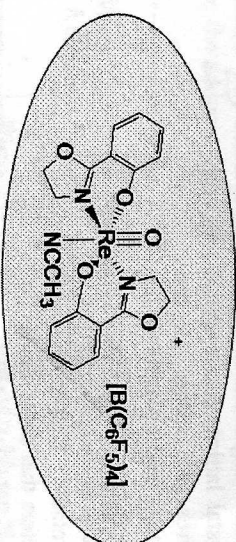
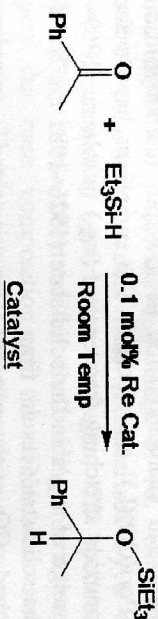
Elon A. Ison, Rex A. Corbin, Evan R. Trivedi,
Jeanette E., Cesarich, Mahdi M. Abu-Omar,
Purdue University

The cationic oxorhenium oxazoline complex $[Re(O)(hoz)_2(CH_3CN)][B(C_6F_5)_4]$ (1) was employed as a catalyst for the dehydrogenative oxidation of organosilanes and the hydrosilation of aldehydes and ketones. Isotopic labeling experiments as well as kinetic studies revealed a new mechanistic paradigm for the activation of Si-H bonds by oxometalate complexes.

Hydrogen Production



Hydrosilation



Recycling Story: Isocyanates and Carbodiimides Derived from Carbon Dioxide.

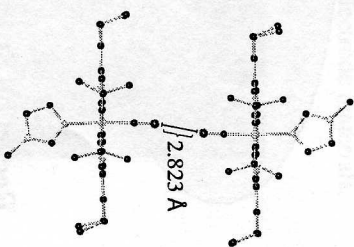
Uriah J. Kilgore, Falguni Basuli, John C. Huffman,
and Daniel J. Mindiola*
Indiana University

Carbon dioxide is a greenhouse gas which is regarded as thermodynamically inert. Though it is typically considered a thermodynamic dead-end, there is considerable interest in incorporation of carbon dioxide into a wide range of commodity products. Hence, complexes capable of both activating and functionalizing carbon dioxide under mild conditions are attractive targets. We report in this paper an imido-zwitterion complex $(Nacnac)Ti=NAr(\mu-CH_2B(C_6F_5)_3)$ ($Nacnac^- = [ArNC(Bu)]_2CH$, $Ar = 2,6-Pr_2C_6H_3$) which mediates clean conversion of carbon dioxide into isocyanates and carbodiimides via ligand metathesis. In addition, the titanium-oxo product generated from the ligand-metathesis reaction can be recycled to the corresponding titanium-imido-transfer reagent. Further reactivity of the zwitterion $(Nacnac)Ti=NAr(\mu-CH_2B(C_6F_5)_3)$ will be presented and discussed.

Structural and Vibrational Study of Heme Carbonyls With Solid-State Interactions

**Nathan J. Silvernail, Arne Roth, Bruce C. Noll
and W. Robert Scheidt**
Notre Dame University

The synthesis and characterization of low-spin (carbonyl)iron(II) porphyrinates, $[\text{Fe}(\text{Por})(\text{CO})(\text{L})]$ are reported. The complexes have a small range of carbon monoxide stretching frequencies (ν_{CO}) in toluene (1969–72 cm^{-1}), but a large range of ν_{CO} 's in the solid-state (1926–1981 cm^{-1}). The large variation in the solid-state, results from interactions of bound CO with adjacent molecules in the crystal lattice. Examination of the crystal structures give insight into the specific interactions that lead to shifts in the ν_{CO} 's of these porphyrinates. The high precision of the structures obtained makes it possible to correlate structural and spectroscopic parameters that describe the Fe–C–O unit. The values of ν_{CO} and the Fe–C and C–O bond distances are strongly correlated and provide a structural as well as a spectroscopic correlation of the π back-bonding model. The interactions of CO described are closely related to the large range of ν_{CO} 's observed in heme proteins and specific interactions observed in carbonylmyoglobin (MbCO).



Afternoon Session:

Cationic porphyrins: synthesis, structure and interaction with DNA.

Kim Andrews, Alexander H. Shelton and David R. McMillin*
Purdue University

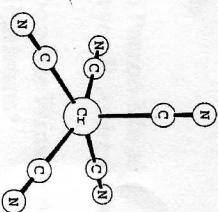
Porphyrins via photodynamic therapy offer a promising non-invasive modality for targeting diseased cells or viruses. Selectivity is possible because the cytotoxic response extends only to the irradiated cell mass. An added bonus is that tumor cells are often unusually avid at taking up the photosensitizer. Porphyrins are attractive sensitizers because they absorb well into the red end of the visible spectrum, i. e., at wavelengths that penetrate tissue relatively efficiently. Hence, a class of new sterically non-demanding, porphyrins have been synthesized via a microwave one pot methodology.

These porphyrins are being used to identify, evaluate and characterize novel DNA binding motifs that vary with the meso substituents on the porphyrins. In structural studies of an intercalated form of the $\text{Cu}(\text{T4})$ derivative, Williams and co-workers identified what may be the critical steric issue for an intercalated form of the porphyrin. In particular, clashes occur in the minor groove due to the fact that two pyridiniumyl groups have to wedge between the sugar-phosphate chains. To avoid this problem, we have synthesized cationic tripyridyl porphyrins since they have fewer bulky aryl substituents and yet preserve a charge of +3. Binding interactions of the cationic porphyrin systems were characterized by a number of physical methods including absorbance, emission, CD spectroscopies as well as viscometry. It was observed that the binding interactions do indeed depend upon the base composition of the DNA and steric factors of the porphyrins. The decisive roles that structural rigidity and steric factors play in shaping the adducts with DNA have become clear.

Why Cyanide Pretends to be a Weak Field Ligand in $[\text{Cr}(\text{CN})_6]^{4-}$

Richard L. Lord and Mu-Hyun Baik*
Indiana University

Cyanide is believed to generate one of the strongest ligand-fields when attached to transition metal centers. Thus, one expects the $d^4\text{-Cr}(\text{II})$ center of the octahedral, homoleptic complex $[\text{Cr}(\text{CN})_6]^{4-}$ to have a large $t_{2g}\text{-}e_g$ gap and consequently be a textbook example of an intermediate-spin ($S=1$) complex. Recently, Joel Miller challenged this textbook paradigm and called the common wisdom of cyanide always being a strong-field ligand a "Myth". He observed that $[\text{Cr}^{\text{II}}(\text{CN})_6]^{3-}$ is the only accessible ionic complex when using non-coordinating $(\text{NEt}_4)^+$ under non-aqueous conditions. $[\text{Cr}(\text{CN})_6]^{3-}$ displays a room temperature magnetic moment of 4.90 μ_B , consistent with a high-spin ($S=2$) $\text{Cr}(\text{II})$ complex, instead of the expected intermediate-spin $\text{Cr}(\text{II})$. The cyanide ligands appear to be weak-field ligands!



We present an intuitive explanation for this apparent violation of common chemical sense that will harmonize the views on the electronic nature of the cyanide ligand.

Notes

Poster Number Assignments

1. Ruthenium Guanidinate Complexes as Access to Electron Rich Metal Centers
Alexander Y. Verat, Kenneth G. Cautlon
2. Synthesis and Reactivity of a Titanium Alkylidyne Complex
Brad C. Bailey, Hongjun Fan, Erich Baum, John Huffman, Daniel J. Mindiola
3. Synthesis, characterization, and reactivity of square planar, 4 coordinate Ru^{II} complexes from [N(SiMe₂CH₂P^tBu)₂]RuCl ((PNP)RuCl).
Amy Walstrom, Nikolai Tsvetkov, Michael Ingleson, Hongjun Fan, Maren Pink, and Kenneth G. Cautlon
4. Synthesis of a monomeric highly reactive tricoordinate iron (I) complex.
Drew Buschhorn, Benji Fuller, Michael Ingleson, Kenneth G. Cautlon
5. Proton-Mediated Electron Configuration Change in High-Spin Iron(II) Porphyrinates
Chuanliang Hu, Bruce C. Noll, Charles E. Schulz, and W. Robert Scheidt
6. Development and Application of Homochiral Magnesium Amide Bases
John F. Allan, Kenneth W. Henderson*, William J. Kerr*, Jennifer H. Moir, Elizabeth R. Specht, Erin Hurley
7. Rh Catalyzed C-H Activation: Why is the N-Heterocyclic Carbene Complex of Iridium Reactive When Its Rhodium Analogue is Not?
Marco Fioroni, Erich W. Baum and Mu-Hyun Baik
8. Theoretical study on the reaction mechanism of C-H activation an pyridine ring opening advocated by a titanium alkylidyne
Hongjun Fan, Brad C. Bailey, Daniel J. Mindiola* and Mu-Hyun Baik*
9. Two-dot Molecular Quantum Cellular Automata Cells
Hua Qi and Thomas P. Fehlner
10. The Mechanism of Diastereoselective Rh-Catalyzed Pauson-Khand Reaction
Huijun Wang, James R. Sawyer, P. Andrew Evans and Mu-Hyun Baik*
11. Characterization and Properties of Magnesium-Carboxylate Frameworks.
Jeffrey A. Rood, Bruce C. Noll, Kenneth W. Henderson*
12. The Art of Stacking: Balance between Rigidity and Flexibility
Justin A. Riddle, John C. Bollinger, and Dongwhan Lee*
13. Synthesis and structural characterization of geminal dimetallics
Katherine L. Hull, Bruce C. Noll, Kenneth W. Henderson*
Leigh J.K. Boerner, Mahendra Nath, Maren Pink, and Jeffrey M. Zaleski
14. Synthesis of Extended Structure Chromophores via Cycloaromatization of Porphyrinic Ene-diyne
Leigh J.K. Boerner, Mahendra Nath, Maren Pink, and Jeffrey M. Zaleski
15. From Clusters to Extended Solids: Using Diphosphonate Ligands to Build Frameworks
Michael W. Hull, Slavi C. Sevov
16. Metal-Carboxylate Extended Frameworks:
Michael T. Scancella

17. Formation Dynamics of Group 14 Nine-Atom Octahedral Clusters in Solution. Ivaylo Petrov and Slavi C. Sevoy
18. R₂D₄ Porphyrin Analogues: DNA Binding Studies of New Cationic Porphyrins A. H. Shelton and David R. McMillin*
19. Thermochemistry of Alane and Dialane Daniel J. Goebbert and Paul G. Wenthold*
20. Multinuclear SSNMR characterization of TiO₂-doped monolayers and nanoparticles and evaluation of visible light photocatalytic activity. Enrique A. Reyes-Garcia; Karla Reyes;; Yanning Sun; Jill Tomlinson; Daniel M. Raftery.
21. Metal Oxo Reactions with Alkylating Agents: Implications for Cancer Prevention Jessica M. Fautsch, Sarah M. Gentry, Elizabeth E. Hamilton, and Jonathan J. Wilker
22. Diastereoselective Intermolecular Rhodium-Catalyzed [4+2+2] Carbocyclization Reactions: A Complete Characterization Robert M. Koffie and Mu-Hyun Baik*
23. Electrochemical Synthesis of Lamellar Structured Cobalt Hydroxide Films Using Anionic Surfactants as Structure Directing Agents Matt Yarger and Kyoung-Shin Choi
24. Towards Resonant Tunneling Molecular Wires, and Nanopatterned and Functional Surfaces. Prem Chand, Kumar Parimal, Kevin Barry, Andrew Share, Kristy McNitt, John Huffman, Amar H Flood
25. Development and Photochemistry of Diazo-Oxochlorins: Toward Phototherapeutic Agents for Hypoxic Environments Tillmann Köpke, Maren Pink, Jeffrey M. Zaleski*
26. A Novel Platinum(II) Tertiaryamine Fused Phenazine Complex and its Photochemical Properties Robert McGuire Jr. and David R. McMillin
27. Rhodium(I) Catalyzed [2+2+1]: A Mechanistic Exploration William Pitcock and Mu-Hyun Baik*
28. Terminal Imines on Cr, Mn, and Fe Corroles: Synthesis and Reactivity with Olefins Michael J. Zilla, Mahdi M. Abu-Omar
29. The Mechanism of Olefin Addition and β -Hydride Elimination in Ir/Rh Catalyzed C-H Activation Catalysis Xiao Dong, Marco Fioroni and Mu-Hyun Baik*
30. A New Class of Metal-Chelating Nucleic Acids Mildred Rodriguez, Megan Lockard, Jonathan J. Wilker
31. On the Reaction of Aryl Azides with a Cationic Oxorhenium(V) Complex in Route to Developing a Nitrene Transfer Catalyst Nicholas E. Trava, Elon A. Ison, and Mahdi M. Abu-Omar
32. Cis,cis-[(bpy)₂Ru^{VO}]₂O₄⁺ Catalyzes Water Oxidation formally via *in situ* Generation of radicaloid Ru^{IV}-O•. Xiaofan Yang and Mu-Hyun Baik*
33. Rhenium catalyzed hydrolytic and alcoholic oxidation of organostanes for on-demand hydrogen production Rex A. Corbin, Elon A. Ison, and Mahdi M. Abu-Omar
34. Energetics of Self-Assembly: Measuring "Ligand Steric Bulk" Xuan Jiang, John C. Bollinger, and Dongwhan Lee*
35. Electrodeposition of nanostructured tin and tin oxide using surfactant templating. Ryan Spray and Kyoung-Shin Choi
36. Ketone Deprotonation Mediated by the Alkaline Earth Metal Amide—Ca(HMDS)₂ - Xuyang He, Bruce Noll, Kenneth W. Henderson*
37. A Role for Metal Ions in Marine Biomaterial Formation Steven M. Howell, Mary J. Sever, Jaime T. Weisser, and Jonathan J. Wilker*
38. AG vs. GA bifunctional binding of Cisplatin to DNA Yogita Mantri, Mu-Hyun Baik
39. Watching Au nanorods grow Zhongqing Wei,*[†], Hua Qi[†] and Francis P. Zamborini[‡]
40. Detoxifying Chlorooxides by Respiration in Dechloromonas aromatica Bennett Streit, Garrett Bassett, John D. Coates, and Jennifer DuBois
41. Covalent Modifications on Ru₂ Units: Towards Novel Materials Weizhong Chen
42. Reactivity of "PNP" complexes of Fe, Ni, and Co Alison R. Fout, Falguni Basuli, Debashis Adhikari, John Huffman, and Daniel J. Mindiola

Restaurant Guide

1. Penn Station
2. Chow Bar - CHINESE
3. Buffa Louie's - WINGS / SANDWICHES
4. Starbucks
5. La Bamba - MEXICAN
6. Kilroy's - PUB GRUB
7. Jimmy John's
8. Falafel's - ISREALI
9. Don Chuy's - MEXICAN
10. Bloomington Bagel Co.
11. Snow Lion - TIBETAN
12. Siam House - THAI
13. Puccini's - ITALIAN
14. Bombay House - INDIAN
15. Casablanca - MOROCCAN
16. Yat's - CALJUN / CREOLE
17. Jiffy Treet - ICE CREAM
18. Nick's English Hut - PUB GRUB / PIZZA
19. Village Deli - SANDWICHES / BREAKFAST
20. Café Pizzaria - PIZZA / SUBS
21. Chipotle - MEXICAN
22. Brave New Deli
23. Greek's Pizzaria - PIZZA
24. Uptown Café
25. Trojan Horse - GREEK
26. Malibu Grill -
27. Opie Taylor's - BURGERS
28. Shanti - INDIAN
29. Esan-Thai - THAI
30. City Grille

