

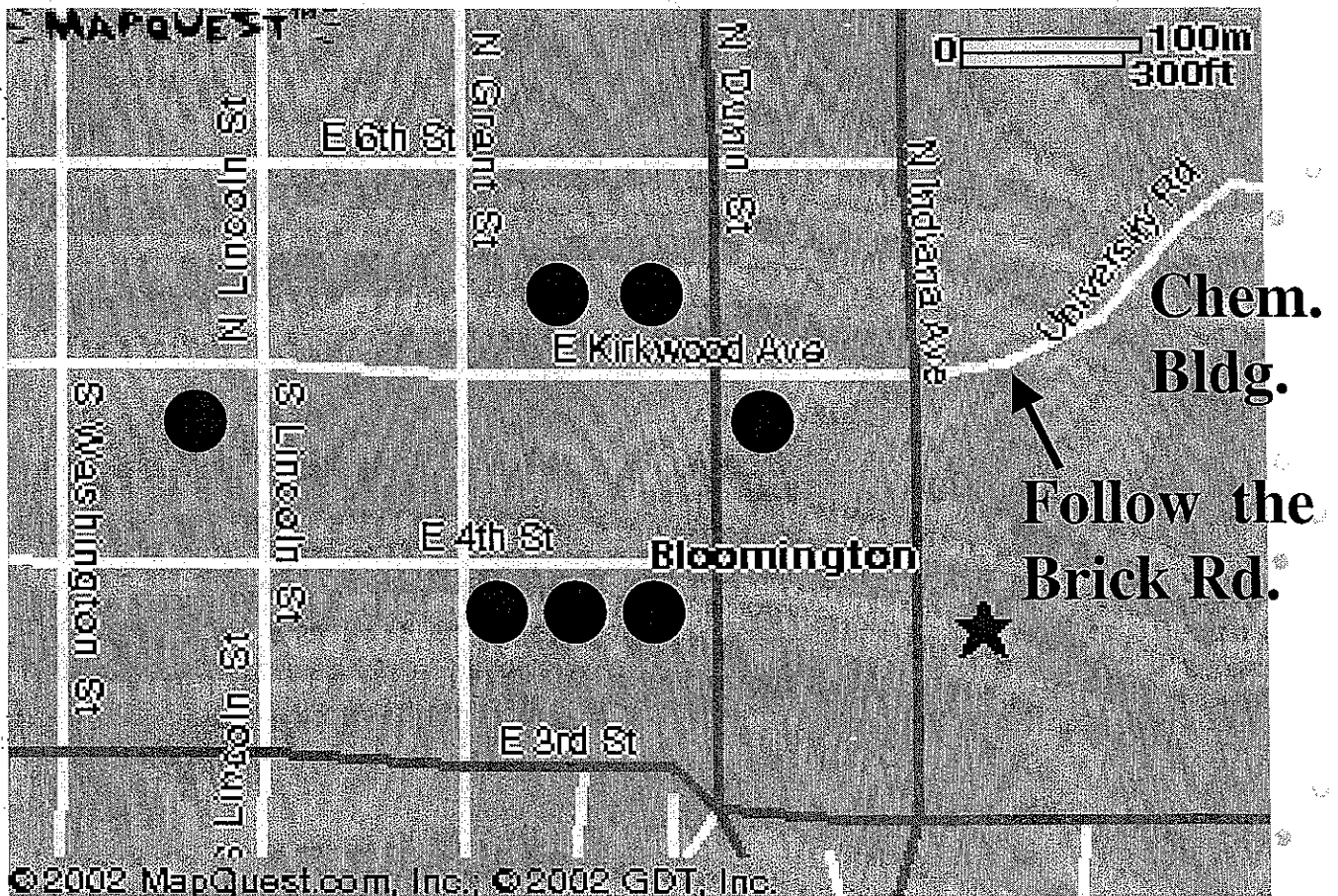
PINDU  
Inorganic Chemistry  
Conference

Abstract Guide

Nov. 2, 2002

Indiana University

# Places to Eat



- Ethnic Foods: Italian, Tibetan, Mediterranean
- Non-Ethnic Foods

# Oral Presentations

(9:30 – 9:50)

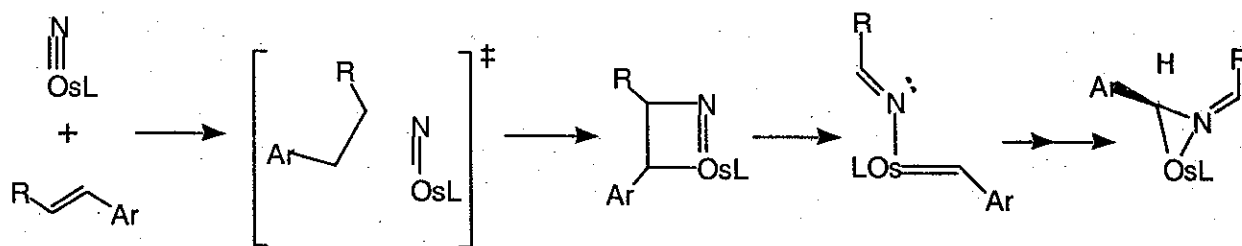
## Novel Insertion Reactions of Electrophilic Osmium(VI) Nitrides with Conjugated Alkenes: Scope and Mechanistic Analysis

Maestri, A. G.; Braunecker, W. A.; Cherry, K. C.; Toboni, J. J.;  
Schuck, S. M.; Brown, S. N.

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### Abstract

Cationic osmium nitrides react with a variety of electron-rich alkenes by completely cleaving the C=C double bonds, inserting the nitrido group between the carbon atoms to yield azametallacycles. The azallenium fragment is bound  $\eta^2$ -(C,N) to the osmium in a regioselective manner, with an aromatic (or alkyl) substituent always bound to C-1 in preference to hydrogen. Mechanistic studies of (formal) alkene cleavage are in progress and to date they have revealed mechanistic support for a [2+2] pathway. The proposed mechanistic model was rationalized by the investigation of kinetic reactivity studies, secondary isotope effects, steric effects, and charge effects. The results are most consistent with the insertion reaction taking place by a concerted, but asynchronous, [2+2] addition of the alkene to the Os-nitrogen triple bond. We have broadened the scope to include the reactions of cyclic alkenes with osmium nitrides to form unusual heterocyclic complexes.



(9:50 – 10:10)

## Novel Germanium(II) Aryloxy and Binaphthoxide Complexes

Charles S. Weinert, Ian P. Rothwell

Department of Chemistry  
Purdue University  
West Lafayette, IN 47907

### Abstract

Two novel chiral germanium (II) binaphthoxide complexes,  $(R,R)$ -[Ge{OC<sub>20</sub>H<sub>10</sub>-(OSiMe<sub>3</sub>)-2'-(SiMe<sub>3</sub>)<sub>2</sub>-3,3'}<sub>2</sub>] and  $(R)$ -[Ge{O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>(SiMe<sub>2</sub>Ph)<sub>2</sub>-3,3'}{NH<sub>3</sub>}], were prepared from Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and the corresponding 3,3'-disubstituted-2,2'-bi-1,1'-naphthols, and were structurally characterized. These two species, which both contain resolved ligands, represent the first examples of germanium (II) binaphthoxide complexes. In the presence of hexamethyldisilazane, Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was found to catalyze the silylation of one of the hydroxyl groups of  $(R)$ -[(HO)<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-(SiMe<sub>3</sub>)-3,3'] to cleanly yield  $(R)$ -[(HO)C<sub>20</sub>H<sub>10</sub>-(OSiMe<sub>3</sub>)<sub>2</sub>-2'-(SiMe<sub>3</sub>)<sub>2</sub>-3,3']. Two other metal (II) bisamide complexes, Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, were also found to catalyze this reaction, but with different rates. The catalytic silylation of three additional 3,3'-disubstituted binaphthols,  $(R)$ -[(HO)<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-(SiR<sub>3</sub>)<sub>2</sub>-3,3'] (R = SiMe<sub>2</sub>Ph, SiMePh<sub>2</sub>, or SiPh<sub>3</sub>), was also studied. In addition, several new germanium(II) aryloxy complexes (ArO)<sub>2</sub>Ge (ArO = 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,6-(<sup>t</sup>Pr)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, 2,6-(Ph)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, and 2,3,5,6-(Ph)<sub>4</sub>C<sub>6</sub>H) were prepared and characterized. Their spectroscopic properties were correlated with their solid-state structures.

(10:10 – 10:30)

## **Understanding Optical SHG in Potassium Niobate Tellurite Glass-ceramic with Structure-property Relationships**

Robert Hart; Josef W. Zwanziger  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405

### **Abstract**

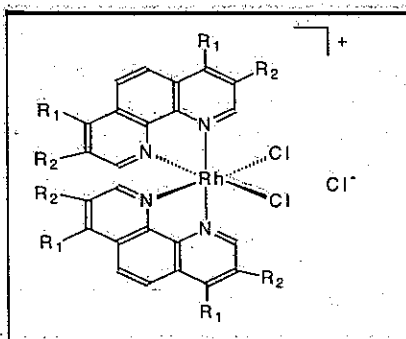
Potassium niobate tellurite glass ceramics are a member of an interesting family of developing nonlinear optical materials that are chemically robust and easy to fabricate (read: inexpensive) for SHG. Since glasses are isotropic, they are highly symmetrical and do not allow properties such as piezoelectricity or optical second harmonic generation. When a glass ceramic is formed by precipitating small crystals within the material, some of the symmetries can be broken and allow these types of properties. However, all previous studies of the KNT glass ceramic have failed to reveal this symmetry breaking, and the SHG mechanism has remained ambiguous. We have undertaken scattering and spectroscopic studies and found several interesting features that can be invoked to explain the relationship between structure and property in this (and by analogy, other) glass ceramics within a well-understood physical theory.

(1:30 – 1:50)

## Photoaquation of methylated *cis*-dichlorobis(1,10-phenanthroline)rhodium(III)chloride compounds by direct population of a photoactive triplet excited state

Devanesan Loganathan; Harry Morrison

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$R_1 = R_2 = H \rightarrow$  BISPHEN  
 $R_1 = CH_3, R_2 = H \rightarrow$  TMBP  
 $R_1 = R_2 = CH_3 \rightarrow$  OCTBP

### Abstract

*cis*-dichlorobis(1,10-phenanthroline)rhodium(III)chloride, *cis*-Rh(phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, BISPHEN, and its analogs are thermally inert and contain replaceable ligands of intermediate lability. They can be activated by broad band UVA irradiation ( $\lambda > 330$  nm) which typically populates metal based [<sup>1</sup>(d-d)] singlet states.<sup>1-3</sup> Intersystem crossing to triplet manifold from the initially generated excited singlet states is highly efficient in these Rhodium complexes<sup>4</sup> and their photoreactivity is generally ascribed to their low-lying [3(d-d)] triplet state.

Analogous photochemistry in two methylated analogs of *cis*-Rh(phen)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, TMBP and OCTBP, can be achieved upon direct excitation into the triplet manifold (i.e., with visible light  $> 500$  nm).<sup>5</sup> It is also noteworthy that methyl substitution of the aromatic rings as in TMBP and OCTBP, increases the triplet [<sup>3</sup>(d-d)] state photoreactivity of these complexes by 10 fold relative to BISPHEN. The otherwise not observable singlet to triplet ( $S_0 \rightarrow T_1$ ) transition in OCTBP is estimated by a combination of the action spectrum for photoaquation in the region between 520 and 600 nm and the phosphorescence spectrum at 77K. The TD-DFT calculation is also in agreement with this estimation.<sup>6</sup> The significant increase in the reactivity of the triplet [<sup>3</sup>(d-d)] state is explained in terms of increasing  $\sigma$ -donation from the methylated phen ligands which stabilize the pentacoordinate rhodium intermediate formed by chloride expulsion.

1. Muir, M.M.; Huang, W.L. *Inorg.Chem.* **1973**, *12*, 1831-1835.

2. Broomhead, J.A.; Grumley, W. *Chem.Commun.* **1968**, 1211.

3. DeArmond, M.K.; Hillis, J.E. *J.Chem.Phys.* **1971**, *54*, 2247-2253.

4. (a) Ford, P.C. *Coord.Chem.Rev.* **1982**, *44*, 61 (b) Ford, P.C.; Wink, D.; DiBenedetto, J. *Prog.Inorg.Chem.* **1983**, *30*, 213 (c) Skibsted, L.H. *Coord.Chem.Rev.* **1985**, *64*, 343.

5. Loganathan, D.; Rodriguez, J.H.; Morrison, H. Submitted for publications in *J.Am.Chem.Soc.*

6. Rodriguez, J.H. Unpublished results.

(1:50 – 2:10)

## Nitrosyl or Nitroxyl Complex from Unsaturated Mono or Polyhydride: Reactivity of Free Radical NO and Hydride Complexes

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### Abstract

Hydride transfer from unsaturated metal hydride complexes ( $\text{RuHCl}(\text{CO})\text{L}_2$ ,  $\text{OsHCl}(\text{CO})\text{L}_2$ ,  $\text{OsH}_3\text{ClL}_2$  and  $\text{OsH}_2\text{Cl}_2\text{L}_2$  ( $\text{L}=\text{P}^i\text{Pr}_3$ )) has been performed by free radical nitric oxide through quenching the radical character of NO to produce HNO.  $\text{MHCl}(\text{CO})\text{L}_2$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) with less than 1 equivalent of NO produces  $\text{MCl}(\text{NO})\text{L}_2$  and  $\text{MHCl}(\text{HNO})\text{L}_2$ . Then,  $\text{MHCl}(\text{HNO})\text{L}_2$  is decomposed in some period time. In the reaction of  $\text{OsH}_3\text{ClL}_2$  with the odd electron donor ligand, NO, we observed mainly two products:  $\text{OsH}_2\text{Cl}(\text{NO})\text{L}_2$  and  $\text{OsHCl}_2(\text{NO})\text{L}_2$ . The first product,  $\text{OsH}_2\text{Cl}(\text{NO})\text{L}_2$ , is formed through losing all the hydride ligands with arriving NO and forming new metal hydride bonds. We observed a four coordinated Os species,  $\text{OsCl}(\text{NO})\text{L}_2$ , as a primary product, as well as the  $\text{H}_2$  adduct of the trihydride compound,  $\text{OsH}_3(\text{H}_2)\text{ClL}_2$ . Then,  $\text{OsCl}(\text{NO})\text{L}_2$  forms the dihydride compound,  $\text{OsH}_2\text{Cl}(\text{NO})\text{L}_2$ , by the addition of  $\text{H}_2$ . The second product,  $\text{OsHCl}_2(\text{NO})\text{L}_2$ , is also observed from some halogen transfer and H loss process. The reaction of  $\text{OsH}_2\text{Cl}_2\text{L}_2$  with NO also forms  $\text{OsHCl}_2(\text{NO})\text{L}_2$ , together with  $\text{OsH}_2(\text{H}_2)\text{Cl}_2\text{L}_2$ , which is the  $\text{H}_2$  adduct of  $\text{OsH}_2\text{Cl}_2\text{L}_2$ . The mechanistic features of these reactions will be discussed.



(2:10 – 2:30)

## Reactions of nine-atoms germanium clusters in solution

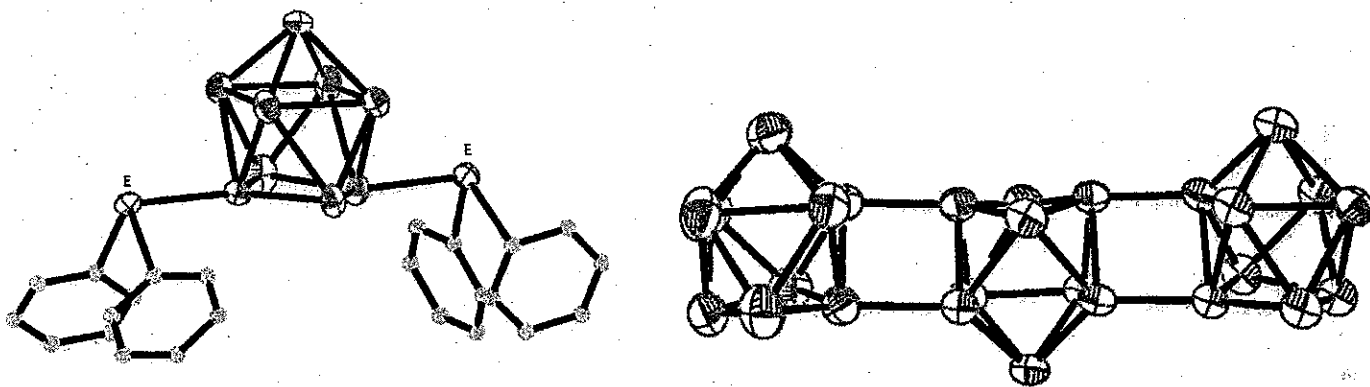
Angel Ugrinov

Department of Chemistry and Biochemistry  
University of Notre Dame  
Notre Dame, IN 46556

### Abstract

Interest in synthesis, isolation and characterization of Zintl cluster ions from solutions dates back to the 19<sup>th</sup> century, and many such species have been discovered since. Ever since the discovery of these clusters, numerous attempts to use them in various reactions have been made, some successful and some not. It has been shown, for the first time in our group, that a “normal” 2-center-2-electron localized covalent bond can exist at a vertex of a deltahedral cluster with delocalized bonding such as  $\text{Ge}_9^{4-}$ . This reverses the popular assumption that it may not be possible to attach main-group substituents to such clusters. Based on the existence of 0-, 1-, and 2-bonded  $\text{Ge}_9$ -species in the monomer  $\text{Ge}_9^{4-}$ , the dimer  $[\text{Ge}_9\text{-Ge}_9]^{6-}$ , and the polymer  $[-(\text{Ge}_9)^{2-}]_\infty$ , respectively, it is only natural to also look for 3- or 4- bonded species.

In my talk I will show our results obtained during our investigation of germanium nine-atom clusters in solution. We show that it is possible to attach group 15 substituents to such clusters. Ethylenediamine solution of precursor,  $\text{K}_4\text{Ge}_9$  reacts with  $\text{Bi}(\text{Ph})_3$  (or  $\text{Sb}(\text{Ph})_3$ ) and gives nine atom germanium cluster ligated by two diphenylbismuth (or diphenylantimony) groups. These groups are exo-bonded to two opposite germanium vertexes of the open face of the cluster,  $[(\text{Ph})_2\text{Bi}(\text{Ge}_9)^{2-}\text{-Bi}(\text{Ph})_2]^{2-}$ . In order to achieve the same product using  $\text{As}(\text{Ph})_3$  and  $\text{P}(\text{Ph})_3$  the linear trimer of germanium clusters,  $[\text{Ge}_9\text{-Ge}_9\text{-Ge}_9]^{6-}$ , was obtained. The most interesting difference between the trimer and the dimer is that in the trimer each cluster is 2-bonded to its neighbor. This means that nine-atom cluster in the middle is actually 4-bonded. The charge of the trimer is 6-, which is in good agreement with the performed Extended-Hückel and Fenske-Hall MO calculations.



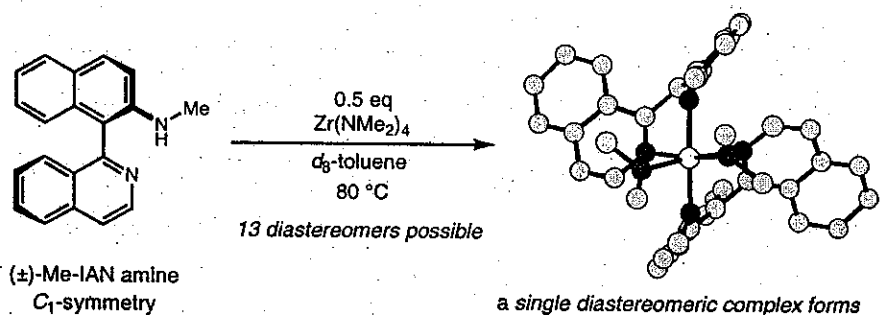
(3:30 – 3:50)

## Highly Diastereoselective Complexation of IAN Amines with Zirconium(IV).

Sarah Cortwright; Jeff Johnston  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405

### Abstract

The first examples of axially chiral  $\beta$ -diketimine ligands have been synthesized. These IAN amines, derived from Isoquinoline and 2-Amino Naphthalene, combine the strengths of the  $\beta$ -diketimine framework with the axial chirality of binaphthyl systems. The ligands are easily accessible and configurationally stable. Remarkable diastereoselectivity has been observed in the reaction of several IAN amines with  $\text{Zr}(\text{NMe}_2)_4$  to form  $C_2$ -symmetric 2:1 complexes which are precursors to active olefin polymerization catalysts.



(3:50 – 4:10)

## **Nuclear Resonance Vibrational Spectroscopy (NRVS): An Exciting New Technique for the Study of Iron Porphyrinates and Heme Proteins.**

Graeme R. A. Wyllie,<sup>1</sup> Mary K. Ellison,<sup>1</sup> Arne Roth,<sup>1</sup> W. Robert Scheidt,<sup>1</sup>  
J. Timothy Sage et al.,<sup>2</sup> Brajesh K. Rai,<sup>3</sup> Stephen M. Durbin et al.,  
<sup>3</sup> Wolfgang Sturhan,<sup>4</sup> E. Ercan Alp<sup>4</sup>

<sup>1</sup>Department of Chemistry and Biochemistry  
University of Notre Dame  
Notre Dame, IN 46556

### **Abstract**

Mössbauer spectroscopy has been traditionally used to obtain information on the coordination environment of a nucleus. The use of synchrotron radiation allows the observation of weaker features resulting in a form of vibrational spectroscopy (NRVS) with a unique sensitivity to the probe nucleus. Unlike traditional vibrational spectroscopy studies, the observed vibrations are specific to only those involving the Mössbauer nucleus and not hampered by interfering vibrations involving other nuclei or selection rules. We report here the NRVS spectra of a series of iron porphyrinate complexes possessing a variety of different axial ligands. We have been able to obtain the complete iron atom vibrational spectra for these and have confirmed the complete normal coordinate analysis upon the basis of heme in-plane and out-of-plane modes. In addition, oriented single crystal measurements have been carried out and demonstrate corresponding changes in the in-plane and out-of-plane modes based upon the crystal orientation. Comparison between calculated and experimental spectra are excellent. We have collected spectra for a number of complexes with the goal of building a suitable library which can then be used for the interpretation of similar spectra of heme proteins and ultimately, the elucidation of the mechanism of biological processes.

2. Department of Physics, Northeastern University, Boston, MA

3. Department of Physics, Purdue University, West Lafayette, IN

4. Advanced Photon Source, Argonne National Laboratory, Argonne, IL

(4:10 – 4:30)

## **Noble Metal Nanoparticle Films Compatible with Photolithography, Microcontact Printing, and Dip-Pen Nanolithography Patterning Technologies**

Lon A. Porter, Jr., Hee Cheul Choi, J. M. Schmeltzer,  
Alexander E. Ribbe, and Jillian M. Buriak  
Department of Chemistry  
Purdue University  
West Lafayette, IN 47907  
E-mail: buriak@purdue.edu

### **Abstract**

Currently, there is considerable interest in producing patterned metallic structures with reduced dimensions for use in technologies such as ultra large scale integration (ULSI) device fabrication, nanoelectromechanical systems (NEMS), and arrayed nanosensors, without sacrificing throughput or cost effectiveness. Research in our laboratory has focused on the preparation of precious metal thin films on semiconductor substrates via electroless deposition. This method provides for the facile interfacing of metal nanoparticles with a group (IV) and III-IV compound semiconductor surfaces. Morphologically complex films composed of gold, platinum, and palladium nanoparticles have been prepared as a result of the immersion of germanium and gallium arsenide substrates into dilute, aqueous solutions of tetrachloraurate (III), tetrachloroplatinate (II), and tetrachloropalladate (II), respectively. Continuous metallic films form spontaneously under ambient conditions, in the absence of a fluoride source or an externally applied current. This facile electroless deposition methodology provides an alternative to complex and expensive vacuum methods of metallization, yet allows for the preparation of both thin and thick nanostructured films with control over surface morphology and deposition rate. Furthermore, precious metal films prepared in this way exhibit excellent adhesion to the underlying semiconductor substrate. The resultant films were characterized utilizing scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and scanning probe microscopy (SPM). In order to apply this novel metallization method toward the development of useful technologies, patterning utilizing photolithography, microcontact printing (CP), and scanning probe nanolithography (SPN) has been demonstrated.

# Poster Presentations

(1)

## CS-Ligated Iron(II)octaethylporphyrinates – Structural and Mössbauer Studies and the Effect of the Sixth Axial Ligand

Sanjay Dahal;<sup>a</sup> M. Shang;<sup>a</sup> C. Chansheng;<sup>a</sup> A. Beatty;<sup>a</sup> C. E. Schulz<sup>b</sup>; W. R. Scheidt<sup>a\*</sup>

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University of Notre Dame

Notre Dame, IN 46556

<sup>b</sup>Department of Physics

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Galesburg, IL 61401

### Abstract

Thiocarbonyl-ligated iron(II)octaethylporphyrinates have been investigated by Mössbauer and single-crystal X-ray crystallography. Crystal structures of [Fe(OEP)(CS)(1-MeIm)], [Fe(OEP)(CS)(Py)] and [Fe(OEP)(CS)(MeOH)] have been solved. The methylimidazole and pyridine derivatives exhibit Fe-C(CS) bond distances of 1.703(4) and 1.707(2) Å which are significantly longer than a value of 1.662(3) Å reported for the five-coordinate derivative. The Fe-N(ligand) distances of 2.112(3) and 2.1550(15) Å observed for the methylimidazole and pyridine complex are ~0.13 Å longer than that observed for the bis-ligated complexes suggesting a significant structural trans effect of the CS ligand. Mössbauer investigations carried out for the five- and six-coordinate thiocarbonyl derivatives bearing pyridine, 4-cyanopyridine, 4-dimethylaminopyridine, 1-methylimidazole and piperidine as the sixth axial ligands reveal several interesting features. All the thiocarbonyl derivatives exhibit very small isomer shift values. The five-coordinate derivative exhibits  $\delta_{\text{Fe}} = 0.08$  mm/s at 4.2 K and the six-coordinate complexes exhibit  $\delta_{\text{Fe}} = 0.14$  to 0.19 mm/s at 4.2 K. The five-coordinate complex exhibits a large quadrupole splitting ( $\Delta E_{\text{Q}} = 1.96$  mm/s at 4.2 K) which gets drastically reduced on coordination of the sixth ligand ( $\Delta E_{\text{Q}} = 0.42$  to 0.80 mm/s at 4.2 K). The differences in the Mössbauer spectra between the five- and six-coordinate complex can be linked to the structural differences observed.

(2)

## Silicon Phthalocyanine SAMs on Silicon and Silicon Dioxide Surfaces

Vallipuram Sarveswaran<sup>a</sup>; Alexander Mintairov<sup>b</sup>; James L. Merz<sup>b</sup>; Marya Lieberman<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry

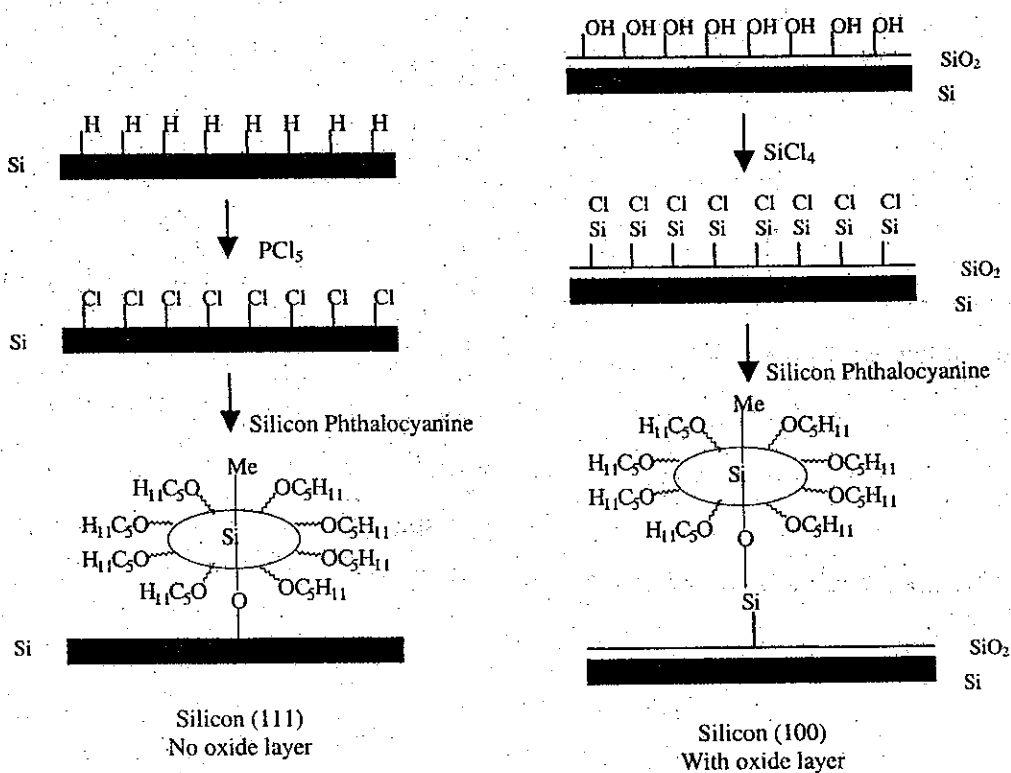
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### Abstract

Thin films of highly oriented phthalocyanines are of particular interest for electronic device applications. The formation of SAM of phthalocyanines at solid surfaces provides a rational approach for fabrication of interfaces having a well-defined composition, structure and reactivity. Silicon and Silicon dioxide surfaces can be modified in order to bind silicon phthalocyanine. One such approach involves radical initiated reaction of Si-H bonds with  $\text{PCl}_5$  which yields Si-Cl bonds. In another approach reaction of  $\text{SiCl}_4$  with the  $\text{SiO}_2/\text{Si}$  surface gives Si-Cl bonds. Both surfaces are found to react with methyl hydroxy silicon phthalocyanine  $[\text{MeSiPc}(\text{OC}_5\text{H}_{11})_8\text{OH}]$ .



(3)

## Electronic Halide Effect On Thermally Induced Bergman Cyclization of Metalloenediynes

Sibaprasad Bhattacharyya; Aurora E. Clark; Maren Pink; Jeffrey M. Zaleski\*

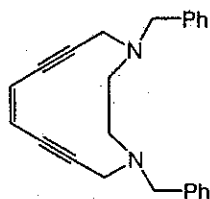
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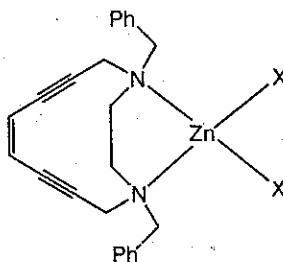
### Abstract

Three zinc dihalide complexes of type  $[LZnX_2]$  ( $X = Cl, Br, I$ ) have been prepared using a newly synthesized N,N donor enediyne ligand, **L**. The ligand and the dihalide complexes have been characterized spectroscopically and by single crystal X-ray diffraction techniques. The X-ray crystal structures of these complexes show that the ethylene bridge of ligand poises the  $ZnX_2$  unit above the enediyne plane and causes the alkyne termini separation to be nearly independent of the ancillary halide ligands and the geometry of the metal center. Upon complexation with  $ZnX_2$  ( $X = Cl, Br, I$ ), the alkyne termini distance is reduced to the same extent, but their Bergman cyclization temperatures (DSC) vary dramatically. As we proceed from the dichloride to diiodide complex, the cyclization temperature gradually decreases (208 to 144 °C). A possible explanation of this interesting observation has been established by density functional theory. The syntheses, structures, and results of the calculations will be discussed.



**L**

DSC 169 °C



**[LZnX<sub>2</sub>]**

X	DSC (°C)
Cl	208
Br	154
I	144



(4)

## Sensor Capabilities of Photoluminescent Tin Surfaces

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### Abstract

Several new surfaces have been prepared by electrochemically or stain etching tin foil with various acids. These high surface area materials were found to photoluminesce when irradiated at 254 nm. Each sample has a unique emission that is temperature dependant. These surfaces also exhibit unique sensing abilities. When amino acids or various common salts (ie. KCl, CaCl<sub>2</sub>) come into contact with the surface, the photoluminescence is visibly altered. Small amounts of water quench the luminescence completely. These effects are not only interesting for sensor applications but also for fundamental studies.

(5)

## Nucleophile Assistance of Electron Transfer Reactions Between Nitrogen Dioxide and Chlorine Dioxide Concurrent with the Nitrogen Dioxide Disproportionation Reaction

Robert H. Becker; Jeffrey S. Nicoson; Dale W. Margerum  
Department of Chemistry  
Purdue University  
West Lafayette, IN 47907

### Abstract

The loss of chlorine dioxide ( $\text{ClO}_2$ ) when reacted with excess  $\text{NO}_2^-$  in the presence of a large concentration of  $\text{ClO}_2^-$  was followed via stopped-flow spectroscopy. The concentrations of these species were set to establish a preequilibrium where nitrogen dioxide ( $\text{NO}_2$ ) is also present. These conditions enable the study of the  $\text{ClO}_2$  reaction with nitrogen dioxide ( $\text{NO}_2$ ) and the  $\text{NO}_2$  disproportionation reaction. The rate of the  $\text{NO}_2/\text{ClO}_2$  electron-transfer reaction is accelerated by different nucleophiles ( $\text{NO}_2^- > \text{Br}^- > \text{OH}^- > \text{CO}_3^{2-} > \text{PO}_4^{3-} > \text{ClO}_2^- > \text{Cl}^- > \text{H}_2\text{O}$ ). This general nucleophile assistance represents a new phenomenon in non-metal electron-transfer reactions for non-metal dioxides. The rate constants for the nucleophile-assisted reactions ( $k^{\text{Nu}}$ ,  $\text{M}^{-2} \text{s}^{-1}$ ) at 25 °C vary from  $4.4 \times 10^6$  for  $\text{NO}_2^-$  to  $2.0 \times 10^3$  when  $\text{H}_2\text{O}$  is the nucleophile. The concurrent  $\text{NO}_2$  disproportionation reaction exhibits no nucleophilic effect and has a rate constant of  $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This reaction system is the third found to exhibit a general nucleophilic acceleration of electron transfer, and also represents an alternative way to study the rate of  $\text{NO}_2$  disproportionation.

(6)

## **Carcinogen Interception: Detoxification and Cancer Prevention from Inorganic Compounds in the Diet**

Elizabeth E. Hamilton ; Jonathan J. Wilker  
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West Lafayette, IN 47907

### **Abstract**

Nitrosamines and polycyclic aromatic hydrocarbons are toxins found in cooked foods and tobacco smoke. The detrimental effects of these compounds are derived from metabolism to alkylating agents and subsequent DNA damage. Also present in the human diet are a variety of inorganic compounds, many of which exist as anionic oxo species under aqueous conditions. Numerous studies report decreased incidences of cancer when diets are supplemented with inorganics such as selenium and vanadium salts. We hypothesize that these bioavailable inorganics react with alkylating agents, thereby preventing genomic damage. We are examining the interactions of vanadium, selenium, and other oxo anions with alkylating agents. Here, we present results showing that simple vanadates detoxify alkylating agents by bringing about transformation to relatively harmless alcohols.

(7)

**Structure and Magnetic Properties of the Electron Transfer Salt  
Tetraarylporphinatomagnesium(II) 2,3,5,6-Tetrafluoro-  
7,7,8,8-tetracyanoquinodimethanide, [TCNQF<sub>4</sub>]<sup>•-</sup>**

Wendy Hibbs;<sup>1</sup> Atta M. Arif;<sup>1</sup> Mark Botoshansky;<sup>2</sup> Menahem Kaftory;<sup>2</sup> Joel S. Miller<sup>1</sup>

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University of Utah,  
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Haifa, 32000 Israel

**Abstract**

The crystal structures of *meso*-tetraphenylporphinatomagnesium(II) 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethanide, [MgTPP][TCNQF<sub>4</sub>]<sup>•-</sup>*x*S, {S = PhMe and 1,2-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>} provide the first structurally characterized examples of 1-D metal-radical chains involving a  $\pi$ -cation radical porphyrins. The compounds are structurally similar to the previously reported 1-D metal-radical chains of [Mn<sup>III</sup>TPP][TCNE] (TCNE = tetracyanoethylene) having *trans*- $\mu$ -N- $\sigma$ -coordination of the cyanocarbon linker to the metal center of the porphyrin. These electron transfer salts form 1-D coordination polymers consisting of parallel chains of alternating ...D<sup>•+</sup>A<sup>•-</sup>D<sup>•+</sup>A<sup>•-</sup>... (D = M(porphyrin); A = radical anion). [Mn<sup>III</sup>TPP][TCNE] (Mn<sup>III</sup>, *S* = 2 and [TCNE]<sup>•-</sup>, *S* = 1/2) displays ferrimagnetic ordering that is solvent dependent between 4 and 15 K. On the contrary, the redox unreactive Mg<sup>II</sup> results in electron transfer from the porphyrin ring to TCNQF<sub>4</sub> resulting in two *S* = 1/2  $\pi$ -delocalized spin sites. The room temperature effective moments for the compounds [MgTPP][TCNQF<sub>4</sub>]<sup>•-</sup>*x*S are consistent with the calculated non-interacting, spin only value of 2.45  $\mu_B$  and display only very weak antiferromagnetic coupling ( $J_{\text{intra}}/k_B \sim -2.9$  K) below 20 K based on fits to several linear chain models. While the structural characteristics of the [Mg<sup>II</sup>TPP]<sup>•+</sup> salts are remarkably similar to those of the [Mn<sup>III</sup>TPP]<sup>•+</sup> counterparts, diminished spin exchange results from the reduced spin magnitude as well as the relocation of the spin site leading to formation of a linear chain compound that is predominantly paramagnetic.

(8)

## Formation, characterization, and sub-50 nm patterning of organosilane monolayers with embedded disulfide bonds

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<sup>1</sup>Department of Chemistry and Biochemistry

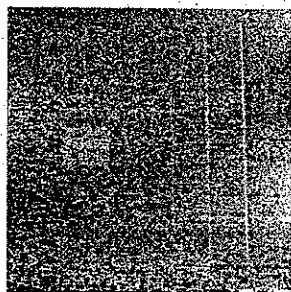
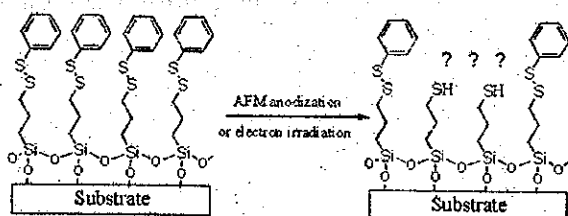
<sup>2</sup>Department of Electrical Engineering

University of Notre Dame

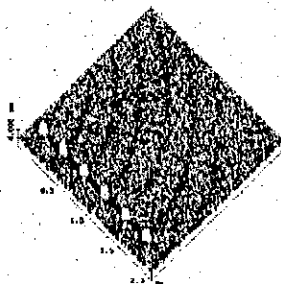
Notre Dame, IN 46556

### Abstract

We demonstrate a procedure for sub-50nm patterning of organosilane monolayers with embedded disulfide bonds on silicon oxide. The weak embedded disulfide bond is accessible to be selectively cleaved by reduction or oxidation. Phenyl(3-trimethoxysilylpropyl)disulfide, and benzyl(3-trimethoxysilylpropyl)disulfide form SAMs on silicon oxide. Ellipsometry measurements and X-ray photoelectron spectra show that the films have monomolecular thickness, and that the embedded disulfide bonds are intact after monolayer formation. These monolayers were used as an electron sensitive ultra-thin film for electron beam lithography and AFM anodization to form sub-50 nm patterns. Based on AFM topographic, phase contrast, and friction images, both electron beam lithography and AFM anodization cause topographic and chemical alteration in the patterned region. In the case of electron beam lithography, these changes are consistent with cleavage of the disulfide bonds. We expect the resulting chemical pattern can be further developed by reaction with other organic and inorganic molecules.



AFM phase contrast image of the monolayer after AFM anodization (image size is 2.75X2.75  $\mu\text{m}$ )



Topographic image of the monolayer after electron beam lithography (image size is 2.0X2.0  $\mu\text{m}$ )

(9)

## Hierarchical self-assembly of double crossover DNA tiles

Koshala Sarveswaran;\* Chris Russo;<sup>φ</sup> Aimee Robinson;\* Paul Huber;\* Craig Lent;<sup>φ</sup>  
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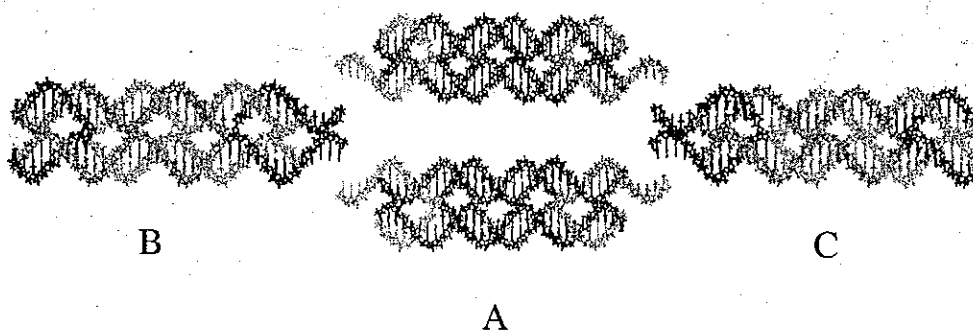
University of Notre Dame

Notre Dame, IN 46556

### Abstract

DNA self-assembly is a methodology for the construction of molecular scale structures. Single stranded DNA self-assemble into DNA crossover molecules (tiles). These tiles are quite rigid, stable and suitable for use in hierarchical self-assembly. Each DNA tile can be designed and constructed to match the ends of certain other DNA tiles, a process that can facilitate assembly into 2-D lattices or 3-D objects.

Our efforts have been focused on exploring the use of DNA tiles for hierarchical self-assembly in two dimensions. By using four different A, B, C and D tiles with complementary "sticky ends" we can program the formation of a finite two-dimensional ABCD raft shown below. These can be visualized directly by atomic force microscopy and inter-tile interactions can be demonstrated using biochemical methods.



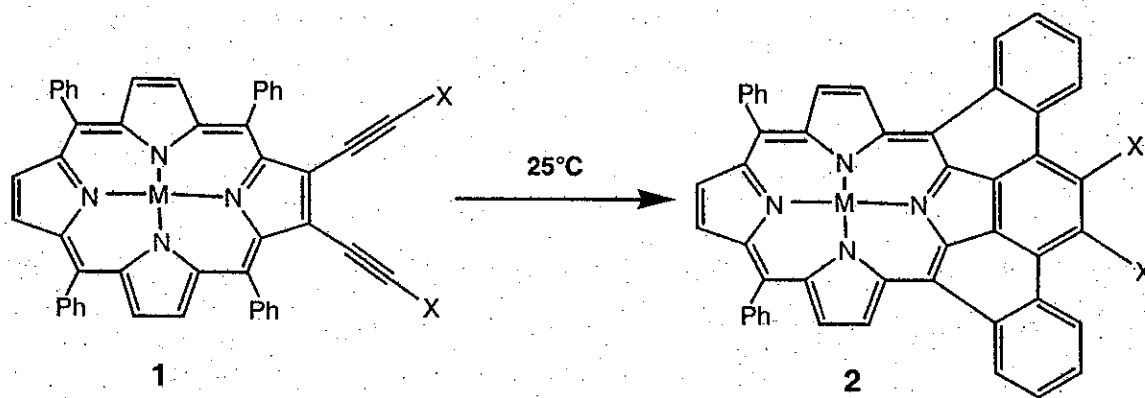
(10)

## Synthesis and Bergman Cyclization of Vicinal Dialkynylporphyrins

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### Abstract

Since porphyrins and their analogs have received much attention as phototherapeutic agents for photodynamic therapy (PDT), we have recently synthesized novel 2,3-diethynylporphyrins and their halo-analogs (**1**). The preparations lead to isolation of the title compounds in good to excellent yields (55-90%). The adjacent acetylenic units on porphyrins behave as an "enediyne" motif, and therefore undergoes Bergman benzannulation at ambient temperature to produce the highly conjugated picenoporphyrins (**2**). The preparation and characterization of these molecules will be presented.



(11)

## Control of reactivity of platinum(II) complexes in alkane oxidative addition: from DFT calculations to experiment

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Indiana University  
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### Abstract

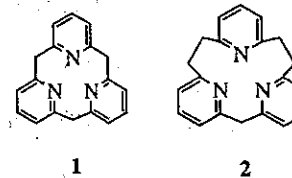
Alkane oxidative addition to  $d^8$  transition metal cyclopentadienyls leading to their  $d^6$  alkyl hydrido derivatives has been described first 20 years ago.



Later it has been discovered that some facially chelating ligands like Tp and *tacn* also stabilize  $d^6$  metal alkyl hydrides both kinetically and thermodynamically. In contrast, monodentate ligands disfavor alkane addition to  $d^8$  metal species. Despite of the knowledge that ligands play so crucial role in determining reactivity of a metal center, particular ligands allowing to "tune" rate and equilibrium of reaction (1) were unknown. In this work we report both a general theoretical and a particular practical solution of this problem.

1. Using *ab initio* and DFT modeling we have found a key to control kinetics and thermodynamics of reaction (1). One of the approaches formulated by us can be referred to as a principle of product adapted geometry.

2. Following to the principle, to tune reactivity of  $d^8$  metal center in alkane activation we suggest here *practical* usage of new macrocyclic ligands of different size, [2.n.1]-(2,6)-pyridinophanes (n=1 (1), and 2 (2)). The macrocycle 1 was designed to allow facile room temperature alkane activation (1), while the compound 2 was expected to allow similar chemistry at much lower temperatures.



3. We have found, that (1)PtR<sub>2</sub>H<sup>+</sup>X<sup>-</sup> species (R = Me, Ph; X = OTf, BAR<sup>F</sup><sub>4</sub>) allow *double* alkane CH bond cleavage at *room temperature*. They eliminate RH to give transient (1)PtR<sup>+</sup> able to add *methane*, or, in the case of linear and cyclic alkanes, to produce related (1)PtH(*olefin*)<sup>+</sup> complexes.

4. Variation of R, X, alkylation or change of size of a macrocycle L in LPtR<sub>2</sub>H<sup>+</sup>X<sup>-</sup> species affects rate of alkane activation dramatically. Thus, platinum complexes formed with macrocycle, 2, allow *double* alkane CH cleavage already at -50°C.

5. Another type of alkane activation, alkane *single* CH bond activation has been achieved using *monohydrocarbyl* dihydrido platinum(IV) complex, (1)PtMeH<sub>2</sub><sup>+</sup>, to give new (1)PtR(H)<sub>2</sub><sup>+</sup> species in high yield at 86°C (R = Cy, n-Am, Ph, Tol etc.). The alkyl ligand exchange at Pt<sup>IV</sup> center is completely reversible.

6. Complexes LPtH(*olefin*)<sup>+</sup> were found to be able to liberate free olefin or undergo carbonylative cyclization under certain conditions so forming a base for development of new catalytic reactions. Perspectives of developing new catalytic hydrocarbon transformations will be described.



(12)

## The Kinetics and Mechanisms of BrCl/Bromite and BrCl/Chlorite Reactions

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### Abstract

The reactions of BrCl/bromite and BrCl/chlorite are studied in phosphate buffer and in a  $p[H^+]$  range of 5.0 to 6.9 by stopped-flow spectrophotometric techniques. The BrCl is generated in small equilibrium concentrations by the addition of excess  $Cl^-$  to HOBr in phosphate buffer. In the BrCl/ $ClO_2^-$  reaction, where  $ClO_2^-$  is in excess, a first-order formation of  $ClO_2$  is observed, indicating a first-order dependence in [BrCl]. The dependencies of the rate on  $[ClO_2^-]$ ,  $[Cl^-]$ ,  $[H^+]$ , and buffer are determined. The loss of absorbance due to  $BrO_2^-$  is followed in the BrCl/ $BrO_2^-$  reaction where [BrCl] is kept constant, and the reaction has a first-order dependence in  $[BrO_2^-]$ . The rate dependencies on  $[Cl^-]$ , [HOBr],  $[H^+]$ , and  $[HPO_4^{2-}]$  were determined for the BrCl/ $BrO_2^-$  reaction. We propose that both the BrCl/ $ClO_2^-$  and BrCl/ $BrO_2^-$  reactions proceed by  $Br^+$ -transfer to form steady-state levels of BrOCIO and BrOBrO, respectively. In the BrCl/ $ClO_2^-$  case, BrOCIO reacts with  $ClO_2^-$  to form two  $ClO_2$  radicals and  $Br^-$ . On the other hand, the hydrolysis of BrOBrO in the BrCl/ $BrO_2^-$  reaction leads to the formation of  $BrO_3^-$  and  $Br^-$ . The rate constants for the transfer of  $Br^+$  in the two reactions are:  $k_2^{Cl} = 3.9(1) \times 10^6 M^{-1} s^{-1}$  and  $k_2^{Br} = 1.5(2) \times 10^5 M^{-1} s^{-1}$ .

(13)

## Electroless Deposition and Patterning of Morphologically Complex Noble Metal Films on Semiconductor Surfaces

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### Abstract

Precious metals are choice materials for a myriad of applications due their high electrical conductivity, resistance to corrosion, and ligand binding specificity. Indispensable in modern electronics fabrication, precious metals also enjoy widespread use as catalysts, support substrates, and sensor elements. Recent progress towards metallization on diminishing size regimes has imposed increasingly stringent demands upon thin film preparation methodologies. Metallization techniques employed in ultra large scale integration (ULSI) device fabrication, nanoelectromechanical systems (NEMS), and arrayed nanosensors will require unparalleled control of surface morphology, deposition rate, and substrate adhesion without sacrificing throughput or cost effectiveness. Furthermore, precious metal films of this type are essential for fundamental investigations aimed at elucidating the intricate nature of interfacial topics ranging from self-assembled monolayers (SAMs) to heterogeneous catalysis. In contrast to complex and expensive vacuum methods of metallization, research in our laboratory has focused on the preparation of precious metal thin films on semiconductor substrates via electroless deposition. Thin and thick films of gold, platinum, and palladium nanoparticles have been prepared as a result of the immersion of germanium and gallium arsenide substrates into dilute, aqueous solutions of tetrachloraurate (III), tetrachloroplatinate (II), and tetrachloropalladate (II), respectively. This methodology yields nanostructured precious metal films with control over surface morphology and deposition rate. Moreover, metal films prepared in this manner exhibit excellent adhesion to the underlying semiconductor substrate. The resultant films were characterized utilizing scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and scanning probe microscopy (SPM). This method provides for the facile interfacing of metal nanostructures with group (IV) and III-IV compound semiconductor surfaces.

(14)

## Anionic Fischer-Type Carbene Complexes in Complex of Complexes Methodology

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South Africa

### Abstract

Fischer type carbene complexes were used as ligands ( $[(\text{CO})_5\text{Cr}=\text{C}(\text{=N}(\text{CH}_3)\text{CH}_2\text{S})\text{O}]^-$  and  $[(\text{CO})_5\text{W}=\text{C}(\text{=N}(\text{CH}_3)\text{CH}_2\text{S})\text{O}]^-$ ) in synthesis of six new complexes, which are described as "complexes of complexes". In all the molecular structures a central metal atom ( $\text{M}^1 = \text{Cr(III)}$  1,  $\text{V(III)}$  2,  $\text{Co(III)}$  3,  $\text{Co(II)}$  4,  $\text{Ti(III)}$  5) is surrounded by three, two or one anionic complex ligands coordinating through the N and O donor atoms. The N and O, in turn, are part of a ligand coordinated to a metal carbonyl complex ( $\text{M}^2 = \text{Cr(0)}$  or  $\text{W(0)}$ ). Synthesis, X-ray structural determinations, and spectroscopic are presented.

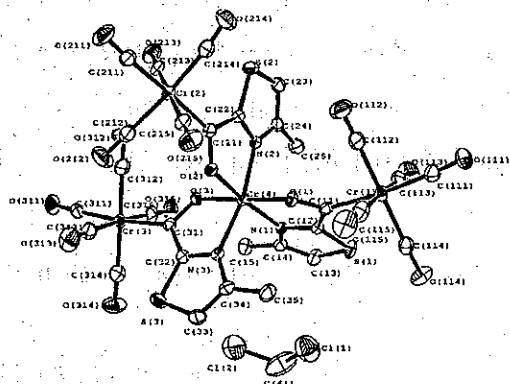


Figure 1. Molecular structure of complex 1  $\text{CH}_2\text{Cl}_2$  showing the numbering scheme.

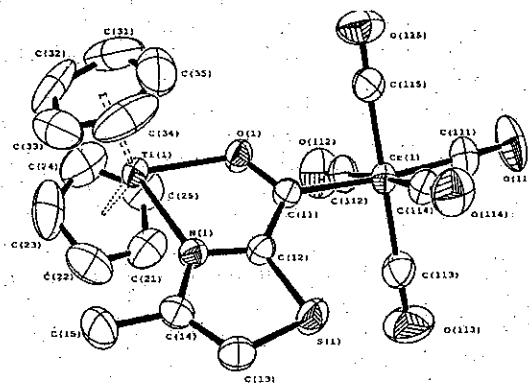


Figure 2. Molecular structure of complex 5 showing the numbering scheme

(15)

## Covalently bonding the bone cement-metal interface of orthopedic joints with a siloxane linker

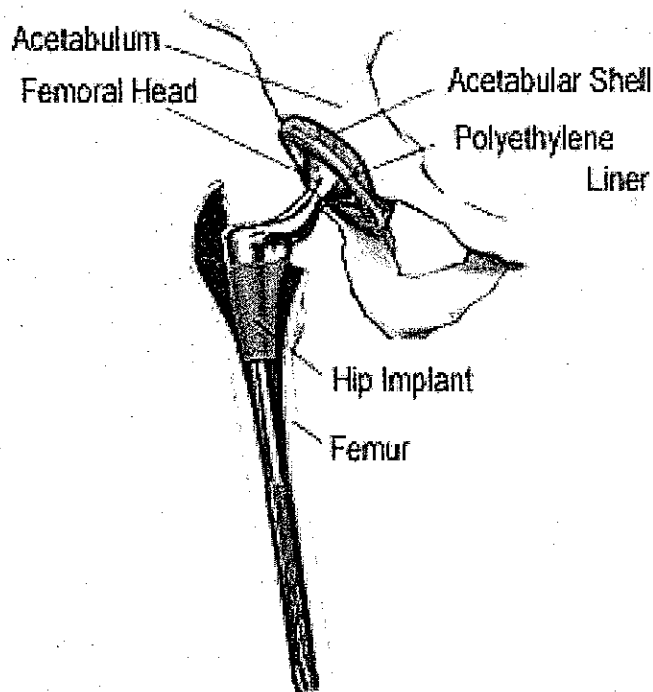
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University of Notre Dame  
Notre Dame, IN 46556

### Abstract

Present joint implants have a finite lifetime, usually within ten to fifteen years. The major mechanism of failure in orthopedic joint implants is the debonding of the metal-bone cement interface. Any improvement to increase interfacial adhesion might extend and improve the implants' lifetimes.

Current available formulas of bone cement consist of methyl methacrylate (MMA) that is mixed with polymethyl methacrylate (PMMA) and an initiator. The mixture polymerizes in a free radical mechanism, linking the bone and metal implant surfaces during the orthopedic surgery.

In order to increase the adhesion between the metal implant and the bone cement, we covalently linked them using a self-assembled monolayer of 3-methacryloxypropyltrichlorosiloxane. We optimized the conditions for derivatization of the metal surface and used X-ray photoelectron spectroscopy, ellipsometry, and contact angle measurements to characterize the SAM on the metal surface. After polymerizing bone cement around the treated rods, we tested the strength of the metal-bone cement bond with a push-out tester. Preliminary results show a marked increase in bonding strength from 7.5 MPa for untreated metal surfaces to 21 MPa for siloxane-treated metal surfaces.



Implant Inside a Femur

(16)

## Functionalization of Porous Silicon with Alkenes and Alkynes via Carbocation-Mediated Hydrosilylation

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Department of Chemistry  
Purdue University  
West Lafayette, IN 47907

### Abstract

Efforts to produce stable, derivatized porous silicon have yielded a number of chemical methods capable of functionalizing this interesting material with organic monolayers. Hydride-terminated porous silicon substrates react with alkenes and alkynes in the presence of dilute triphenylcarbenium salt solutions to respectively produce alkyl- and alkenyl-functionalized materials. Characterization by transmission FTIR and solid-state NMR suggests the formation of highly stable silicon-carbon bonds to yield covalently bound organic moieties. Porous silicon passivated in this fashion exhibits a greater resistance than that of the native material to chemical degradation, indicating that the organic functionalities may serve to sterically shield the nanocrystallites from nucleophiles. Hydrosilylation is proposed to proceed via hydride abstraction from the substrate followed by electrophilic attack by the subsequent species upon the alkene/alkyne, a mechanism previously hypothesized for the formation of stabilized beta-silyl carbocations. The reaction is tolerant of a variety of substrate functional groups and native porous silicon surfaces but depends markedly upon the identity of the salt counteranion, among other solution parameters.

(17)

## **A Role for Metal Ions in Marine Biomaterial Formation**

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### **Abstract**

Marine organisms such as the common blue mussel (*Mytilus edulis*) affix themselves to surfaces by producing protein-based glues. The soluble precursor protein of this biomaterial contains high levels of 3,4-dihydroxyphenylalanine (DOPA) and cross-links into a hardened matrix for adhesion. Interesting properties of this adhesive include a transition metal (e.g., iron, zinc, copper, manganese) content up to 100,000 times that of the surrounding waters. To better understand the bonding interactions of these marine biomaterials, we are studying the roles of transition metals in adhesive synthesis. We show that DOPA-containing peptides react with metals to provide models for inorganic cross-links. Similar bonding schemes are observed in both metal-cured precursor protein and intact mussel plaques. The resulting products are studied by materials engineering and spectroscopic techniques.

(18)

## Reactivity Studies of Lanthanide Complexes Supported by $\beta$ -Diketiminato Ligands

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### Abstract

A series of lanthanide complexes containing the sterically demanding amido-imine ligand  $\text{ArNC(R)CHC(R)NAr}$ . ( $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ;  $\text{R} = \text{CH}_3, ^t\text{Bu}$ ) have been prepared and structurally characterized. Redox and reactivity studies stemming from these systems will be presented and discussed.

(19)

## Vanadium Metalloenediynes: Initiating Bergman Cyclization via Photothermal Excitation

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### Abstract

The ability of enediynes to cleave DNA via diradical formation upon Bergman cyclization has created much interest in this class of compounds for potential therapeutic applications. Recent studies have shown that the Bergman cyclization temperatures of enediyne ligands can be controlled through metal ion coordination and the geometry of the resulting complexes. In many cases, ligands can be designed to be thermally quite labile and will generate Bergman cyclized product at modest temperatures. This low thermal barrier provides an opportunity to induce cyclization via a photo-thermal route. The significant long wavelength absorptivities ( $\epsilon \sim 5,000\text{-}10,000 \text{ M}^{-1}\text{cm}^{-1}$ ,  $\lambda \sim 600\text{-}1100 \text{ nm}$ ) associated with vanadium (V) catecholato compounds provides a potentially useful pathway for initiation of this cyclization. Through the judicious choice of an enediyne ligand with a low thermal cyclization barrier, compounds which generate cyclized diradical intermediates upon photo-excitation can be designed. The synthesis and reactivity of these novel metalloenediynes will be described.



(20)

## Synthesis, structure and apical group exchange reactions of Ti(IV) aminetrisulfonamid and aminetriphenoxide complexes

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University of Notre Dame  
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### Abstract

Titanium(IV) peroxo species represent an active component in a number of homogeneous and heterogeneous oxidation reactions of organic substrates by hydrogen or alkyl peroxides. In order to prepare Ti(IV) peroxo complexes and test them for epoxidation activity, complexes of two types of tripodal, trianionic ligands were synthesized. The tosylated TREN derivative  $N(\text{CH}_2\text{CH}_2\text{NHTs})_3$  reacts with  $\text{Ti}(\text{NR}_2)_4$ ,  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ , to give moisture- and air sensitive Ti-aminetrisulfonamide complexes. The nitrilotricresol  $N[\text{CH}_2\text{C}_6\text{H}_2(4,6\text{-}^t\text{Bu}_2)\text{OH}]_3$  reacts with  $\text{Ti}(\text{O}^t\text{Bu})_4$  to give an air- and moisture stable aminetriphenoxide complex. A number of aminetriphenoxide complexes with different apical groups, including terminal hydroxo and  $\mu$ -oxo derivatives, have been prepared and structurally characterized. The equilibrium for the apical ligand exchange reactions between Ti(IV) alkoxy complexes and various alcohols and phenols were studied. Bidentate ligands, such as acetylacetonate, form six-coordinate complexes which show complex fluxional behavior.

(21)

**Structure and magnetic property of  $\text{Ba}_5\text{In}_4\text{Bi}_5$ :  
A new Zintl phase**

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University of Notre Dame  
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**Abstract**

For several decades, many investigators have studied Zintl phases. Classically, a Zintl compound is a “polar intermetallic compound” and it has alkali or alkaline-earth metals as electropositive donors and p-block elements as electronegative acceptors. The electron transfer from the donor to the acceptor allows the latter to fulfill the octet rule. To do so, the p-block elements can form  $2c-2e^-$  bonds between each other and/or carry lone pairs of electron. Zintl phases are diamagnetic but in some rare cases can exhibit a metallic character due to delocalized extra electrons.

In this poster, we will discuss the structure and properties of the new Zintl phase  $\text{Ba}_5\text{In}_4\text{Bi}_5$ .

(22)

## DNA Studies with Bis 2-Pyridyl Porphyrin, Bis 4-Pyridyl Porphyrin

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### Abstract

Tetra N-methylpyridium-2-yl porphyrins have and continue to be extensively studied in various systems, in particular, DNA binding agents. A plethora of researchers have shown that the free tetrakis porphyrin preferentially groove binds to DNA. The binding is accomplished by the coulombic interactions between the anionic phosphate backbone and the cationic porphyrin. Groove binding is preferred because steric hindrance between the *meso* substituents and the minor groove destabilizes the intercalation form. We have focused on reducing the steric hindrance by synthesizing compounds with only two pyridyl groups and determining the effects on the binding between ligand and DNA. The resultant *trans* pyridyl porphyrin ligand would only have to fit one pyridyl group in the minor groove, and hydrophobic DNA interior may help drive the ligand to bind intercalatively. Recent experiments point to the *o*- and *p*- bis pyridyl ligands finding a niche as universal intercalators. We report binding studies on the bis pyridyl porphyrin and compare them with their tetrakis counterparts.

(23)

**Group (IV) and (V) transition metal alkyl, amido, chloro complexes supported by optically active binol ligands.**

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Purdue University  
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**Abstract**

Optically active binaphthyl ligands are used to prepare Zr(IV), Hf(IV), and Ta(IV) binol complexes. The (S)-[Ta(O<sub>2</sub>C<sub>20</sub>H<sub>10</sub> 3,3'-SiPh<sub>3</sub>)(NHMe<sub>2</sub>)(NMe<sub>2</sub>)Cl<sub>2</sub>] complexes has been isolated and fully characterized. Reactions of those species with a variety of substrates, including RLi, SiCl<sub>4</sub>, and Lewis bases will be discussed. Those complexes have provided an opening for interesting asymmetric chemistry such as kinetic resolution. In the presence of a racemic mixture of achiral alcohol the Ta(V) complexes has been found to react in a non-stereospecific fashion in the solution phase. Further reactivity of the complexes and efforts to prepare new species containing optically active binol ligand will be discussed.

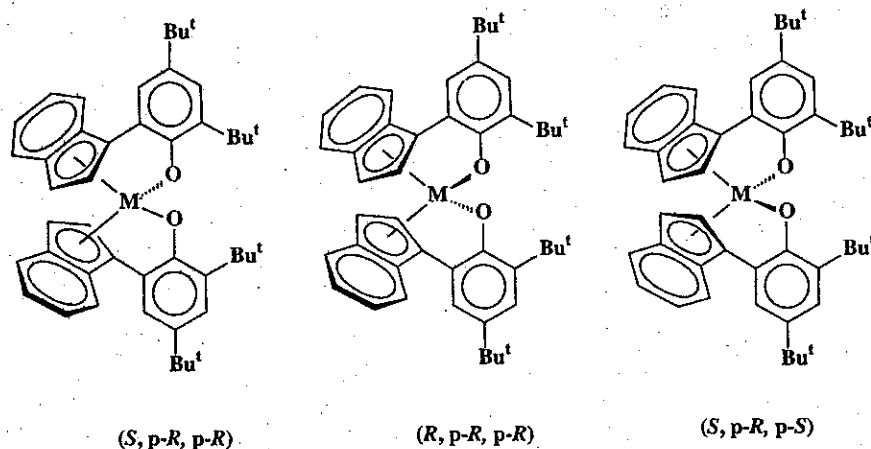
(24)

## Diastereoselectivity and Isomerism in a Series of bis(2-indenyl-phenoxy) Group 4 Metallospiranes

Luke E. Turner; Ian P. Rothwell  
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Purdue University  
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### Abstract

A series of constrained geometry ligands based on 4,6-ditertbutyl-2-(inden-3-yl) phenol (**1**) have been synthesized for application as Group 4 metallocene analogues.<sup>1</sup> The planar chirality of the indenyl moiety induces an asymmetry upon coordination to Group 4 metal centers. The reaction of Group 4 amides with two equivalents of **1** results in the formation of a spirocyclic metal center. The asymmetry of the indenyl rings coupled with the chirality at the metal center presents three diastereomeric possibilities (Figure 1). The diastereoselectivity and interconversion of the metallospiranes was found to vary not only with the identity of the metal, but also with the indenyl ring substitution and solvent.



1. Thorn, M. G.; Fanwick, P. E.; Chesnut, R. W.; Rothwell, I. P. *Chem. Commun.* 1999, 2543.

(25)

## Polypyridine Platinum(II) Lumaphors

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Purdue University  
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### Abstract

Pt(trpy)Cl<sup>+</sup> derivatives has been an area of interest for several years. More recently a superior polypyridyl system, php [2-(2'-pyridyl)-1,10-phenanthroline], was developed. It possesses several appealing properties, such as a more rigid framework, substantial hydrophobic character, and a compatibility with various solvents including water. In this study phenyl derivatives of the php family, ph $\phi$  [2-phenyl-1,10-phenanthroline], are being studied. While they possess the same attractive qualities of the php family complexes of these ligands are more emissive and possess longer lived lifetimes. For example Pt(ph $\phi$ )Cl<sup>+</sup> has a lifetime of 0.34  $\mu$ s while Pt(ph $\phi$ )Cl has a lifetime of 8.4  $\mu$ s. Other derivatives such as phQ [2-(8-quinolyl)-1,10-phenanthroline] and phNp [2-(1-naphthyl)-1,10-phenanthroline] are also being studied.

(26)

## Organolithium Aggregates as Synthons in Supramolecular Synthesis

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Department of Chemistry and Biochemistry

University of Notre Dame

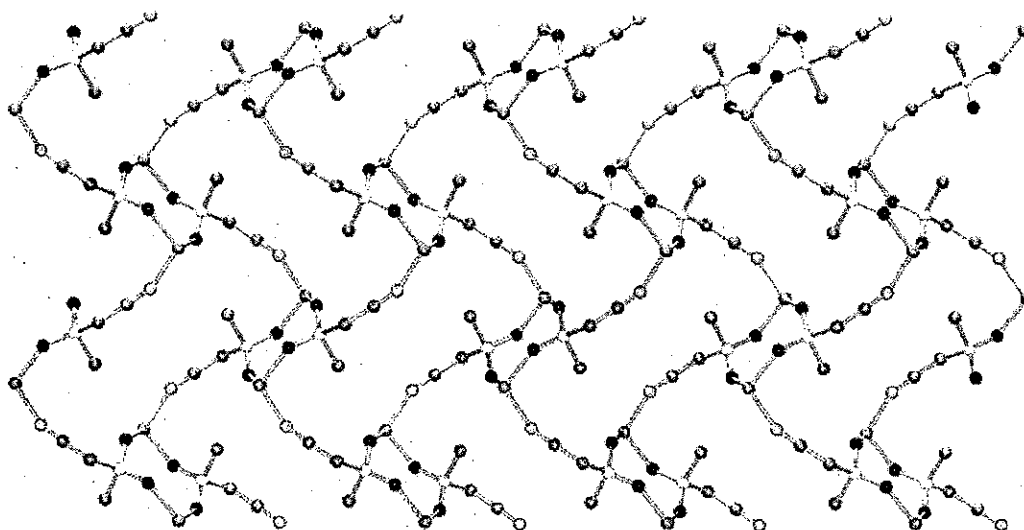
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### Abstract

The synthesis and characterization of well-defined network assemblies is an area of intense interest due to the potential of these materials in applications as diverse as catalysis, chemical separation, optics and electronics. Although there have been remarkable advances in our understanding of the principles of self-assembly, the development of rational routes to well-organized solid state materials remains a real challenge to the synthetic chemist. In this regard, two main strategies have been adopted in the formation of molecular networks, firstly through use of hydrogen bonded organic solids and secondly using inorganic coordination polymers containing transition elements and ligand spacer molecules. However, to our knowledge, the deliberate use of *s*-block metals, and more precisely organolithium aggregates, to control the formation of complex 2-D network architectures has not previously been reported. In contrast, the molecular coordination chemistry of organolithium compounds is well developed, with a wealth of information known regarding their solid state and solution aggregation behavior.

Our aim was to prepare, in a rational manner, a series of extended polymeric structures, which retain the core organolithium aggregate as supramolecular synthons, and utilize 'internal' Lewis base donors as linking agents. We will describe the use of lithiated  $\alpha$ -cyanophosphonates as building blocks, where the core aggregates are  $\text{Li}_2\text{O}_2$  ring dimers and the cyano ( $\text{C}\equiv\text{N}$ ) groups act as Lewis base linking groups. The overall result is the formation of 2-dimensional sheets composed of 4+4 nets. This work has now been extended to other functional groups and we will focus on the synthesis and structural characterization of a series of lithiated (organosulfonyl)acetonitrile complexes, culminating in the tailored synthesis of a sheet containing  $(\text{LiSO}_2)_2$  rings as part of a macroassembly of linked twenty-four membered rings (Fig. 1).

**Figure 1.** Section of  $[\text{MeSO}_2\text{CHCNLi}\cdot\text{THF}]$ , the THF groups are omitted for clarity.



(27)

## Aromaticity in Sn- and Pb - based Zintl Phases. Some Interesting Clathrate Compounds of Si and Ge.

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### Abstract

Although aromaticity has been extensively studied for more than a century, there is still no generally acceptable definition. The most significant feature of aromatic compounds is a planar structure with a delocalized system of  $(4n+2)$   $\pi$ -electrons. The most general point of view on aromaticity combines geometry (bond length equality), energy (aromatic stabilization energy) and magnetism (diamagnetic susceptibility exaltations). However this property has never been investigated carefully and systematically in all-metal species. Here we report the discovery of two isostructural Zintl phases containing aromatic anionic pentagonal rings made of Sn and Pb,  $\text{Sn}_5^{6-}$  and  $\text{Pb}_5^{6-}$ . These are the first heavy main-group species with an aromatic ring. It is very unusual that such heavy atoms can form aromatic structures.

Thermoelectric materials can be used for refrigeration and energy recovery, in special applications where small size, absence of moving parts, reliability, or environmental restrictions are important. According to theory cage compounds that have an atom inside the cages, that can "rattle" will have good thermal conductivity. Clathrates are periodic solids in which tetrahedrally coordinated atoms form cages that surround metal cations and are therefore, good candidates for thermoelectric materials. We present two unprecedented clathrate compounds:  $\text{Cs}_8\text{Ga}_8\text{Si}_{36}$  and  $\text{Ba}_8\text{Ge}_{42}$ .