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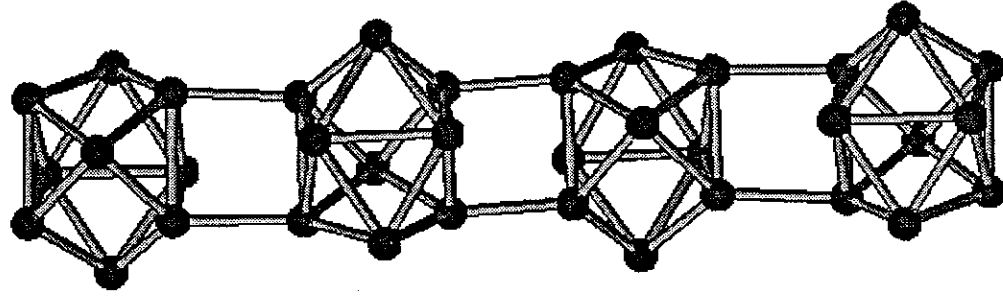
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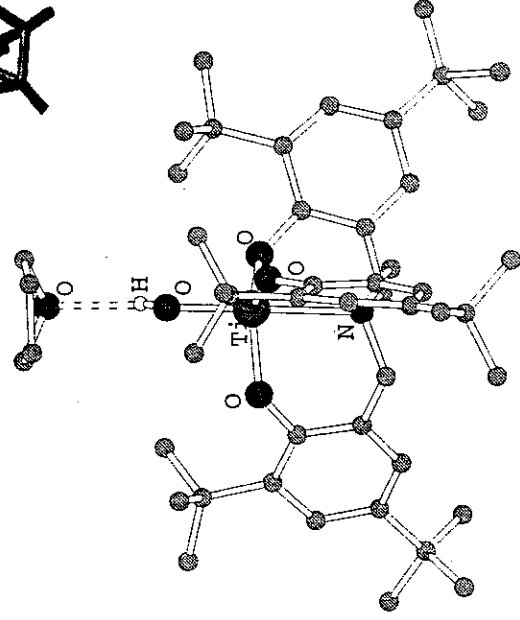
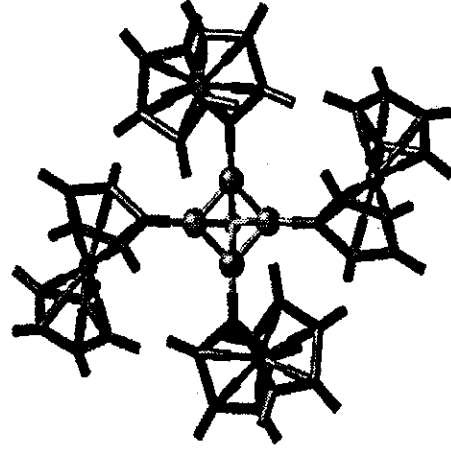
Universities



The University of
Notre Dame Presents

PINDU

October 11,



2003

Schedule

8:30 – 9:25am

Welcome Reception & Poster Hanging, Stepan Hall Lobby

9:25 – 9:30am

Opening Remarks, 123 Nieuwland Science Hall

Talk Session, Session Chair: Brad Bailey

9:30 – 9:50am

“DNA Binding Studies of New Cationic Porphyrins”, A. H. Shelton, Stephanie A.

Bejune and David R. McMillin - Purdue University.

9:50 – 10:10am

“s-Block Metal Aggregates as Supramolecular Synthons”, Dugald MacDougall and Kenneth W. Henderson - University of Notre Dame.

10:10 – 10:30am

“Os(H)₂CIL₂X (L=PPr₃, X=OTf or B(C₆H₃(CF₃)₂)₄) with Terminal Alkynes: the Formation of a 4 Electron Donation Adduct Alkyne and its Isomerization to an Os Carbyne.”, Joo-Ho Lee, Yegor D. Smurniy and Kenneth G Caulton - Indiana University.

10:30 – 11:30am

Odd Numbers Poster Session, Stepan Lobby

11:30 – 1:00pm

Lunch (see the last 2 pages)

Talk Session, 123 Nieuwland Science Hall, Session Chair: Alex Shelton

1:00 – 1:20pm

“Synthesis, structure and catalytic activity of Ti(IV) aminetriphenoxy complexes”, Yesela Ugrinova, Greg Ellis and Seth Brown - University of Notre Dame.

1:20 – 1:40pm

“Thermal and Photochemical Bergman Benzannulation of Porphyrinic Eneidyynes”, Mahendra Nath, John C. Huffinan and Jeffrey M. Zaleski - Indiana University.

1:40 – 2:00pm

“Peptide Mimics of Marine Mussel Adhesive Cross-Links”, Mary J. Sever and Jonathan J. Wilker - Purdue University.

2:00 – 3:00pm

Even Numbers Poster Session, Stepan Lobby

Talk Session, 123 Nieuwland Science Hall, Session Chair: Angel Ugrinov

3:00 – 3:20pm

“A Four-Coordinate and Terminal Titanium Alkylidene: Synthesis, Reactivity, and Mechanistic Features”, Brad C. Bailey, Falguni Basuli and Daniel Mindiola - Indiana University.

3:20 – 3:40pm:

“Isolation and Characterization of a Charged 4-Dot Molecular Quantum Cellular Automata Cell”, Jieying Jiao, Gary J. Long, Fernande Grandjean, Alicia M. Beatty and Thomas P. Fehlner - University of Notre Dame.

3:40 – 3:45pm

Concluding Remarks

TALKS

DNA Binding Studies of New Cationic Porphyrins

A. H. Shelton, Stephanie A. Bejune and David R. McMillin

Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084

Porphyrin/DNA interactions have and continue to be studied extensively in light of many fascinating results and future possibilities. Tetrakis N-methyl-pyridyl porphyrins (H_2TX X = 2,4) have been extensively studied in conjunction with B-form DNA. It has been found that tetra-substituted H_2T_2 porphyrin predominantly bind externally to DNA for steric reasons. The pyridyl groups of H_2T_4 have greater rotational freedom and will preferentially intercalate into DNA that has >50% G=C base pairs. To minimize the potential steric clashes between pyridyl groups and the DNA phosphate backbone, we have to date synthesized two bis pyridyl porphyrin series. These porphyrins have been variably studied with DNA and will be compared. The first series involves 5,15-di-(N-methylpyridium-2-yl)porphyrin (H_2D2) and 5,15-di-(N-methylpyridium-4-yl)porphyrin (H_2D4), while the second series includes 5,15-di-(N-methylpyridium-2-yl)-10,20-di-methylporphyrin (R_2D4) and 5,15-di-(N-methylpyridium-4-yl)-10,20-di-methylporphyrin (R_2D4). Also the results of (ZnD4) with DNA are reported. A qualitative energy-level diagram will be proposed to assess the forces that influence porphyrin/DNA binding.

s-Block Metal Aggregates as Synthons in Supramolecular Synthesis

Kenneth W. Henderson and Dugald J. MacDougall

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Fax: 574-631-6652, e-mail: khenders@nd.edu

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 1-D and 2-D 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 rationally prepare a series of extended polymeric structures, which retain the core organolithium aggregate as supramolecular synthons, and utilize 'internal' Lewis base donors as linking agents. To this end we have been developing the use of alkali metal derivatives of α , α' -stabilized carbanions as starting materials. We will describe the use of lithiated α -cyanophosphonates as building blocks, where the core aggregates are Li_2O_2 ring dimers and the cyano ($C\equiv N$) 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)acetone nitrile complexes, culminating in the tailored synthesis of a sheet containing $(LiSO_2)_2$ rings as part of a macroassembly of linked twenty-four membered rings. Furthermore, new aggregation patterns are now being established for these α , α' -stabilized carbanions and we will outline their relationship to the known ring-stacking and ring-laddering principles that have been developed for related alkali metal complexes.

Os(H)₂ClL₂X (L=PⁱPr₃, X=OTf or B(C₆H₃(CF₃)₂)₄) with Terminal Alkynes: the Formation of a 4 Electron Donation Adduct Alkyne and its Isomerization to an Os Carbyne.

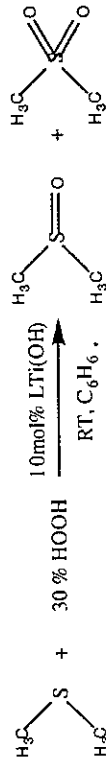
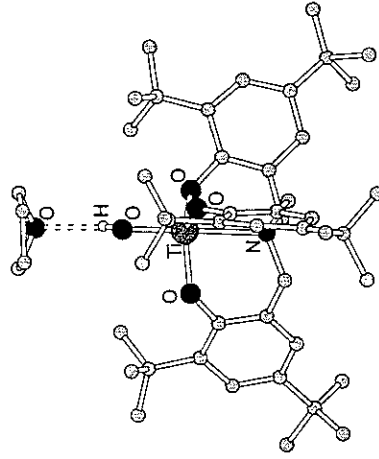
Jojo-Ho Lee, Yegor D. Smurniy, Kenneth G Caulton.
Indiana University

In studying the reactivity of unsaturated hydride metal complexes toward various organic compounds, the chemical reactivity of an Os cationic compound, Os(H)₂ClL₂X, L=PⁱPr₃, X=OTf or B(C₆H₃(CF₃)₂)₄, toward terminal alkynes (PhCCH, ¹BuCCH, HCCH) was investigated. Variable temperature multinuclear NMR shows the primary product of this reaction in benzene or methylene chloride was a 4e donor πadduct alkyne. In the case of HCCH with the Os/OTf complex, the alkyne was isomerized to a carbyne species at room temperature, possibly promoted by additional nucleophile (OTf, HCCH, or solvent). In addition, with long reaction time (over one day), a black precipitate of polyacetylene was also observed from the Os/OTf complex and HCCH. When X in the Os compound is B(C₆H₃(CF₃)₂)₄, the carbyne species was not observed in the NMR spectra of room temperature reaction in CD₂Cl₂. Instead, the black precipitate was seen within hours. The mechanism of the formation of the carbyne was studied by variable temperature NMR experiments and DFT calculations.

Synthesis, structure and catalytic activity of Ti(IV) aminetriphenoxide complexes

Vesela Ugrinova, Greg Ellis and Seth N. Brown
Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, IN

Titanium(IV) peroxy species represent an active component in a number of homogeneous and heterogeneous oxidation reactions of organic substrates by hydrogen peroxide or alkyl hydroperoxides. In order to prepare a Ti(IV) peroxy complex and test it for oxidation activity, nitrilotriresol N[CH₂C₆H₂(4,6-^tBu₂)OH]₃ was reacted with Ti(O^tBu)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 phenols were studied. Hydroxoaminetriphenoxide complex was reacted with hydrogen peroxide to give a peroxy derivative that was an active catalyst for sulfide oxidation.



Thermal and Photochemical Bergman Benzannulation of Porphyrinic Eneidyne

*Mahendra Nath, John C. Huffman and Jeffrey M. Zaleski**

Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, IN, 47405, USA

Abstract: Natural product eneidyne have shown high order of anti-cancer efficacy since they undergo Bergman cyclization and form reactive 1,4-benzoid diradical intermediate, which abstract hydrogen atoms from the sugar backbone of DNA and causes cell death. The discovery of photochemical Bergman cyclization as a novel approach to drive eneidyne reactivity in controlled manner prompted us to design eneidyne molecules with strongly absorbing chromophores and low excited state thermal barriers to cyclization. For this purpose, we have recently synthesized novel 2,3-dialkynylporphyrins and their halo-analogs in good to excellent yields (55-90%). The terminal alkyne units on these porphyrins, coupled with the double bond at the pyrrole backbone, behave as an "enediynes" motif, and therefore undergoes Bergman cycloaromatization thermally and photochemically to produce the highly conjugated picenoporphyrins. The preparation and characterization of these molecules will be presented.

Peptide Mimics of Marine Mussel Adhesive Cross-Links

Mary J. Sever and Jonathan J. Wilker

Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084

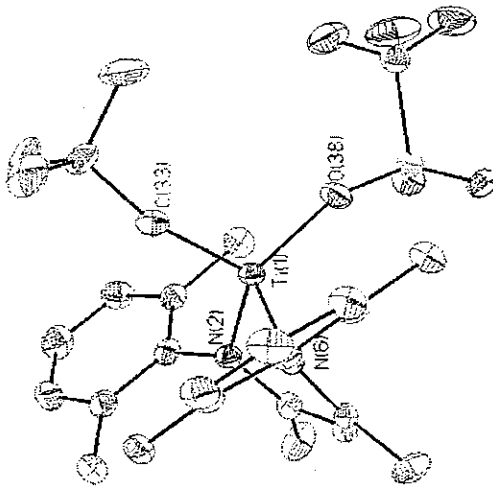
Marine organisms such as the common blue mussel (*Mytilus edulis*) affix themselves to surfaces by producing a protein-based glue. The soluble precursor protein of this biomaterial contains high levels of the unusual amino acid 3,4-dihydroxyphenylalanine (DOPA) and cross-links into a hardened matrix 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. Peptide mimics of marine mussel adhesives are prepared and reacted with various metal ions to produce soluble cross-linked model complexes suitable for spectroscopic characterization. Ultraviolet-visible absorption spectroscopy, electron paramagnetic resonance spectrometry, and mass spectrometry of these models have led to the identification of a variety of potential inorganic and oxidative cross-links.

A Four-Coordinate and Terminal Titanium Alkylidene: Synthesis, Reactivity, and Mechanistic Features

Brad C. Bailey, Falguni Basuli, and Daniel Mindiola*

Contribution from the Chemistry Department at Indiana University,
Bloomington, IN (USA)

A four-coordinate and terminal titanium alkylidene supported by the Nacnac⁻ ligand, namely (Nacnac)Ti=CH^tBu(OTf), was prepared via an oxidatively-induced ⁻hydrogen abstraction using silver trifluoromethanesulfonate and a Ti(III) precursor (Nacnac)Ti(CH₂Bu)₂. It was found that alkylidene (Nacnac)Ti=CH^tBu(OTf) thermally rearranges by a Wittig-like reaction. The chloro, bromo and iodo derivatives of the triflate-alkylidene were prepared and were found to transform upon thermolysis. Kinetic studies and DFT calculations reveal that the reaction occurs through an intramolecular rearrangement with a four-membered titanacycle being the likely intermediate. Reactivity studies of the titanium-alkylidene prepared herein display Wittig-type chemistry at the alkylidene moiety, and also nucleophilic reactivity at the ⁻carbon the Nacnac⁻ ligand. Cross-metathesis, salt-metathesis, and deprotonation studies concerning the chemistry of the titanium-alkylidenes will be described.

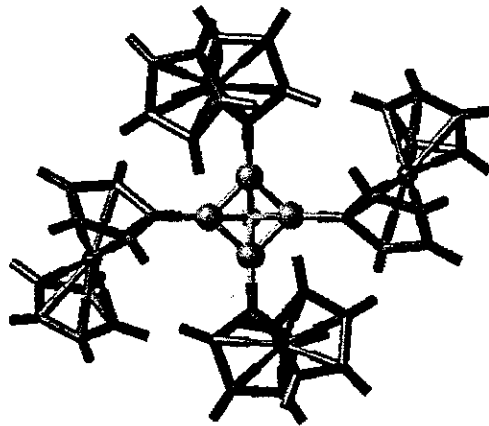


Isolation and Characterization of a Charged 4-Dot Molecular Quantum Cellular Automata Cell

Jieying Jiao[†], Gary J. Long[†], Fernande Grandjean[‡], Alicia M. Beatty[†], and Thomas P. Fehner^{†*}

[†]Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, IN 46556-5670, [‡]Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409-0010, [§]Department of Physics, B5, University of Liège, B-4000 Sart-Tilman, Belgium

The mixed-valence compound, $\{(\text{C}_5\text{H}_5)_2\text{Fe}(\text{C}^-\text{C}_5\text{H}_4)\}_4(\text{C}^-\text{C}_4)\text{Co}(\text{C}^-\text{C}_5\text{H}_5)[\text{PF}_6]_2$ ($[\text{I}][\text{PF}_6]_2$), was evaluated as a potential building block for constructing molecular quantum cellular automata (QCA) circuits. The preparation, isolation and characterization of the neutral compound **1** and mono and dicationic mixed-valence complexes will be presented. XRD of **1** and $[\text{I}][\text{PF}_6]$ as well as IR, EPR and Mössbauer spectra plus magnetic susceptibility measurements will be described. The mixed-valence compounds have valence-trapped electronic structure on the IR, EPR and Mössbauer time scale. In common with most mixed-valence compounds, the cations in $(\text{CD}_3)_2\text{CO}$ have intervalence charge transfer bands in near-IR region yielding an estimated thermal electron transfer rate of the dication appropriately fast for the QCA application.



POSTERS

1. Reactivity of $[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}(\text{tBu})_2)_2]\text{RuCl}$ with small organic molecules

Amy Walstrom

Indiana University

The molecule $[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}(\text{tBu})_2)_2]\text{RuCl}$ (PNPRuCl), a very unique 14 electron, square planar, ground state triplet, has proven to be highly reactive toward small, sterically accessible organic unsaturated compounds. Reaction of the aforementioned PNPRuCl with ethylene gives solely the π bound olefin in an apical position of a square pyramidal structure, as determined by ^1H NMR, $^31\text{P}\{^1\text{H}\}$ NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and X-ray crystallographic studies show. Other olefins, such as acetylenes and allyl halides, give similar products shown by the same techniques. DFT calculations were also carried out upon some of the resultant products.

2. Some Rare Cases of Zintl Phases: New Metallic Zintl Compounds with In and Bi

Ara Cho and Slavi C. Sevov

Department of Chemistry & Biochemistry,

University of Notre Dame

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.

For several decades, many investigators have studied Zintl phases. In this poster, we will discuss the structure and properties of some Zintl phases with alkali (and/or alkaline-earth) metal, In, and Bi.

3. Reactions of nine-atoms germanium clusters in solution

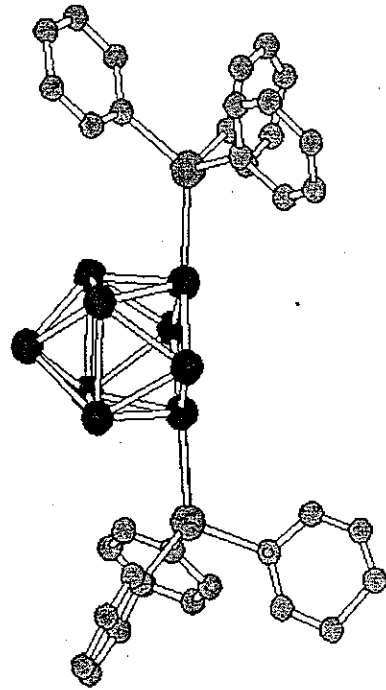
Angel Ugrinov and Slavi Sevov

Department of Chemistry and Biochemistry,

University of Notre Dame, Notre Dame, IN

Interest in synthesis, isolation and characterization of deltalhedral Zintl ions from solutions dates back to the 19th century. Numerous attempts to use these species in various reactions have been made, some successful and some not. It has been shown, for the first time in our group, that "normal" 2-center-2-electron bonds can form between such clusters with delocalized bonding, Ge_9^{4-} for example. Based on the existence of the dimers of $[\text{Ge}_9\text{-Ge}_9]^{6-}$, and the chain of $[-(\text{Ge}_9)^2]_{\infty}^-$, it is only natural to look also for oligomers of various sites.

The poster presents some of the results of our investigation of reactions with the germanium nine-atom clusters in solution. We show that it is possible to attach group 15 or group 14 substituents to such clusters. Ethylenediamine solutions of the precursor A_4Ge_9 (A=K or Rb) react with SbPh_3 , BiPh_3 or SnPh_4 and give yield of $[\text{Ph}_2\text{SbGe}_9\text{SbPh}_2]^{2-}$ (same for Bi), $[\text{Ph}_2\text{SbGe}_9\text{Ge}_9\text{SbPh}_2]^{4-}$, $[\text{PhGe}_9\text{SbPh}_2]^{2-}$, $[\text{Ph}_3\text{SnGe}_9\text{SnPh}_3]^{2-}$ and $[\text{Ge}_9\text{SnPh}_3]^{3-}$. The same reactions with AsPh_3 and PPh_3 provide linear trimer of germanium clusters, $[\text{Ge}_9\text{-Ge}_9\text{-Ge}_9]^{6-}$. Later we found that the trimer can be synthesized just using high concentration of precursor in an appropriate cation sequestering agent. Following the same idea but changing the cation sequestering agent we obtained a tetramer, $[\text{Ge}_9\text{-Ge}_9\text{-Ge}_9\text{-Ge}_9]^{8-}$. It was supposed, based on these results, that the mechanism of these reactions is nucleophilic addition between anions. The best proof is the fact that the reactions between K_4Ge_9 and Ph_3Sn^- or Ph_3Ge^- , or Me_3Sn^- are produced $[\text{Ph}_3\text{SnGe}_9\text{SnPh}_3]^{2-}$, $[\text{Ph}_3\text{GeGe}_9\text{GePh}_3]^{2-}$ and $[\text{Me}_3\text{SnGe}_9\text{MePh}_3]^{2-}$ respectively.



4. Metaloenediyne Incorporating Salen Like Ligands

David Dye, Jeff Zalesk

Indiana University

Naturally occurring compounds containing enediyne moieties have proven to be potent anti-tumor agents through their ability to undergo Bergman cyclization and cleave DNA via the 1,4-phenyl diradical intermediate's abstraction of H atoms from the DNA backbone. Though potent, the non-selective nature of these compounds makes them toxic to both healthy and diseased cells, limiting the scope of their therapeutic applicability. Attempts to synthesize synthetic analogues incorporating metal centers to regulate the reactivity of the enediyne moiety have been ongoing in the Zaleski Lab, and to that end we have synthesized several new enediyne ligands that have been designed to mimic the classic ligand salicylaldehyde ethylenediamine (salen). The synthesis and reactivity of these ligands and some of their metal complexes will be presented.

5. Carcinogen Interception: Detoxification and Cancer Prevention from Inorganic Compounds in the Diet

Elizabeth E. Hamilton, Jessica M. Fautsch and Jonathan J. Wilker

Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084

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 inorganics prevent DNA damage and detoxify alkylating agents by bringing about transformation to relatively harmless alcohols.

6. Four-Coordinate Alkylidene and Phosphinidene Complexes of Vanadium(IV)

*Falguni Basuli,[†] Uriah J. Kilgore,[†] Xile Hu,[†] Karsten Meyer,[†] Maren Pink,[†] John C. Huffman,[†] and Daniel J. Mindiola**

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One electron oxidation of the η^5 -diketiminato vanadium (III) bis-neopentyl complex (Nacnac)V(CH₂^tBu)₂ (Nacnac⁻ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-(CHMe₂)₂C₆H₃) promotes η^5 -abstraction to afford the cationic four-coordinate neopentylidene complex [(Nacnac)V=CH^tBu(THF)][BPh₄]. The neutral vanadium neopentylidene complex (Nacnac)V=CH^tBu(I) was prepared by the reaction of cationic complex [(Nacnac)V=CH^tBu(THF)][BPh₄] with I₂ or MgI₂. This family of alkylidene complexes are one electron paramagnets and display well-resolved EPR spectra. Gentle heating of [(Nacnac)V=CH^tBu(THF)][BPh₄] affords the vanadium(II) zwitterion [(Nacnac)V(-C₆H₅BPh₃) and neopentane, while thermolysis of (Nacnac)V=CH^tBu(I) produces the terminal imido species [(Ar]NC(Me)CHC(Me)=CH^tBu)V=NAr, a compound formed via intramolecular cross-metathesis. Reaction of the alkylidene cation [(Nacnac)V=CH^tBu(THF)][BPh₄] with N-benzylidene-methyl-amine affords the cationic imido complex [(Nacnac)V=NMe(THF)₂][BPh₄] along with the corresponding olefin BuCH=CHPh by-product. In addition, novel four-coordinate phosphinidene complexes (Nacnac)V=PR(CH₂^tBu) (R = C₆H₁₁, 2,4,6-Pr₃C₆H₂, 2,4,6-^tBuC₆H₂) were prepared from salt metathesis of (Nacnac)V=CH^tBu(I) with LiPHR followed by η^5 -hydrogen migration of the putative phosphide (Nacnac)V=CH^tBu(PHR). Solid and solution magnetic measurements, EPR spectra, and single crystal X-ray diffraction studies have been carried out for all the complexes described.

7. Aromaticity in Sn- and Pb- based Zintl Phases.

*Liya Todorov and Stavi Sevoy**

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

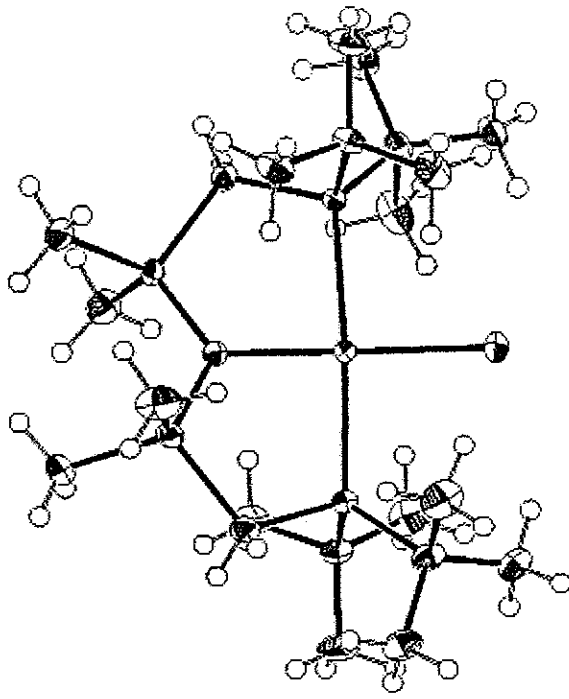
Although aromaticity has been extensively studied for more than a century, there is still no generally acceptable definition. This concept was invented to account for the unusual stability of certain organic molecules: the aromatic compounds. The most significant feature that they exhibit is a planar structure with a delocalized system of $(4n+2)$ π -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 three isostructural Zintl phases with aromatic anionic pentagonal rings made of Sn and Pb, Sn_5^{6-} and Pb_5^{6-} . Furthermore two other phases having anionic pentagonal rings have been discovered in a detailed study of the Li-Eu-Sn system, $\text{Li}_6\text{Eu}_5\text{Sn}_9$ and Li_7EuSn_6 .³³ In addition a quaternary phase $\text{LiMgEu}_2\text{Sn}_4$ with infinite chains in cis conformation have been made. This phase is related to $\text{Li}_6\text{Eu}_5\text{Sn}_9$ where the Sn_5^{6-} rings are separated by infinite chains in trans conformation. All compounds have been synthesized by direct fusion of the elements at 800°C and characterized by single crystal X-ray diffraction. These are the first heavy main-group species with an aromatic ring. It is very unusual that such heavy atoms can form aromatic structures.

8. Structure and reactivity of $[\text{N}(\text{Si}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{Bu})_2)_2\text{RuCl}]$: the first 4-coordinate, planar, d^6 complex of Ruthenium

Lori A. Watson, Amy Walstrom, Oleg Ozerov, Maren Pink, Kenneth G. Caulton

Indiana University

The use of a diphosphine amido ligand, $[\text{N}(\text{Si}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{Bu})_2)_2]$ (PNP-Bu), provides a convenient way to stabilize highly unsaturated transition metal complexes and has resulted in the successful synthesis of $(\text{PNP-Bu})\text{RuCl}$. This 4-coordinate, d^6 ruthenium complex has been shown to have a square planar geometry by X-ray crystallography and be paramagnetic through NMR and SQUID methods. The geometric and electronic structure of this complex as well as its reactivity toward small molecules (O_2 , NO , N_2 , H_2 , and CO) will be discussed.



9. Enhancing the Luminescence of Pt(II) Polypyridine Complexes

Michael H. Wilson, Randolph P. Thummel, and David R. McMillin
Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084

In recent years there has been considerable interest in platinum(II) complexes of 2,2',6,6'-terpyridine and its derivatives, because of its DNA interactions. However, chloro(2,2',6,6'-terpyridine)platinum(II) is non-luminescent in solution because of a thermally accessible deactivating d-d state. Altering the terpyridine ligand to 2-(2-pyridyl)-1,10-phenanthroline lowers the energy of the excited state, and moving it away from the deactivating d-d state. With a lower energy excited state the complex becomes emissive in solution, having a lifetime of 230 ns in degassed dichloromethane solution. Temperature studies showed that the deactivating d-d state and lies about 1840 cm⁻¹ above the excited state. To further move the excited state away from the deactivating d-d state two routes are being explored. One route is to open the N-Pt-N bond angle to relieve bond strain. A second route is to replace the bound chloride with an acetylene ligand, lowering the energy through Pt-C bond formation.

10. Metal - Linked Nucleic Acids

Mildred Rodriguez, Megan Lockard, and Jonathan J. Wilker
Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084

Antisense therapy is a potentially powerful tool to combat genetic diseases. In this approach, a nucleic acid drug is bound to mRNA thereby inhibiting expression of a protein responsible for the disease. The major benefits of this method are its high specificity for a given genetic target and broad applicability. However, these polyanionic nucleic acids suffer from low transport into cells, nuclease degradation, and low affinity for the irregular structures of target mRNA. We are developing a new class of oligodeoxynucleosides to improve antisense therapy. By changing the phosphate linkage in nucleic acids to a metal - ligand complex we can obtain better control of charge, improve transport into cells, and provide structural variety. Preliminary work replacing a base with bipyridine, piperazine, and dithioether ligands has shown some promise. We will present synthetic results and initial biochemical binding assays for these new metal - DNA conjugates.

11. Characterization of a Kinetically Stable, Highly Ordered, Octamer Form of Lithium tert-Butoxide and its Implications Regarding Aggregate Formation

John F. Allan, Roger Nassar, Kenneth Henderson*
Department of Chemistry & Biochemistry, University of Notre Dame,
Notre Dame, Indiana 46556, USA; massar@nd.edu

Since 1965, the structure of lithium tert-butoxide has been believed to be exclusively hexameric, **1₆**,¹ this was confirmed by a series of spectroscopic data.² It was only in 2002 that this aggregation state was observed by single crystal X-ray diffraction.³ Herein, we present the characterization of a novel octameric, **1₈**, aggregation of 'BuOLi (Figure 1).

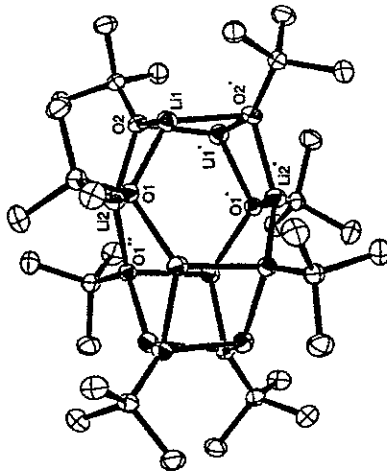


Figure 1. Crystal structure of Octameric lithium tert-butoxide.

The formation of **1₈** results from the reaction of 'BuLi with molecular oxygen in hexane or pentane. Cryoscopy and powder and single crystal X-ray diffraction are the only studies that reveal differences between **1₆** and **1₈**. Experimental and computational results prove that **1₈** is a kinetically stable aggregation state of 'BuOLi. The influence of the reaction conditions on the resulting aggregation state and proposed formation mechanisms will be discussed.

- (1) Huml, K. *Czech. J. Phys.* 1965, **15**, 699.
- (2) Kahn, J. D.; Haag, A.; Schleyer, P. v. R. *J. Phys. Chem.* 1988, **92**, 212.
Cihsholm, M. H.; Drake, S. R.; Naimi, A. A.; Streib, W. E. *Polyhedron* 1991, **10**, 337.
Thomas, R. D.; Boff, S. G.; Gravelle, P. W.; Nguyen, H. D. *Abstracts of Papers*, 215th ACS National Meeting, Dallas, 1998, Part 1, INOR 291.
- (3) Nekola, H.; Olbrich, F.; Behrens, U. *Z. Anorg. Allg. Chem.* 2002, **628**, 2067.

12. A Unique Example of Mo(IV) Induced Ene-diyne Activation

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Bloomington, IN, 47405, USA

A new ene-diyne dithiolate ligand, dipotassium salt of 3,10-dialkylthiacyclododec-1,6-ene-4,8-diyne-1,2-dithiolate (L) was prepared in few steps. First the 5,13-dihydro-8-ene-6,10-diyne-1,3-dithiol[4,5-b]-dithiacyclododecanone-2-thione (I) was prepared by the reaction between 1,8-dibromooct-4-ene-2,6-diyne and dicesium salt of 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) in 20% yield. Stirring the slurry of mercury(II) acetate and I in chloroform-acetic acid afforded 4,11-dialkylthiacyclododec-1,7-diene-5,9-diyne-1,3-dithiol-2-one, 2, in 60% yield. Addition of 2 eq of EtOK to a slurry of 2 in methanol gave a light yellow solution of L. Heating the L (*in situ* prepared from 2) with dichlorobis(η^7 -cyclopentadienyl)molybdenum in methanol at 60 °C for 0.5 h afforded molybdenum bound purple colored Bergman product in 28% yield. The mechanism and cause of cyclization have been studied thoroughly. All the compounds in this work have been characterized by spectroscopic techniques. The structural identities of some representative compounds were confirmed by X-ray crystallography.

13. Metal-Mediated Cross-Linking in the Generation of a Marine Mussel Adhesive

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Marine organisms such as the common blue mussel (*Mytilus edulis*) affix themselves to surfaces by producing a protein-based glue. 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 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 intact mussel plaques and extracted precursor protein. The resulting products are studied by materials engineering and spectroscopic techniques.

14. Synthesis and Structure of Bimetallic Alkali and Alkaline Earth Metal Enolates

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Enolate anions are key intermediates in numerous transformations including alkylations, Michael reactions, protonations, acylations and aldol additions. Magnesium bisamides have previously been shown to have contrasting reactivity and selectivity to their lithium analogues¹. We now report the extension of this work to include calcium and potassium. The preparation and characterization of a series of mixed metal (Ca/K) enolates will be discussed.

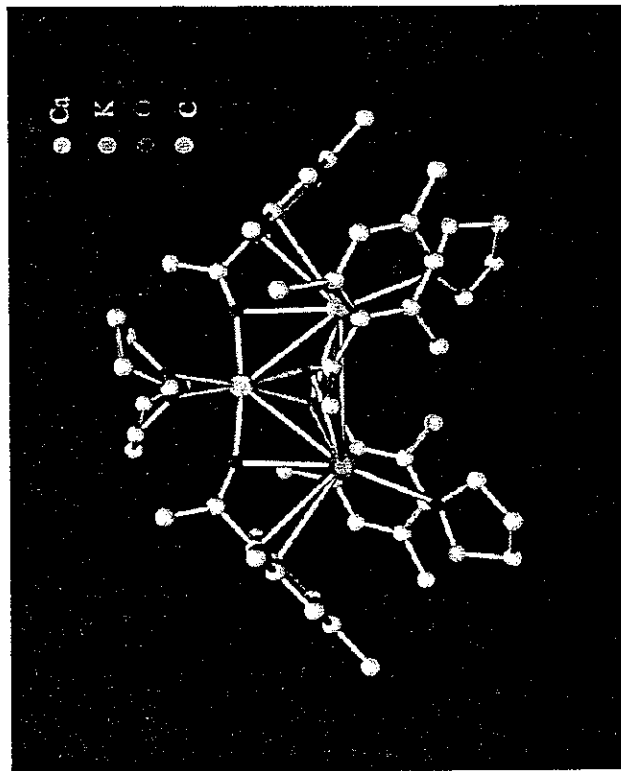


Fig.1 Molecular Structure of $[K_2Ca\{OC(Mes)=CH_2\}\cdot THF_4]$ (Mes=2,4,6-Me₃C₆H₂)

1. H. B. Mehlburger and C. S. Wilcox, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 3, ch. 14.
2. K. W. Henderson and W. J. Kerr, *Chem-Eur J.*, 2001, 7(16), 3430.

15. Electrochemical Fabrication of Nanostructured ZnO Films

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Semiconducting mesoporous films (with pore sizes between 2nm and 50 nm) have excellent potential for applications such as battery electrodes, photovoltaics, sensors, and photo- and electro-catalysts due to the combination of their high surface areas and useful optical, electrical, and catalytic properties. The synthesis of semiconducting films with ordered mesopores, however, has been limited to only a few systems because conventional sol-gel based supramolecular templating methods do not produce sufficiently robust mesoporous frameworks for many of these materials. Therefore, developing a method capable of fabricating semiconducting films with tunable robust mesostructures will be extremely advantageous for tailoring functional properties of the films.

We are currently developing a new synthetic strategy that combines a soft solution electrochemical process with supramolecular templating. In this approach we organize amphiphilic molecules in various ways on the electrode surface by tuning chemical and electrochemical conditions and utilize these organic matrices to template inorganic nanostructures. This method provides a new mechanism for assembling amphiphilic molecules as well as for building inorganic wall structures, which makes it possible to produce a variety of semiconducting films with new porous architectures. In this presentation, we will discuss principles and mechanisms of our new method and present preliminary results on the fabrication of ZnO films with various ordered nanoporous structures.

16. Reactivity of Electron-Rich Alkenes with a Cationic Rhenium Carbene

Markos M. Papadakis and Seth N. Brown

University of Notre Dame

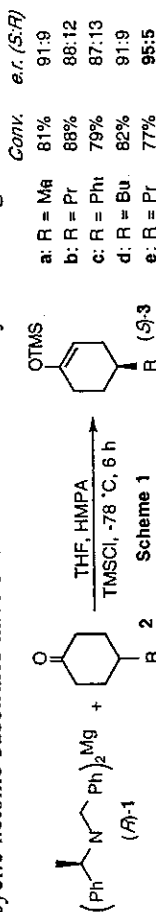
Eighteen-electron cationic carbene complexes have exhibited reactivity as electrophiles, but no carbon-carbon bond forming reactions of metal carbenes with alkenes have been observed. The cationic carbene complex $[(C_5H_5)Re(CO)_2(C_6H_5)]^+BARF^-$ has been prepared in three steps from $CpRe(CO)_3$ and its spectroscopic and structural features will be summarized. The reactivity of this carbene with a variety of electron-rich alkenes, including enamines, dienes and aryl-substituted alkenes, will be described.

17. Development and Application of Homochiral Magnesium Reagents

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Recently, we have embarked upon preliminary investigations into the utility of enantiomerically pure Mg bisamide species, $(R_2N)_2Mg$, as potential reagents for asymmetric deprotonation reactions. Our initial investigations have involved the use of the readily accessible and structurally very simple homochiral base, bis(*N*-benzyl- α -methylbenzylamido)magnesium **1** as a benchmark reagent to judge against the known selectivity of the Li analogues. Reactions with a series of 4-substituted cyclic ketonic substrates have shown enantioselectivity in the range 87:13 - 95:5 e.r.



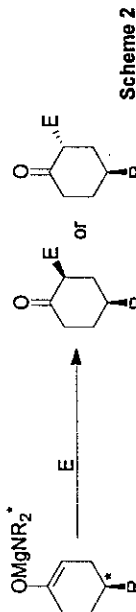
(Scheme 1).

It is worth noting that the general enantioselection displayed by the use of our novel Mg system is appreciably higher than the equivalent Li-based process (e.g., 75:5:24:5 e.r. for **2d**). Furthermore, by changing the ketone to *cis*-di-isopropylcyclohexanone we have been able to achieve the highest asymmetric induction yet observed for such an enantioselective deprotonation reaction, >99:5:0:5 e.r.

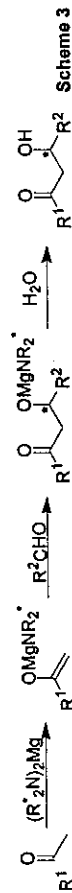
Following these initial results we are now extending these novel protocols in asymmetric addition reactions.

Addition of Electrophiles to In Situ Prepared Chiral Complexes

The chiral enolates prepared using our Mg-based enantioselective deprotonation strategy may be reacted with various electrophiles to yield numerous functionalized products. Scheme 2 shows the addition of an electrophile, to an *in situ* prepared chiral Mg enolate. Importantly, this creates an additional new stereogenic center, and in our case, the selectivity of this reaction will be influenced not only by the chiral center of the enolate but also by the *chiral amide attached to the metal*. Therefore, within this program our asymmetric strategies will be extended to establish conditions for the stereoselective reaction of our optically enriched Mg enolates with a range of electrophiles in order to create two stereogenic centers in a single practical process.



Yet another clear advantage to having a covalently bound chiral directing group is that this opens up the possibility of inducing asymmetry in addition reactions involving *achiral* enolates. For example, aldol reactions of enolates derived from methyl ketones will be influenced by the presence of a chiral group on the metal center (Scheme 3). In this respect, we have recently demonstrated that Mg bisamides can mediate the aldol addition reactions under kinetic conditions. This discovery will be further studied in an asymmetric sense to produce optically-enriched β -hydroxy ketones.



Lunch in Lafortune Hall

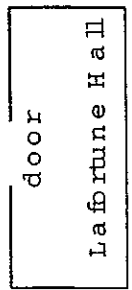
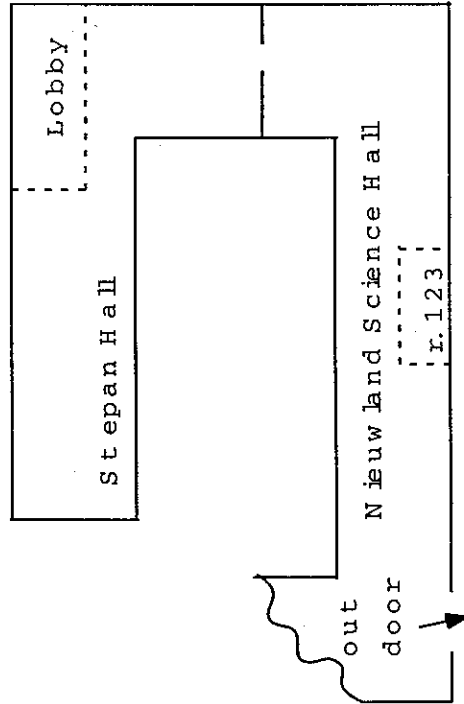
Resources:

- 1st floor
- *Burger King*
- *iBuen Provecho!* – burritos, nachos, tacos, taco salads, fajitas
- *Subway*
- *Starbucks coffee*

Basement floor

- *Sbarro* – pizza, pasta, heroes, wings

Advantages: very close, TVs, Internet connection



Directions for lunch off campus

From the parking turn left onto the street. On the STOP turn left onto Bulla Road. Turn right at the 1st light, Juniper Road. After that take a left at the 2nd light, Douglas Road. On the next light take a right, US-31-BR/US-33 (aka S. DIXIE WAY). That is the street with the restaurants.

On the US-31 the restaurants are as follow: On your left side – *Perkins*, *Denny's*, light cross section, *Taco Bell*. On your right side – *Wendy's*, "*Great Wall*"-chinese restaurant, *Bob Evans*, *Pizza King*, light cross section, - 2nd light cross section, *Mikado- Japanese steakhouse*. After the 3rd light cross section you can find more restaurants on the both sides as *Arbys*, *Pizza Hut*, *Burger King* ...

