40th Inorganic Discussion Weekend

Book of Abstracts

and

Official Program

Welcome to the 40th Inorganic Discussion Weekend!

The Department of Chemistry at the University of Toronto is delighted to host the 40th annual Inorganic Discussion Weekend from Nov. 2nd- Nov. 4th, 2007. The Chemistry Department is located at 80 St George St., Toronto.

IDW 2007 – Schedule

Friday, November 2nd

19:00 - 22:30 Registration, Mixer and Posters (Davenport Atrium, Chem. Dept.)

Saturday, November 3rd (MORNING)

8:00 - 15:20 Registration (Lash Miller, Chem. Dept.)

8:30 - 8:40 Introductions and Welcome (Lash Miller, rooms 159 and 162)

8:40 - 10:20 Oral Presentations (Lash Miller, rooms 159 and 162)

10:20 - 10:40 *DIMA GLASS* Coffee Break (Lash Miller Lobby)

10:40 - 12:00 Oral Presentations (Lash Miller, rooms 159 and 162)

Saturday, November 3rd (AFTERNOON)

12:00 - 13:40 Lunch

13:40 - 15:00 Oral Presentations (Lash Miller, rooms 159 and 162)

15:00 - 15:20 *Strem Chemicals* Coffee Break (Lash Miller Lobby)

15:30 - 16:20 Dalton Pharma Services Plenary Lecture: Prof. Thomas Rauchfuss
(Bahen Centre, room 1160)
"Iron Carbonyl Comes to Life: Inorganic Chemistry and the Hydrogenase Enzymes."

16:20-16:30 Summation and Break

16:30 - 19:30 *Sigma-Aldrich* Poster Session (Lash Miller Lobby and Davenport Atrium)
  16:40 -17:40: Presenters of even-numbered posters stay with their posters
  17:40-18:40: Presenters of odd-numbered posters stay with their posters

20:00 - 22:30 *Bruker Spectrospin* Banquet (Bright Pearl Restaurant, 346 Spadina Ave., see map)

Sunday, November 4th (MORNING)

8:00 - 9:00 Registration (Lash Miller Lobby)

8:30 - 8:40 Introductions (Lash Miller, room 159)

8:40 - 10:20 Oral Presentations (Lash Miller, rooms 159 and 162)

10:20 - 10:40 *MBraun* Coffee Break (Lash Miller Lobby)

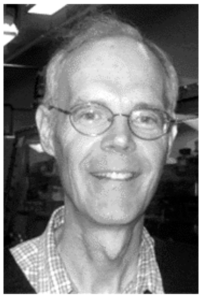
10:40 - 11:20 Oral Presentations (Lash Miller, rooms 159 and 162)

11:25 - 12:15 40th IDW Plenary Lecture: Prof. Geoffrey Ozin (Lash Miller room 159)
“P-Ink and Elast-Ink Lab to Market”

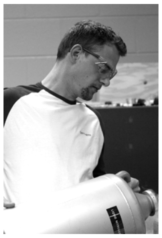
12:15 - 12:45 Summation/Awards (Lash Miller room 159)

Organizing Committee and Helpers

Conference Chair: Prof. Robert H. Morris



Program: Prof. Ulrich Fekl, graduate students Daniel J. Harrison and Anthonio G. De Crisci,



Social activities: Prof. Datong Song and student helpers

Organizing Judging: Prof. Douglas W. Stephan, Dr Douglas McIntosh

Fundraising:
Prof. Vy Dong, Robert H. Morris,
Ulrich Fekl, Datong Song

Conference secretary: Nina Lee

Finance: Maggie Cameron

Chemistry Chair: Professor Scott Mabury

Chemistry office: Penny Ashcroft Moore

And our <u>many volunteers</u>, UofT Inorganic Chemistry Graduate Students and Postdoctoral fellows.

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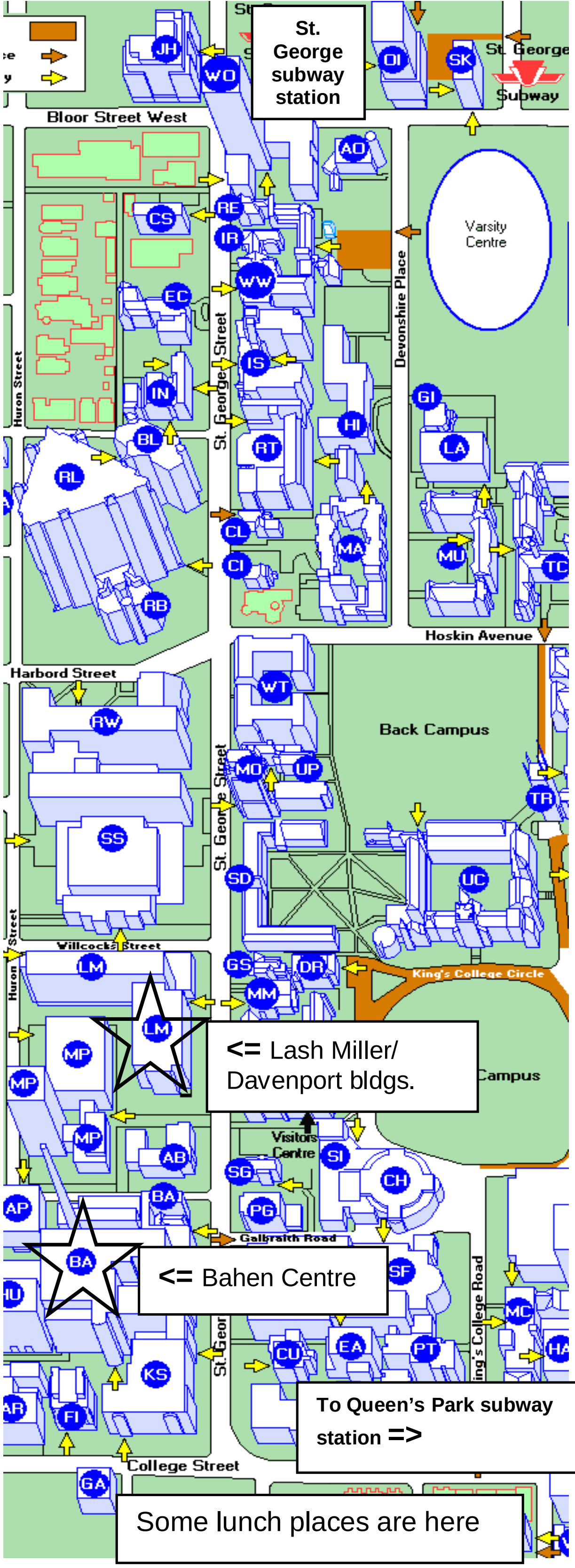
- **The Department of Chemistry, University of Toronto**
- **The Faculty of Arts and Sciences, University of Toronto**
- **Inorganic Chemistry Division, Canadian Society for Chemistry**

Partial University of Toronto Map



St. George subway station

<= Lash Miller/ Davenport bldgs.

<= Bahen Centre

To Queen's Park subway station =>

Some lunch places are here

Registration: Lash Miller/Davenport (80 St. George Street)

Mixer: Lash Miller/Davenport

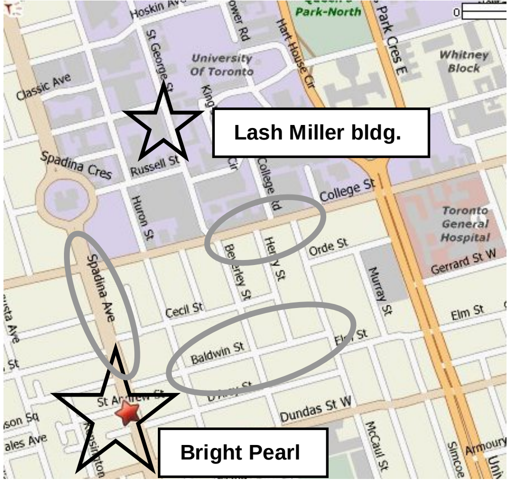
Poster Session: Lash Miller/ Davenport

Talks (except Rauchfuss Plenary Lecture): Lash Miller/ Davenport

Rauchfuss Plenary Lecture: Bahen Centre room 1160 (40 St. George Street)

Summation/Awards: Lash Miller LM159

Banquet: Bright Pearl Restaurant (346 Spadina Avenue, see map below)



Lash Miller bldg.

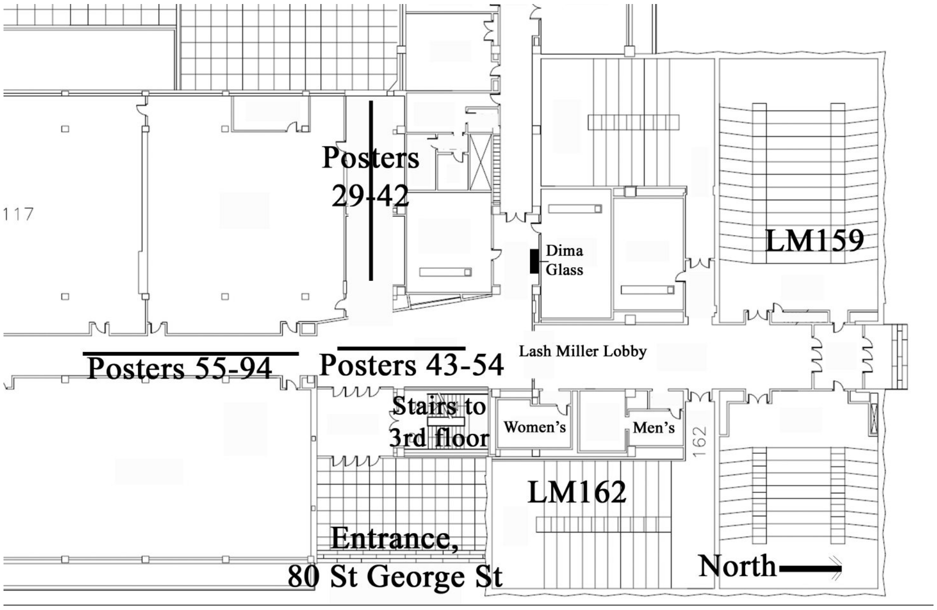
Bright Pearl

A variety of lunch options (pubs/restaurants, etc.) can be found on College Street, Spadine Avenue south of College St., as well as on Baldwin St, see areas inclosed in grey ellipses above:

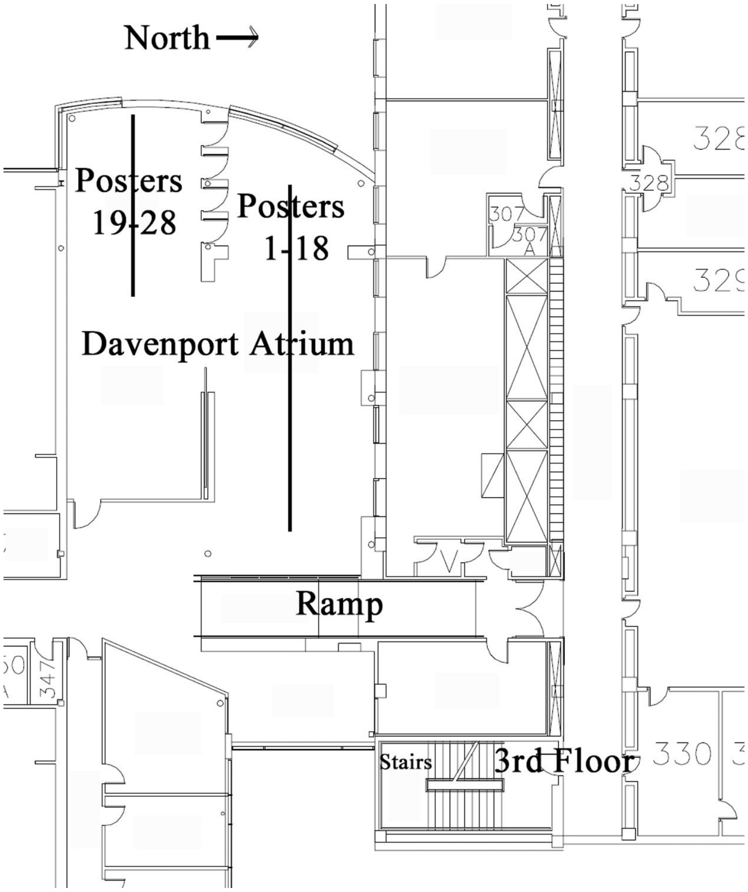
The subway stations nearest to campus are St. George station (near top of map) and Queen's Park station (East on College, not shown on map)

Floor Plan for Poster Space (All in 80 St. George St.)

A) Lash Miller Labs, Ground Floor Lobby



B) Davenport Atrium (3rd Floor. Easily accessed via the 3rd floor of the Lash Miller Building)



Scientific Program

Saturday

Session 1 (Lash Miller room 159)

Talks 1-5: Chemistry of Lanthanides and Early Transition Metals

8:30 – 8:40 Opening Remarks

8:40 – 9:00 T01 **Synthesis and Reactivity of *f*-Block Complexes with Hemi-Labile p-bonding Ligands**
Ilia Korobkov and Sandro Gambarotta
Department of Chemistry, University of Ottawa

9:00 – 9:20 T02 **Rapid probing of reactions at metal centers using MALDI-TOF mass spectrometry**
Nduka Ikpo and Francesca M. Kerton
Department of Chemistry, Memorial University

9:20 – 9:40 T03 **CEST properties of lanthanide(III) macrocyclic complexes with hydroxyl proton exchangeable sites**
Ching-Hui Huang and Janet R. Morrow
Department of Chemistry, University of Buffalo

9:40 – 10:00 T04 **Novel Tantalum(V) Boronate Clusters Exhibiting a Lewis Acid Cavity**
Christian N. Garon and Frédéric-Georges Fontaine
Département de Chimie, Université Laval

10:00 – 10:20 T05 **Chiral Analogues of Titanocene Dichloride as Potential Anti-Tumour Agents**
Gregory D. Potter, Mike C. Baird and Susan P.C. Cole
Department of Chemistry, Queen's University; Cancer Research Laboratories, Queen's University

10:20 – 10:40 **Break**

Talks 6-9: Coordination Chemistry

10:40 – 11:00 T06 **Synthesis of cobalt dinitrogen complexes and comparison to their iron analogues**
Keying Ding and Patrick L. Holland
Department of Chemistry, University of Rochester

11:00 – 11:20 T07 **Ligand-Centered Alkene Reactivity of Metal Bis- and Trisdithiolenes**
Daniel J. Harrison, Alan J. Lough, Neilson Nguyen, and Ulrich Fekl
Department of Chemistry, University of Toronto at Mississauga; University of Toronto, X-Ray Crystallography Lab

11:20 – 11:40 T08 **Aspects of Ruthenium Benzoquinone Chemistry**
Christopher Dares, Daria Kalinina, Julia Krainova, A. B. P. Lever, and Pierre G. Potvin
Department of Chemistry, York University

11:40 – 12:00 T09 **Electrocatalytic Reduction of CO_2: Preparation, Coordination Chemistry and Complex Properties**
Tharsini Manivannan, S. Hawa, K. Davis, Pierre G. Potvin, A. B. P. Lever
Department of Chemistry, York University

12:00 – 13:40 **Lunch**

Talks 10-13: New Main Group Molecules and New Phosphorous Donors

13:40 – 14:00 T10 **Main Group Catalyzed Hydrogenations Utilizing H_2**
Preston A. Chase, Gregory C. Welch, Titel Jurca and Douglas W. Stephan
Department of Chemistry and Biochemistry, University of Windsor

14:00 – 14:20 T11 **Towards the development of new indolylphosphines: reactivity at N1 and C7 of indole**
M. T. C. Ang, J. O. Yu, A. Mulani, C. S. Browning and D. H. Farrar
Department of Chemistry, University of Toronto

14:20 – 14:40 T12 ***N*-Heterocyclic Phosphenium Cations: Synthesis, Group 10 Metal Complexes and Reactivity Studies**
Christine A. Caputo, Jacqulyn T. Price, Michael C. Jennings, Robert McDonald and Nathan D. Jones
Department of Chemistry, University of Western Ontario; University of Alberta

14:40 – 15:00 T13 **A New Convenient Approach to Low Oxidation State Phosphorus Compounds**
Erin L Norton and Charles L. B. Macdonald
Department of Chemistry and Biochemistry, University of Windsor

15:00 – 15:20 **Break**

Session 2 (Lash Miller room 162)

Talks 14-18: Fluorescence and Photophysics

8:30 – 8:40 Opening Remarks

8:40 – 9:00 T14 **Organometallic-Pigment Dyads and Triads: Model Compounds for Photonic Polymers**
Diana Bellows and Pierre D. Harvey
Département de chimie, Université de Sherbrooke

9:00 – 9:20 T15 **Fluorescent N^2-Guanosines as Metal Ion Sensing Probes**
Sanela Martić, Dr. Gang Wu and Dr. Suning Wang
Department of Chemistry, Queen's University

9:20 – 9:40 T16 **Ruthenium(II) Complexes of Carboxylated Tridentate Ligands**
Arta Stublla and Pierre G. Potvin
Department of Chemistry, York University

9:40 – 10:00 T17 **New hexametallic light-harvesting assembly based on a rhodium(II) tetraamidinate dimer**
Daniel Chartrand and Garry S. Hanan
Département de Chimie, Université de Montréal

10:00 – 10:20 T18 **Bright, Oxygen and Fluoride Sensitive Ambient Temperature Phosphorescence of Triarylboron-Containing Metal Complexes**
Shu-Bin Zhao and Suning Wang
Department of Chemistry, Queen's University

10:20 – 10:40 **Break**

Talks 19-22: Main Group Synthesis

10:40 – 11:00 T19 **Neutral and Cationic Carbene complexes of Germanium(II)**
Paul A. Rupar, Viktor N. Staroverov, Paul J. Ragogna and Kim M. Baines
Department of Chemistry, University of Western Ontario

11:00 – 11:20 T20 **Persistent silylium ions stabilized by polyagostic Si-H···Si interactions**
Andrey Yu. Khalimon, Zihua Lin, Razvan Simionescu, and Georgii I. Nikonov
Department of Chemistry, Brock University

11:20 – 11:40 T21 **Unprecedented Coordination Chemistry at an Electron Rich, Lewis Acidic Selenium Centre. A New Route to E à Se Bond Formation**
Jason L. Dutton and Paul J. Ragogna
Department of Chemistry, University of Western Ontario

11:40 – 12:00 T22 **Synthesis, Structure and Bulk Properties of a Selenium-Containing Family of Neutral Radical Conductors**
Craig M. Robertson, Alicea A. Leitch, Kristina Cvrkalj, Daniel J. T. Myles, Robert W. Reed, Paul A. Dube and Richard T. Oakley
Department of Chemistry, University of Waterloo; Brockhouse Institute for Materials Research, McMaster University

12:00 – 13:40 **Lunch**

Talks 23-26: Metal Clusters and Bioinorganic Chemistry

13:40 – 14:00 T23 **A Molecular Approach to Nanoscale Magnetic Materials: Design and Synthesis of Polynuclear Metal Complexes Using Oximate Ligands**
Thushan Pathmalingam, Terra Burchell, Anne-Catherine Bédard, André Beauchemin, Rodolphe Clérac and Muralee Murugesu
Department of Chemistry, University of Ottawa; CRPP-CNRS

14:00 – 14:20 T24 **Development of Precursors for Atomic Layer Deposition of Tin-doped Indium Oxide**
Matthew J. Ward, Glen P. A. Yap and Sean T. Barry
Department of Chemistry, Carleton University; Department of Chemistry and Biochemistry, University of Delaware

14:20 – 14:40 T25 **Synthesis of Trimethylsilylchalcogenolate complexes of Manganese(II) and Cobalt(II): Precursors to Ternary Nanoclusters**
Chhatra B. Khadka and John F. Corrigan
Department of Chemistry, University of Western Ontario

14:40 – 15:00 T26 **Development of platinum(II) luminescence-based probes for the investigation of aptamer folding**
Elyse D. Bernard and Maria C. DeRosa
Department of Chemistry, Carleton University

15:00 – 15:20 **Break**

Dalton Pharma Services Plenary Lecturer
Bahen Centre, room 1160

15:30 – 16:20 **Carbonyl Comes to Life: Inorganic Chemistry and the Hydrogenase Enzymes**

Professor Thomas Rauchfuss

University of Illinois

Poster Session
Lash Miller Lobby and Davenport Atrium

16:30 – 19:30 **Poster Session**
Please stand by your posters for the duration of judging

16:40 -17:40: Presenters of even-numbered posters stay with their posters
17:40-18:40: Presenters of odd-numbered posters stay with their posters

Please see below (after the abstracts for talks) for poster abstracts and numbering

Banquet
Bright Pearl Restaurant

19:30 – 20:00 **Break/walk to Banquet**

20:00 – 22:30 **Banquet**

Sunday

Session 1 (Lash Miller room 159)

Talks 27-31: Solid State NMR

8:30 – 8:40 Opening Remarks

8:40 – 9:00 T27 **Chlorine solid-state NMR and Computational Studies of Bioinorganic and Inorganic Systems**
Rebecca. P. Chapman, Miranda Boggild, and David L. Bryce
Department of Chemistry, University of Ottawa

9:00 – 9:20 T28 **Solid-state ^{35}Cl NMR Studies of Early Transition Metal Organometallic Complexes**
Aaron J. Rossini, Ryan W. Mills, Graham A. Briscoe, Erin L. Norton and Robert W. Schurko
Department of Chemistry and Biochemistry, University of Windsor

9:20 – 9:40 T29 **Probing the Local Structure of Ionic Liquid Salts with ^{35}Cl, ^{79}Br and ^{127}I Solid State NMR**
Peter G. Gordon, Darren H. Brouwer and John A. Ripmeester
Department of Chemistry, Carleton University; Steacie Institute for Molecular Sciences, National Research Council

9:40 – 10:00 T30 **Solid State NMR Studies with Fast Magic Angle Spinning of $LiFePO_4$**
Linda J. M. Davis amd Gillian R. Goward
Department of Chemistry, McMaster University

10:00 – 10:20 T31 **^{6,7}Li 2D Exchange NMR and ^{6}Li{^{31}P} REDOR to Study Lithium Ion Dynamics in Phosphates and Fluorophosphates for Cathode Materials**
Lindsay S. Cahill, Gillian R. Goward, Chris W. Kirby, Linda F. Nazar and Yasutoshi Iriyama
Department of Chemistry, McMaster University; University of Western Ontario; University of Waterloo

10:20 – 10:40 **Break**

Talks 32 and 33: Organometallics and New Instrumentation

10:40 – 11:00 T32 **High-throughput tools for optimization of tandem reactions and the development of reactivity profiles in olefin metathesis**
Johanna M. Blacquiere and Deryn E. Fogg
Department of Chemistry, University of Ottawa

11:00 – 11:20 T33 **The First [1]Ferroceniumphane: Synthesis, Structure, and Reactivity**
Georgeta Masson, Alan J. Lough and Ian Manners
Department of Chemistry, University of Toronto; School of Chemistry, University of Bristol

Session 2 (Lash Miller room 162)

Talks 34-38: Transition Metal Catalysis

8:30 – 8:40 Opening Remarks

8:40 – 9:00 T34 **Development of Ruthenium Based Ionic Hydrogenation Catalysts for the Selective Deoxygenation of Sugar Polyalcohols**
Kylie L. Luska and Marcel Schlaf
Department of Chemistry, McGill University; University of Guelph

9:00 – 9:20 T35 **Hydrogenation of Benzonitrile to Benzylamine Catalyzed by Ruthenium Hydride Complexes with P–NH–NH–P Tetradentate Ligands: Evidence for a Hydridic–Protonic Outer Sphere Mechanism**
Marco Zimmer-De Iuliis, Tianshu Li, Ines Bergner, F. Nipa Haque and Robert Morris
Department of Chemistry, University of Toronto

9:20 – 9:40 T36 **Ligand Promoted Carbene Insertion of Grubbs Ruthenium Carbene Complexes**
Brandon R. Galan, Jerome B. Keister and Steven T. Diver
Department of Chemistry, University of Buffalo

9:40 – 10:00 T37 **Competition studies of vinyl arenes in cationic rhodium-catalyzed hydroboration systems**
Christopher J. Lata, David R. Edwards and Cathleen M. Crudden
Department of Chemistry, Queen's University

10:00 – 10:20 T38 **Synthesis, characterization and electrochemical studies of novel POCN Pincer type complexes of Ni**
Denis M. Spasyuk, Davit Zargarian
Département de Chimie, Université de Montréal

10:20 – 10:40 **Break**

Talks 39 and 40: Computational Organometallic Chemistry

10:40 – 11:00 T39 **Metal-metal bonds. Believe none of what you hear and a half of what you see**
Serge I. Gorelsky and Sougandi Ilango
Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa

11:00 – 11:20 T40 **Simulating the Dynamics of Catalytic Reactions: Transition Path Sampling in Organometallic Chemistry**
Christopher N. Rowley and Tom. K. Woo
Department of Chemistry, University of Ottawa

40th IDW Plenary Lecture
Lash Miller room 159

11:25 – 12:15 **P-Ink and Elast-Ink Lab-to-Market**

Professor Geoffrey Ozin
University of Toronto

Summation and Awards
Lash Miller room 159

12:15 – 12:45 Summation and Awards

Plenary Lecture Sponsor: Dalton Pharma Services

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We thank Dalton Pharma Services for generously supporting the IDW.

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IDW2007 Dalton Pharma Services Plenary Lecturer: Professor Thomas B. Rauchfuss

Department of Chemistry, University of Illinois, Urbana, IL, 61801, USA, E-mail: rauchfuz@uiuc.edu

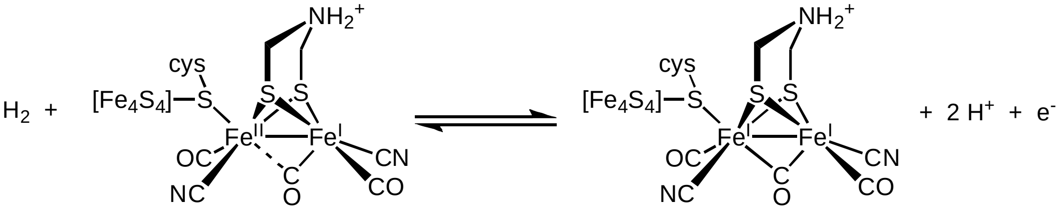
Thomas. B. Rauchfuss, Professor of Chemistry: Professor Rauchfuss received his undergraduate degree from the University of Puget Sound (1971) and his Ph.D. from Washington State University (1976). He has studied overseas at the following institutions: the Australian National University, University of Auckland, University of Strasbourg, and the Technical University of Karlsruhe. He is interested in all aspects of the synthesis and reactivity of inorganic, organometallic, and main-group compounds and materials.

Awards and Honors:
- ACS Award in Inorganic Chemistry
- Fellow, Japan Society for the Promotion of Science
- Humboldt Foundation Senior Scientist
- Guggenheim Fellowship
- University of Illinois Scholar
- Alfred P. Sloan Fellowship
- Dreyfus Teacher-Scholar Award
- Union Carbide Innovative Recognition Award
- DuPont Young Professor Award

Iron Carbonyl Comes to Life: Inorganic Chemistry and the Hydrogenase Enzymes

The growing concerns about energy and the environment has led to intense interest in bio-inspired processing of energy feedstocks. Nature indeed has evolved elaborate systems for the processing of H_2, a fundamental component of our energy future. The three known classes of hydrogenases feature $Fe(CO)_x$ centers at their active sites, but are phylogenetically distinct proteins. This striking example of convergent evolution indicates that the Fe-H-CO system merits special scrutiny, because Nature chose it three times.

The [FeFe]-hydrogenases are highly efficient catalysts for the reduction of protons to H_2. The active site exists in two functional states (see Scheme below), one of which is $S = 0$, and the other is $S = 1/2$. This lecture will survey recent studies that provide insights into the mechanisms of the enzymatic catalysis as elucidated though synthetic analogues, molecules that resemble to varying degrees, the functional states of the active site.



Themes to be reviewed include mechanisms of hydrogen production, the role of the second coordination sphere imposed through the dithiolate cofactor, and the nature of the mixed valence state in the catalytic cycle.

Leading references:

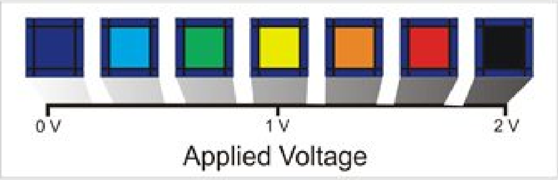
van der Vlugt, J. I.; Rauchfuss, T. B.; Whaley, C. M.; Wilson, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 16012-16013.
Justice, A. K.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 6152-6154
Linck, R. C.; Rauchfuss, T. B. In “Bioorganometallics: Biomolecules, Labeling, Medicine”; Jaouen, G., Ed.; Wiley-VCH: Weinheim, 2005.

40th IDW Plenary Lecturer: Professor Geoffrey Ozin

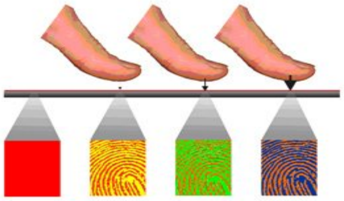
Materials Chemistry Research Group and Opalux Inc, Center for Inorganic and Polymeric Nanomaterials, Chemistry Department, 80 St. George St., University of Toronto, Toronto, Ontario, Canada M5S3H6

Geoffrey Ozin studied at King's College London and Oriel College Oxford University, before completing an ICI Postdoctoral Fellowship at Southampton University. Currently he is the Tier 1 Canada Research Chair in Materials Chemistry, Distinguished University Professor at the University of Toronto, and a Founding Fellow of the Nanoscience Team at the Canadian Institute for Advanced Research. Internationally he is an Honorary Professor at The Royal Institution Great Britain and University College London, External Advisor for the London Centre for Nanotechnology, Alexander von Humboldt Senor Scientist at the Max Planck Institute for Surface and Colloid Science Potsdam, and Guest Professor at the Centre for Functional Nanostructures at Karlsruhe Institute of Technology (KIT). Over a four decade career he has made important scientific and technological advances in Nanochemistry, which have help shape the course of Nanotechnology. He has made benchmark discoveries in the emerging fields of Nanomaterials, Nanoporous Materials and Photonic Crystals.

P-Ink and Elast-Ink Lab to Market



A notable trend these days amongst academics, especially in the fields of information technology, biotechnology and nanotechnology, is the increasing tendency to transfer the fruits of their research into the marketplace. Nowhere is this more apparent than in the globally burgeoning and highly competitive area of nanotechnology. Particularly interesting is the large number of spin-off companies now emerging from universities all racing to develop, manufacture and commercialize nanotechnology based on the potential of a cornucopia of new nanomaterials in diverse areas from electronics to photonics, biometrics to cancer therapy. In this lecture I will present a personal account of some of our recent research in the area of photonic crystals that has evolved over the last ten years from a laboratory curiosity to two new nanotechnology platforms, affectionately called P-Ink and Elast-Ink. These nanotechnology platforms are both founded on active color tuning of opals, a capability that provides electrical and mechanical access to materials with any visible color you want, including the invisible ultraviolet and near infrared wavelength range. P-Ink is made of a metallopolymer opal gel that reversibly swells and shrinks with application and removal of a voltage. Elast-Ink is made of an elastomeric opal that undergoes reversible dimensional changes on applying and removing a mechanical force. P-Ink and Elast-Ink actively tuned opals show considerable promise for the development of a new generation of full color display, energy saving surface coatings and biometric security systems.



Talks 1- 5: Chemistry of Lanthanides and Early Transition Metals

T01, Session 1	8:40 Saturday	Lash Miller room 159

Synthesis and Reactivity of *f*-Block Complexes with Hemi-Labile p-bonding Ligands.

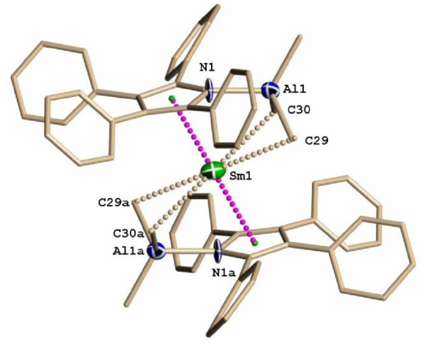
Korobkov, I.[a], Gambarotta, S[a].
[a] *Department of Chemistry, University of Ottawa, Ottawa, ON. K1N 6N5. korobkov@uottawa.ca, Sandro.Gambarotta@uottawa.ca*

Concept of utilization of hemi-labile ligands to generate organometallic catalysts has been a topic of much interest in recent years. While there have been several important breakthroughs in the chemistry of transition metals, chemistry of f-block elements remains relatively unexplored, yet promising.

In our research project we are currently exploring the possibility of using a series of oxygen and nitrogen based anionic ligands to achieve hemi-labile ligand coordination. Such a coordination mode is obtained by introducing a highly Lewis acidic center into the molecule with consequent formation of a zwitter-ionic structure. Hemi-lability of the ligand system provides sufficient stability without quenching the reactivity of the metal center. Formation of the precursors and their subsequent reaction with Lewis acid appears to be a winning strategy to isolate compounds with low-valent metal centers.

Utilization of this approach in chemistry of f-block elements leads to the formation of compounds with unusual reactivity patterns of the metal center.

The presentation will highlight several new, low-valent f-block complexes and discuss the most exciting examples of their reactivity.

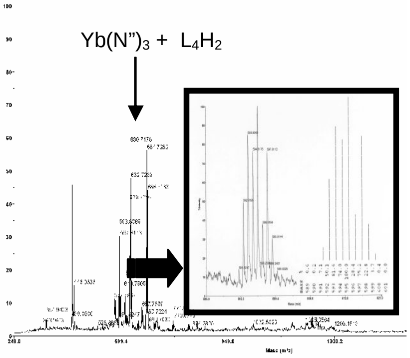


T02, Session 1	9:00 Saturday	Lash Miller room 159

Rapid probing of reactions at metal centers using MALDI-TOF mass spectrometry. Nduka Ikpo., Francesca M. Kerton, *Department of Chemistry, Memorial University of Newfoundland,St. John's NL, A1B 3X7.* induka@mun.ca, fkerton@mun.ca

The screening of metal-ligand reactions in catalyst development is very important, in order to be certain that the desired complexes have been obtained. Often, catalytically active complexes are not easily isolated and are produced *in situ*. NMR spectroscopy is a powerful technique used to analyze the structures of such complexes in solution. However, NMR is not as useful when applied to paramagnetic compounds. MALDI-TOF mass spectrometry (MS) has been developed and used to analyze macromolecules and rapidly probe the binding affinity of small molecules at enzyme active sites.[1] We reasoned it could be used as a fast technique for the determination of ligand coordination with lanthanide and other paramagnetic metal centers. This presentation will show how MALDI-TOF MS can be used for rapid screening in the synthesis of water-sensitive paramagnetic organometallic compounds.[2] Unexpected reactions occurring within the mass spectrometer, such as arene-adduct formation, will also be discussed.

Ref. (1) Webb M. E.; Stephens, E.; Smith, A. G.; Abell, C. *Chem. Commun*., **2003**, 24164. (2) Ikpo, N.; Collins, K. L.; Kerton, F.M. *Chem.Commun*., submitted B715214K



T03, Session 1	9:20 Saturday	Lash Miller room 159

CEST properties of lanthanide(III) macrocyclic complexes with hydroxyl proton exchangeable sites. Ching-Hui Huang and Janet R. Morrow Professor *Department of Chemistry, University of Buffalo, Amherst, NY. 14260*

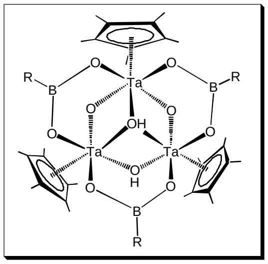
Chemical exchange saturation transfer (CEST) has been proposed as a new type of magnetic resonance imaging technique to provide contrast with agents possessing sites which exchange protons with the surrounding water environment. Recently we reported the CEST properties of a Eu(III) complex which possesses five magnetically inequivalent hydroxyl proton exchangeable sites at low water concentration(1). In order to understand the CEST properties of the same type of hydroxyl proton exchangeable agents, the symmetrical ligand THED (1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane) complexed with different lanthanide metal ions was studied. The ^{1}H NMR spectra of these complexes showed nine magnetically inequivalent proton peaks with only one proton exchangeable site observed in CEST spectra at low water concentrations. The CEST effect was observed when these complexes were dissolved in dry d_3-acetonitrile and up to 5% water for the Eu(III) complex. However, the hydroxyl peak of $[Yb(THED)]^{3+}$ was no longer observed in ^{1}H NMR upon addition of only 1% of water to d_3-acetonitrile. These results indicated that the CEST effect of complexes with the hydroxyl proton exchangeable sites is not only affected by the fast proton exchange rate in the presence of small concentrations of water, but also by the pK_a of the hydroxyl groups of the complex. Thus the selection of the lanthanide ions and the structure of the ligand are essential for the CEST agents with the hydroxyl proton sites.

Ref. (1) Woods, M.; Woessner, D. E.; Zhao, P. Y.; Pasha, A.; Yang, M. Y.; Huang, C. H.; Vasalitiy, O.; Morrow, J. R.; Sherry, A. D. *J. Am. Chem. Soc.* **2006**, *128*, 10155-10162.

T04, Session 1	9:40 Saturday	Lash Miller room 159

Novel Tantalum(V) Boronate Clusters Exhibiting a Lewis Acid Cavity.

Christian N. Garon and Frédéric-Georges Fontaine. *Département de Chimie, Université Laval, Québec, Qc, G1V 0A6.* christian-n.garon.1@ulaval.ca, frederic.fontaine@chm.ulaval.ca



We recently reported the synthesis of boronate tantalum clusters having a unique supramolecular structure.[1] Some of these novel complexes feature a Lewis acid type cavity allowing for substrate binding in both the solid and liquid state using a unique type of dual interaction with a Lewis acid and a hydrogen bond. The ease of synthesis and the commercial availability of precursors allow for great versatility in fine-tuning the shape of the cavity to suit one's needs. Several novel supramolecules featuring the interesting Ta-O-B fragment have been synthesized and characterized by NMR and X-ray diffraction, and the steric and electronic effects on the boronate ligands have been investigated. The physical properties of the interaction between our cages and different substrates have been studied and evidence of a strong interaction is observed. Some of these complexes also exhibit a certain potential in hosting highly reactive species such as $\mathrm{AlMe_2}$.

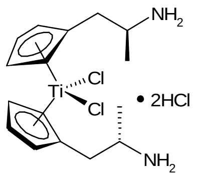
(1) Sigouin, O.; Garon, C. N.; Delaunais, G.; Fontaine, F.-G. *Angew. Chem. Int. Ed.*, **2007**, *119*, 5067-5070.

T05, Session 1	10:00 Saturday	Lash Miller room 159

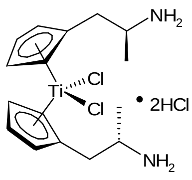
Chiral Analogues of Titanocene Dichloride as Potential Anti-Tumour Agents.

Gregory D. Potter,[a] Mike C. Baird,[a] Susan P.C. Cole.[b]
[a]*Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.* [b] *Cancer Research Laboratories, Botterell Hall, Queen's University, Kingston, Ont. K7L 3N6.* potterg@chem.queensu.ca, bairdmc@chem.queensu.ca

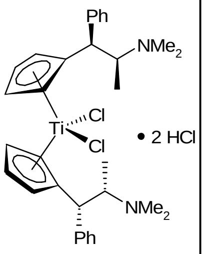
Although *cis*-$\mathrm{PtCl_2(NH_3)_2}$ (cisplatin) has been widely used as a chemotherapeutic agent, its use can be accompanied by toxic side effects and the development of drug resistance. Consequently, much research has been focused on the discovery of novel transition metal compounds which produce elevated cytotoxicities coupled with reduced toxic side effects and non-cross resistance. Recently, research in our lab has focused on preparing titanocene dichloride (TDC) derivatives, a highly active chemotherapeutic agent, with pendant alkylammonium groups on one or both rings. Our earlier results have demonstrated that derivatives containing either cyclic or chiral alkylammonium groups had increased cytotoxic activities; we are therefore investigating a new series of TDC derivatives bearing chiral alkylammonium groups. We have systemically prepared enantiomerically pure titanocene dichloride derivatives (two examples (S,S)-**1** and (R,R)-**R** are shown) in an effort to determine if cytotoxic activity is dependent on chirality. We have also prepared a derivative bearing an ephedrine group (**2**). The cell lines used include A549 and H209, representing both standard candidates for which new drugs exist and cell lines for which new drugs are urgently needed.



(S,S)-**1**



(R,R)-**1**



2

Talks 6-9: Coordination Chemistry

T06, Session 1	10:40 Saturday	Lash Miller room 159

Synthesis of cobalt dinitrogen complexes and comparison to their iron analogues

Keying Ding, Patrick L. Holland *Department of Chemistry, University of Rochester, Rochester, NY 14627*

The development of late transition metal dinitrogen chemistry remains a challenging goal.[1] β-Diketiminate ligands ($\mathrm{L^{tBu}}$) stabilize a three-coordinate cobalt chloride complex ($\mathrm{L^{tBu}CoCl}$), which can be reduced by potassium to give cobalt dinitrogen complexes $\mathrm{L^{tBu}CoNNCoL^{tBu}}$ and $\mathrm{K_2L^{tBu}CoNNCoL^{tBu}}$. Both of these species were crystallographically characterized, and the structures show similarities and differences when compared to their iron analogues.[2] The mixed-metal compound $\mathrm{L^{tBu}FeNNCoL^{tBu}}$, which is a rare example of a heterometallic dinitrogen complex, is also accessible. In contrast to the iron system, it was possible to synthesize cobalt-dinitrogen complexes directly from hydride sources. Treating $\mathrm{L^{tBu}CoCl}$ with 2 equiv of $\mathrm{KBEt_3H}$ under $\mathrm{N_2}$ cleanly gave $\mathrm{K_2L^{tBu}CoNNCoL^{tBu}}$. Reaction of $\mathrm{L^{tBu}CoCl}$ with 1 equiv of $\mathrm{KBEt_3H}$ under argon gave impure, metastable samples from which crystals of $\mathrm{[L^{tBu}CoH]_2}$ could be isolated. This dimeric cobalt-hydride complex reacts with $\mathrm{N_2}$ to give $\mathrm{L^{tBu}CoNNCoL^{tBu}}$.

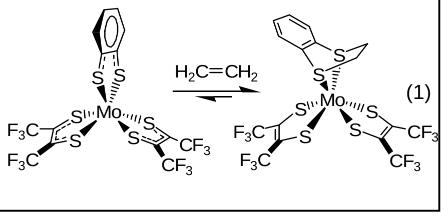
(1) M. P. Shaver et al., *Adv. Synth. Catal.* **2003**, *345*, 1061.
(2) J. M. Smith et al., *J.Am.Chem.Soc.* **2006**, *128*, 756

T07, Session 1	11:00 Saturday	Lash Miller room 159

Ligand-Centered Alkene Reactivity of Metal Bis- and Trisdithiolenes.

Daniel J. Harrison,[a] Alan J. Lough,[b] Neilson Nguyen,[a] and Ulrich Fekl.[a] [a]*Department of Chemistry, University of Toronto at Mississauga, Ont. L5L 1C6.* [b]*Department of Chemistry, University of Toronto, X-Ray Crystallography Lab, Ont. M5S 3H6.*

Certain nickel bisdithiolenes ($Ni(S_2C_2R_2)_2$) react with alkenes at the ligand sulfur atoms, rather than at the metal center. Interligand alkene addition to sulfur centers of nickel bisdithiolenes gives stable alkene adducts. Electrochemical reduction of interligand adducts releases the dithiolene-bound alkene and affords a reduced form of the metal complex, which may be oxidized to regenerate the neutral species. It has been proposed that such an electrochemical cycle might be useful for purifying alkenes.[1] However, we showed that the addition of simple alkenes to $Ni(S_2C_2(CF_3)_2)_2$ proceeds, preferentially, in an intraligand fashion, forming free dihydrodithiins and decomposed metal dithiolene species, unless monoanionic $[Ni(S_2C_2(CF_3)_2)_2]^-$ is present. The monoanion reverses the product selectivity in favor for stable interligand adducts.[2] Recently, we have been investigating the reactions of ethylene with molybdenum *tris*dithiolenes. We discovered that "push-pull" molybdenum trisdithiolenes, with a combination of electron-withdrawing and electron-releasing dithiolene ligands (Mo(dithiolene)$_2$(dithiolene')) react rapidly with ethylene, in an intraligand fashion, affording isolable intraligand adducts (e.g., eq. 1). We have provided the first structurally characterized product of intraligand alkene addition to a metal bisdithiolene. The metal-bound dihydrodithiins can be displaced by a variety of donor ligands, allowing access to highly unsymmetrical new molybdenum dithiolenes. Finally, we demonstrated that ethylene addition to $Mo(S_2C_2(CF_3)_2)_2(S_2(C_6H_4))$ is reversible, such that ethylene is released from the metal trisdithiolene upon heating (eq. 1).[3]



(1)

Ref. (1) Wang, K.; Stiefel, E. I. *Science*, **2001**, *291*, 106.
Ref. (2) Harrison, D. J.; Nguyen, N.; Lough, A. J.; Fekl, U. *J. Am. Chem. Soc.* **2006**, *128*, 11026.
Ref. (3) Harrison, D. J.; Lough, A. J.; Nguyen, N.; Fekl, U. *Angew. Chem. Int. Ed.* **2007**, *46*, 7644.

T08, Session 1	11:20 Saturday	Lash Miller room 159

Aspects of Ruthenium Benzoquinone Chemistry.

Christopher Dares,[a] Daria Kalinina,[b] Julia Krainova,[c] A. B. P. Lever,*[d] and Pierre G. Potvin.*[e] *Department of Chemistry, York University, Toronto, Ont. M3J 1P3.* [a]**cdares@yorku.ca**, [b]**dkalinin@yorku.ca**, [c]**juliak@yorku.ca**, [d]**blever@yorku.ca**, [e]**pgpotvin@yorku.ca**

The successful syntheses of Ru(acac)$_2$**X**-bqdi (where *acac* = acetylacetonato ligand, and ***X**-bqdi* = benzoquinone diimine ligand with **X** = N-(SO_2CH_3) or **X** = N,N'-(SO_2CH_3)$_2$ have been confirmed by NMR, MS and FT-IR data. The large degree of covalent metal-bqdi mixing observed for these complexes gives rise to unique properties which were analyzed through the use of electronic, electrochemical and spectroelectrochemical methods. The data are interpreted in the context of metal-ligand mixing and are supported by molecular-orbital composition computations using both semi-empirical INDO/S and TD-DFT methods. Correlations between the substituents present and the extent of π-back-donation are also reported.

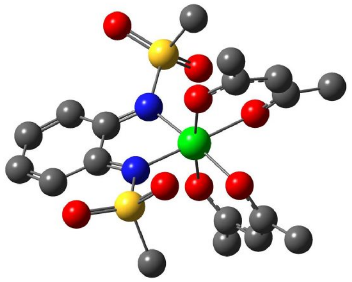


Figure 1. Ru(acac)$_2$((SO_2Me)$_2$-bqdi). Hydrogen atoms have been omitted for clarity.

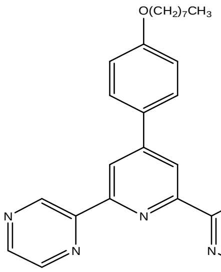
Ref. (1); Rusanova, J.; Rusanov, E.; Gorelsky, S. I.; Christendat, D.; Popescu, R.; Farah, A. A.; Beaulac, R.; Reber, C.; Lever, A. B. P. *Inorg. Chem.*, **2006**, *45*, 6246. (2) Krainova, J.; Lever, A. B. P. Proceedings of the 35th Southern Ontario Undergraduate Student Chemistry Conference, Oshawa, **2007** Abstract #062. (3) Kalinina, D.; Dares, C.; Kaluarachchi, H.; Lever, A. B. P.; Potvin, P. G., *Inorg. Chem.*, **2007** in preparation. (4) Kalinina, D.; Krainova, J.; Lever, A. B. P.; Potvin, P.G. *Inorg. Chem.*, **2008** in preparation.

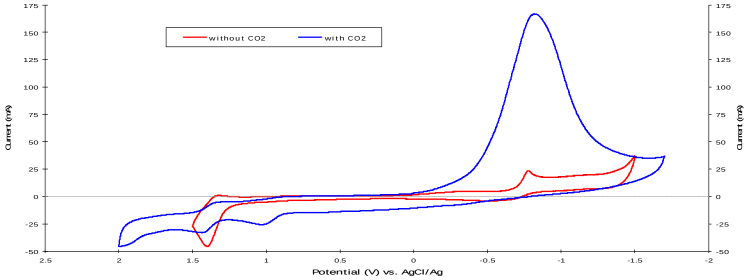
T09, Session 1	11:40 Saturday	Lash Miller room 159

Electrocatalytic Reduction of CO_2: Preparation, Coordination Chemistry and Complex Properties.

Tharsini Manivannan[a], S. Hawa, K. Davis, Pierre G. Potvin[b], A. B. P. Lever[c]. *Department of Chemistry, York University, 4700 Keele Street, Toronto, Ont. M3J 1P3.* [a]**ttharsi@yorku.ca**, [b]**pgpotvin@yorku.ca**, [c]**blever@yorku.ca**.

We have previously reported *trans/cis* isomeric complexes of **L**Ru(CO)Cl_2 (where **L** = 4-(4-octoxyphenyl)-2,6-di(2-pyrazinyl)pyridine). These have been fully characterized *via* FAB-MS, elemental analysis, and by ^{1}H-NMR, ^{13}C-NMR, ^{15}N-NMR, UV-visible and FT-IR spectroscopies. Cyclic voltammetry showed that the *trans* complex acts as an excellent electrocatalyst for CO_2 reduction. In this presentation, we discuss a possible mechanism for the reduction process, and introduce new variants of the catalyst, using new ligand designs. Details of the synthesis,characterization, and coordination chemistry of these new catalysts will be presented.

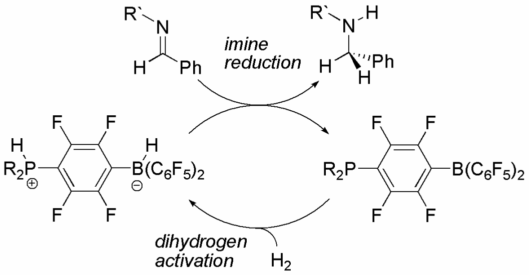




Talks 10-13: New Main Group Molecules and Exotic Phosphines

T10, Session 1	13:40 Saturday	Lash Miller room 159

Main Group Catalyzed Hydrogenations Utilizing H_2. Chase, Preston A.; Welch, Gregory C.; Jurca, Titel and Stephan, Douglas W. *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **pachase@uwindsor.ca**, stephan@uwindsor.ca



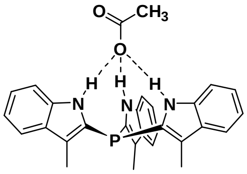
Hydrogenation is one of the most important reactions in the chemical industry and in synthesis.[1] In terms of atom economy, H_2 gas is the most desirable reducing source and is the cleanest. Transition metal catalysts, typically based on Pd, Pt or Rh, are the standard systems that can hydrogenate organic compounds utilizing H_2. While wildly successful, these metals are very expensive and can be quite toxic so alternatives are desired. We have recently shown that sterically "frustrated" Lewis pairs (FLPs) consisting of a bulky borane and phosphine that do not form a traditional adduct can heterolytically cleave H_2.[2] This is an exceptionally rare example of a well defined main-group system that reacts directly with H_2. The borohydride produced ($[HBAr^F_3]^-$) in this reaction is similar to the well known stoichiometric reducing agents $NaBH_4$ or $LiAlH_4$ and has been implicated in the hydrosilylation of ketones and imines.[3] Here, we will detail our efforts to employ these H_2-activating systems for the catalytic hydrogenation of a variety of organic substrates,[4] including ketones, imines and nitriles as well as in the reductive ring opening of aziridines.

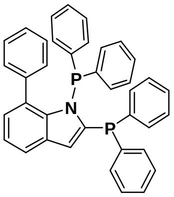
Ref. (1) Blasser, H.U.;*et al. Adv. Synth. Catal.* **2003**, *345*, 103. (2) Welch, G. C. *et al. Science*, **2006**, *314*, 1124; *J. Am. Chem. Soc.* **2007**, *129*, 1880. (3)ex. Parks, D.J. *et al. J. Am.Chem. Soc.* **1996,** *118*, 9440; Blackwell, J.M. *et al. Org. Lett.* **2000**, *2*, 3921. (4) Chase, P.A. *et al. Angew. Chem. Int. Ed.* **2007**, *46*, 8050.

T11, Session 1	14:00 Saturday	Lash Miller room 159

Towards the development of new indolylphosphines: reactivity at N1 and C7 of indole. M. T. C. Ang, J. O. Yu, A. Mulani, C. S. Browning, D. H. Farrar. *Davenport Chemical Research Building, Department of Chemistry, University of Toronto, Toronto, Ont. M5S 3H6.*

The well-developed synthetic routes to, and modifications of indole provide the opportunity to create indolylphosphines with potentially interesting and useful properties. For example, tris(3-methylindolyl)phosphine **1** has demonstrated the ability to act as an anion receptor in which the three NH moieties act as hydrogen bond donors to bind halides and other anions. Utilizing the reactivity at the N1 and C7 position of indole, developments toward the synthesis of more complex indolylphosphines such as the potentially atropisomeric P-P bidentate phosphine **2** will be discussed.



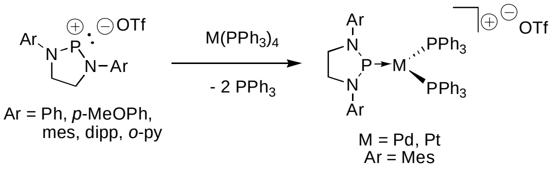


2

T12, Session 1	14:20 Saturday	Lash Miller room 159

N*-Heterocyclic Phosphenium Cations: Synthesis, Group 10 Metal Complexes and Reactivity Studies.** Christine A. Caputo,[a] Jacqulyn T. Price,[a] Michael C. Jennings,[a] Robert McDonald[b] and Nathan D. Jones[a] [a] *Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7* [b] *University of Alberta, Edmonton, Alta. T6G 2G2* ***ccaputo2@uwo.ca, njones26@uwo.ca.

N-Heterocyclic phosphenium cations (NHP) are two-coordinate, formally cationic species that are analogous to the now ubiquitous Arduengo-type carbenes (NHC). These species are isostructural, but electronically inverse: NHP are weak σ-donors and good π-acceptors, while NHC are strong σ-donors and weak π-acceptors. While the NHC class has been used with great success as a phosphine replacement ligand, the NHP class has been largely ignored (particularly in catalysis). Although a number of metal-NHP complexes (*e.g.*, of Mo, Fe, Co, Rh and Pt)[1-6] have been made, the onward reactivity of these compounds has not been investigated thoroughly.



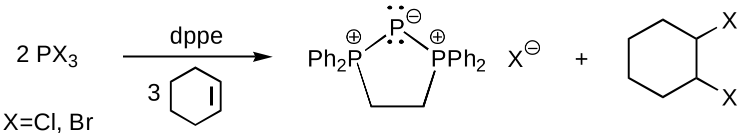
We have developed an improved and highly efficient route for the synthesis of a small library of NHP and some of their Pd(0) and Pt(0) complexes. The shown Pt compound has been made previously by Baker from $Pt(PPh_3)_3$.[5] The goal of this project is to uncover the hitherto unexplored reactivity of NHP-containing group 10 metal compounds with the general formula $[M(NHP)(PPh_3)_2]^+$. We are currently investigating the reactions of these complexes with small molecules, such as bidentate phosphine ligands, alkenes, alkyl halides, thiols, MeLi, H_2O, as well as CO and H_2. Progress in this area will be presented.

(1) Nakazawa, H., *J. Organomet. Chem.* **2000**, *611*, 349. (2) Cowley, A.H., Kemp, R.A. *Chem. Rev*. **1985**, *85*, 367. (3) Hutchins, L.D. *et. al. Inorg. Chem.* **1982**, *18*, 2345. (4) Abrams, M.B., *et. al. Organometallics* **2000**, *19*, 4944. (5) Spinney, H.A et. al. *Organometallics* **2006**, 25, 3541. (6) Hardman, N.J., *et. al. Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 1955.

T13, Session 1	14:40 Saturday	Lash Miller room 159

A New Convenient Approach to Low Oxidation State Phosphorus Compounds. Erin L Norton,[a] and Charles L. B. Macdonald[a]

[a]*Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **nortone@uwindsor.ca**, **cmacd@uwindsor.ca**



Synthetic methods to make low oxidation phosphorus compounds have made use of external reducing agents, such as SnCl$_2$, which ultimately leads to the formation of undesirable anions.[1] Recently, the iodide salts have become available through the disproportionation of PI$_3$ or P$_2$I$_4$ into "PI" fragments which are stabilized through coordination of dppe.[2] The high reactivity of X$_2$ (for X=Cl, Br) has hindered the isolation of other pure halide salts until now. Using a simple halogen-scavenging reagent, the reaction to generate the bromide salts (Eq. 1) proceeds in quantitative yields. The synthesis of the chloride salts are somewhat more complicated, however some salts are still accessible through this route. This methodology is presently being used to produce other new types of compounds containing low oxidation state main group elements.

[1] Ellis, B. D.; Macdonald, C. L. B. *Coord. Chem. Rev.* **2007**, *251*, 936-973.
[2] Ellis, B. D.; Macdonald, C. L. B. *Inorg. Chem.* **2006**, *45*, 6864-6874.

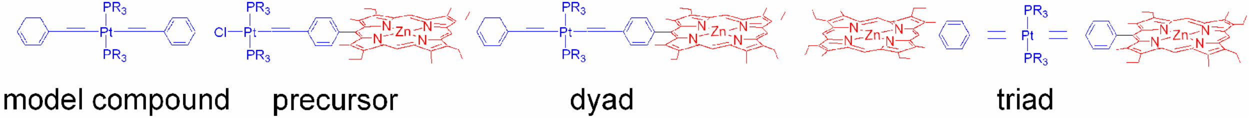
Talks 14-18: Fluorescence and Photophysics

T14, Session 2	8:40 Saturday	Lash Miller room 162

Organometallic-Pigment Dyads and Triads: Model Compounds for Photonic Polymers, Diana Bellows, Pierre D. Harvey

Département de chimie, Univesité de Sherbrooke, Sherbrooke, PQ, J1N 2X8. Pierre.Harvey@USherbrooke.ca

The quest for conjugated and luminescent materials potentially useful in photonic devices such as photovoltaic cells and light emitting diodes (LED) is ever increasing due to the obvious consequences on environment and energy savings. Target materials for white light emitters are currently investigated and the common strategy is the use of heavy metal-containing precursors in order to promote triplet state emission in addition to the fluorescence, hence covering a wide window of wavelengths. The incorporation of such heavy atom into a polymer backbone provides this property added to the common property of a plastic desired for industrial applications. In this respect, the long term objective of this research program is the design of organometallic polymers of the type (C$_6$H$_4$-C≡C-PtL$_2$-C≡C-C$_6$H$_4$-M(porph))$_n$ (L = PR$_3$ (R = Et, Bu); M = H$_2$, Zn; porph = porphyrin unit) where the organometallic fragments C$_6$H$_4$-C≡C-PtL$_2$-C≡C-C$_6$H$_4$ and the pigment porphyrin exhibit together fluorescence and phosphorescence ranging from 350 to 750 nm. This presentation focuses on the synthesis and characterization of the precursor Cl-PtL$_2$-C≡C-C$_6$H$_4$-Zn(porph), model compounds Ph-C≡C-PtL$_2$-C≡C-Ph and Zn(porph)-C$_6$H$_4$-C≡CH, the dyad Ph-C≡C-PtL$_2$-C≡C-C$_6$H$_4$-Zn(porph), and the triad Zn(porph)-C$_6$H$_4$-C≡C-PtL$_2$-C≡C-C$_6$H$_4$-M(porph). The electronic spectra and the photophysical parameters addressing the electronic communication between the organometallic residue and the Zn-containing pigment will be presented in the light of possible singlet and triplet energy transfer (Ph-C≡C-PtL$_2$-C≡C-Ph to Zn(porph)).

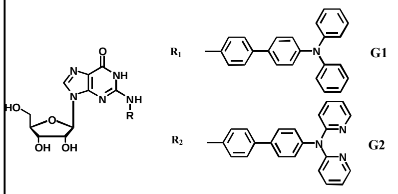


model compound precursor dyad triad

T15, Session 2	9:00 Saturday	Lash Miller room 162

Fluorescent N^2-Guanosines as Metal Ion Sensing Probes. Sanela Martić,[a] Dr. Gang Wu[a] and Dr. Suning Wang[a]

[a]*Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.*
martics@chem.queensu.ca



Fluorescent guanosines are potentially used as sensors due to their water solubility and biological relevance. While such biological probes are highly desirable, they are rare due to the challenges associated with the chemical modification when attaching fluorescent chromophores to guanine core. The arylation of exocyclic amine of guanosine is most challenging and it typically requires protection/ deprotection chemistry. We have now developed new synthetic methods that allow facile N^2-arylation. The new method is based on Ullmann condensation. Using this method we have synthesized and isolated several N^2-arylated guanosine derivatives (**G1** and **G2**) without any use of protecting groups on the ribose unit. These new fluorescent N^2-guanosines are bright blue emitters that are highly sensitive to Zn(II), Tb(III) and Eu(III) ions in aqueous or organic solutions. While guanosines are known to be ineffective Tb(III) activators, we have found that luminescent N^2-guanosines are efficient Tb(III) sensitizers. Our findings suggest that the chelating guanosine (**G2**) is a more effective sensing probe than its non-chelating analogue (**G1**). A facile and selective N^2-arylation synthesis was successfully used to fine tune the photoelectronic properties of guanosine analogues which exhibit remarkable and selective response to metal ions.

T16, Session 2	9:20 Saturday	Lash Miller room 162

Ruthenium(II) Complexes of Carboxylated Tridentate Ligands. Arta Stublla[a] and Pierre G. Potvin.[a]

[a]*Department of Chemistry, York University, 4700 Keele Street, Toronto, ON M3J 1P3***.**
arta@yorku.ca, pgpotvin@yorku.ca

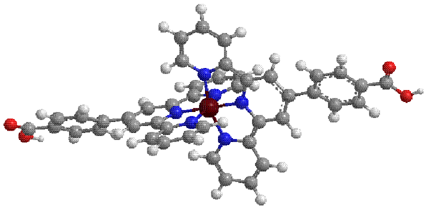


Figure 1.** DFT-computed structure of a photovoltaic dye.**

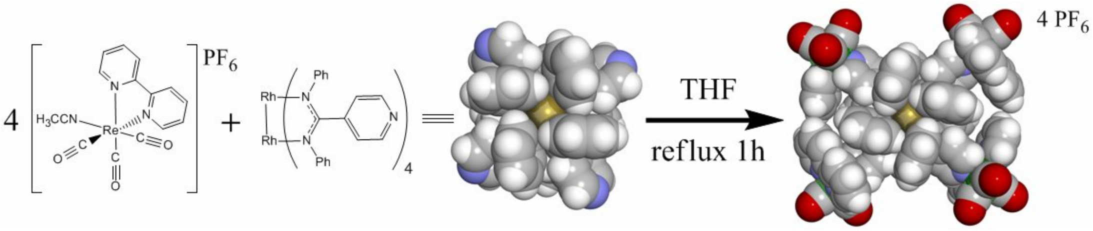
Dye-sensitized solar cells (DSSCs) have emerged as promising and inexpensive alternatives to solid-state silicon devices, where light is directly converted into electrical energy. This development exemplifies chemists' ability to design, prepare and manipulate Ru^{II} polypyridine complexes in order to understand fundamental photochemistry and address practical problems, such as the production of clean and renewable energy. Among the Ru^{II} chromophores employed in photoactive devices, particularly attractive are tridentate ligands, as the $[RuL_2]^{2+}$ unit is achiral when substituted at the 4′ positions, and appropriate substitution there can usefully enhance the luminescent metal-to-ligand charge transfer (MLCT) excited state lifetime. Carboxyl groups are most often used to anchor the dyes on photovoltaic anatase (TiO_2) surfaces, and will influence the dye's photophysical and electrochemical properties. In this talk, we will present the preparation and characterization of a systematically designed family of homoleptic Ru^{II} complexes of new carboxylated tridentate ligands, and their direct application in DSSCs.

T17, Session 2	9:40 Saturday	Lash Miller room 162

New hexametallic light-harvesting assembly based on a rhodium(II) tetraamidinate dimer. Daniel Chartrand and Garry S. Hanan.

Départment de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7. **daniel.chartrand.1@umontreal.ca**, garry.hanan@umontreal.ca

In our general objective of forming assemblies of chromophoric units for photocatalysis, the rhodium dimers, with their paddlewheel motif, offer an excellent structural backbone for polynuclear assemblies. It has already been shown that a carboxylate group can be used to attach chromophores to the metal dimers, however, the inherent lability of these ligands can cause ligand scrambling.[1] Using an amidine ligand, N,N'-diphenyl-isonicotamidine, the tetra amidinate metal dimer formed is much more resilient to ligand scrambling and can be bonded to other metals, under mild conditions, through the free pyridyl moiety of the ligand. Here a rhodium(II) dimer bonded to four rhenium(I) chromophores formed a new hexametallic light-harvesting assembly and was characterized by X-ray crystallography, UV-vis spectroscopy and electrochemistry.



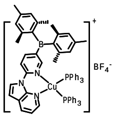
Ref. (1) M. W. Cooke, G. S. Hanan, F. Loiseau, S. Campagna, M. Watanabe and Y. Tanaka*, J. Am. Chem. Soc.*, **2007**, 129, 10479.

T18, Session 2	10:00 Saturday	Lash Miller room 162

Bright, Oxygen and Fluoride Sensitive Ambient Temperature Phosphorescence of Triarylboron-Containing Metal Complexes.

Shu-Bin Zhao, and Suning Wang. *Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.*

Triarylboron-containing metal complexes are a class of compounds with versatile applications in the areas of catalysis, luminescent lighting and colorimetric anion sensing (H^-, OH^-, F^- and CN^-), which when combined with phosphorescence become especially attractive as bifunctional electron transport-phosphorescent emitters in high efficiency OLEDs as well as potential sensors for triplet state oxygen. Despite the great potentials and the increasing number of examples of boron-containing metal complexes in recent literature, phosphorescent metal complexes that contain a triarylboron group remain elusive. In search of bright phosphorescent emitters with a triarylboron functional group, we have developed a new ligand system (Bnpa). In sharp contrast to their 5,5'-B2bipy analogues, we have found that Cu(I) (**1**) and Pt(II) (**2a**) complexes of Bnpa display bright room temperature phosphorescence with an unprecedented high emission quantum yield (88%) for the Cu(I) in the solid state. The phosphorescence of these complexes is highly sensitive toward molecular oxygen and has distinct response to fluorides. For **1** the fluoride ion causes phosphorescent quenching and Bnpa dissociation, whereas for **2a** it switches phosphorescent color from yellow to green. The detail of our investigation will be discussed.



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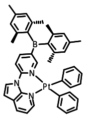
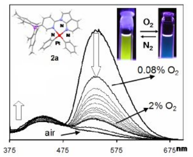


2a



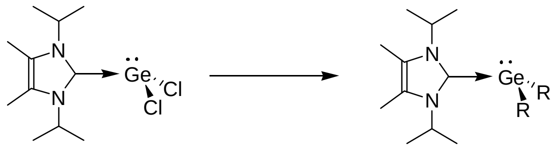
Talks 19-22: Main Group Synthesis

T19, Session 2	10:40 Saturday	Lash Miller room 162

Neutral and Cationic Carbene complexes of Germanium(II)

Paul A. Rupar, Viktor N. Staroverov, Paul J. Ragogna and Kim M. Baines *Department of Chemistry, University of Western Ontario, London, Ont.* parupar@uwo.ca, kbaines2@uwo.ca

N-Heterocyclic carbenes (NHC) are strong Lewis donors that readily form complexes with Lewis acidic metal centres. Recently, we demonstrated that an NHC can stabilize an otherwise transient diorganogermanium(II) species by donating electron density into the empty p-orbital on Ge.[1] Currently, we are studying NHC-GeX_2 complexes (where X = halogen)[2] as precursors to more complex carbene-germylene systems. We now report that the halogens can be displaced by nucleophiles resulting in numerous novel germylenes. The synthesis, structural characterization and reactivity of both neutral and cationic carbene complexes of germanium(II) will be discussed.



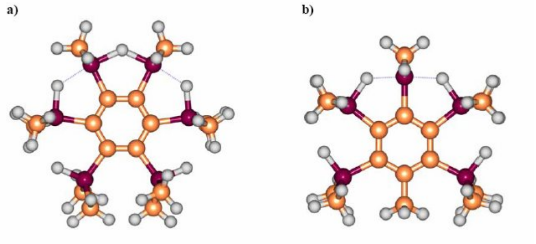
(1) Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M. *Organometallics* **2007**, *26*, 4109
(2) Arduengo, A. J., III; Dia, V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541

T20, Session 2	11:00 Saturday	Lash Miller room 162

Persistent silylium ions stabilized by polyagostic Si-H···Si interactions.

Andrey Yu. Khalimon, Zihua Lin, Razvan Simionescu, and Georgii I. Nikonov. *Department of Chemistry, Brock University, 500 Glenridge Ave., St. Catharines, Ont. L2S 3A1.* ak06ty@brocku.ca, gnikonov@brocku.ca

Herein we report the case of polyagostic Si-H-Si interactions in the series of silylium ions derived from polysilyl-substituted benzenes and their study with spectroscopic methods (NMR, IR) and DFT calculations. Hydride abstraction[1] from $C_6(SiHMe_2)_6$ by $[Ph_3C][B(C_6F_5)_4]$ generates the silylium ion **1**. NMR studies showed that compound **1** is highly fluxional at room temperature but at -80 °C exhibits a symmetric structure with a 3c-2e Si-H-Si bond supported by two additional Si←H-Si agostic interactions. Methyl-substituted analog **2** prepared by reacting persilylated toluene $MeC_6(SiHMe_2)_5$ with $[Ph_3C][B(C_6F_5)_4]$ is temperature-independent down to -80 °C. Cation **2** is stabilized by two Si-H bond coordinations to the cationic silicon centre. Silylium ions **1** and **2** present the first examples of a compound in which two Si-H bonds serve as ligands to a hypervalent silicon center. Or, if an alternative view is adopted, the structures **1** and **2** exhibit multiple agostic interactions induced by the silylium ion.[2]



a) DFT-calculated structure of agostically stabilized silylium ion 1. b) DFT-calculated structure of agostically stabilized silylium ion 2.

Ref. (1) Lambert J.B., Zhao Y. *Angew. Chem. Int. Ed. Engl.,* **1997**, *36*, 400; (2) Khalimon A.Yu., Lin Z., Simionescu R., Nikonov G.I. *Angew. Chem. Int. Ed.,* **2007**, *46*, 4530.

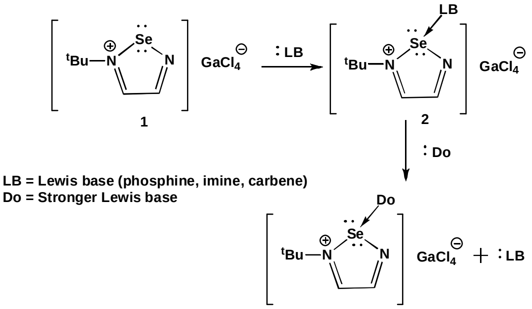
T21, Session 2	11:20 Saturday	Lash Miller room 162

Unprecedented Coordination Chemistry at an Electron Rich, Lewis Acidic Selenium Centre. A New Route to E à Se Bond Formation

Jason L. Dutton and Paul J. Ragogna *Department of Chemistry, The* University *of* Western Ontario, jldutton@uwo.ca

Investigation of the coordination chemistry for heavier (n > 2) Group 16 compounds is exceeding difficult, due to the propensity of these chalcogen molecules to participate in REDOX reactions in the presence of Lewis bases. A lack of suitable chalcogen starting materials, which are resistant towards reduction, has historically been the limiting factor. In this context, we have developed an electron rich, cationic Se-N heterocycle, where the Se centre is formally in the +2 oxidation state, and highly unsusceptible to further reduction (**1**). This has allowed for the synthesis and comprehensive characterization of the first true coordination complexes of selenium (*e. g.* **2**). The coordinative bonding model is confirmed by ligand exchange reactions at Se. A variety of neutral two electron donors (phosphines, imines, carbenes) may be used, and the resulting complexes represent a novel method of selenium-heteroatom bond formation, adding to the main group "toolbox" of synthetic methodologies.

Representative references (1) Dutton, J.L. Tabeshi, R. Lough, A. J. Jennings, M. C. Ragogna, P. J. *Inorg. Chem.* **2007**, 8594-8602.
(2) Dutton, J. L. Tindale J. T. Jennings, M. C. Ragogna, P. J. *Chem. Commun.* **2006**, 2474-2476.



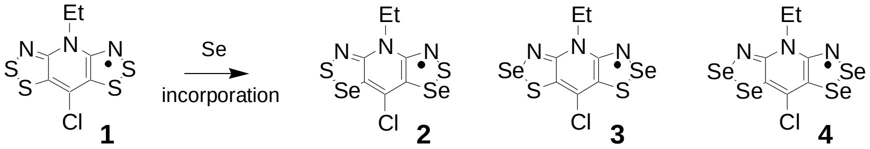
T22, Session 2	11:40 Saturday	Lash Miller room 162

Synthesis, Structure and Bulk Properties of a Selenium-Containing Family of Neutral Radical Conductors.

Craig M. Robertson,[a] Alicea A. Leitch,[a] Kristina Cvrkalj,[a] Daniel J. T. Myles,[a] Robert W. Reed,[a] Paul A. Dube[b] and Richard T. Oakley.[a] [a]*Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1.* [b]*Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ont. L8S 4M1*. cmrobert@uwaterloo.ca, oakley@uwaterloo.ca

Single component, non-metal containing molecular compounds displaying both conductive and magnetic properties in the solid state hold great potential for the development of spintronic materials. The basic electronic requirement for such molecules is the availability of at least one unpaired electron that can serve as both charge carrier and magnetic coupler. In principle, these criteria could be met by molecular radicals; however, there are limited numbers of materials displaying either property, let alone both.

In this paper we report the synthesis, structure, and bulk properties of a selenium-containing radical family based on the dithiazolyl framework **1**. This family demonstrates a rich diversity of magnetic properties, including spin canting (**2**) and ferromagnetism (**3**[1] & **4**); improved electrical conductivities (up to 3 orders of magnitude) in the solid state have also been observed upon Se incorporation.



Ref. (1) Robertson, C. M., Myles, D. J. T., Leitch, A. A., Reed, R. W., Dooley, B. M., Frank, N. L., Dube, P. A., Thompson L. K., Oakley, R. T. *J. Am Chem. Soc.,* **2007**, *129*, 12688 - 12689.

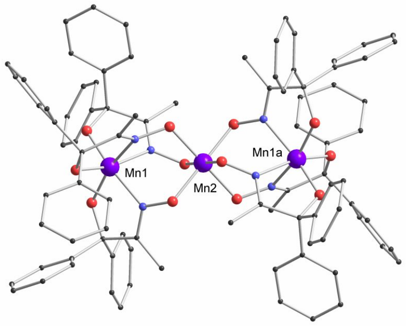
Talks 23-26: Metal Clusters and Bioinorganic Chemistry

T23, Session 2	13:40 Saturday	Lash Miller room 162

A Molecular Approach to Nanoscale Magnetic Materials: Design and Synthesis of Polynuclear Metal Complexes Using Oximate Ligands.

Thushan Pathmalingam.[a] Terra Burchell,[a] Anne-Catherine Bédard,[a] André Beauchemin,[a] Rodolphe Clérac,[b] and Muralee Murugesu,[a] *Department of Chemistry, 10 Marie Curie,University of Ottawa, Ottawa, ON, K1N 6N5.* [b]*CRPP-CNRS 8641, 115 Ave. du Dr. A. Schweitzer, 33600 Pessac, France.* tpath063@uottawa.ca, m.murugesu@uottawa.ca

Over the past few decades there has been great research emphasis put into the synthesis of manganese cluster complexes mainly due to the potential applications it holds for the near future, such as molecular electronic storage devices (Single Molecule Magnets) and remodeling of enyzmes. The greatest challenge in this field is designing the appropriate ligand systems, which has the optimum capability to bridge and interact between metal centers to produce magnetically interesting complexes. What is even more challenging is modifying the ligand system and studying the effect of variation through structure activity relationship. Herein we report, the use of tridentate oximate ligands which provide a great control and tunability in the design of polynuclear maganse complexs. A series of Mn cluster compexes has been obtained using aforementionned ligand system, amoung which, a rare species of a trinuclear manganese complex is reported here to contain high oxidation state (Mn^{IV}_3), ferromagnetically coupled to yield a high spin ground state (S= 9/2).



$[Mn^{IV}_3(dpo)_6(CH_3CN)_3]$

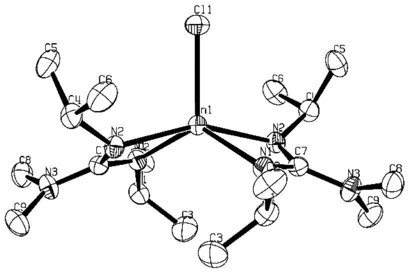
T24, Session 2	14:00 Saturday	Lash Miller room 162

Development of Precursors for Atomic Layer Deposition of Tin-doped Indium Oxide.

Matthew J. Ward,[a] Glen P. A. Yap,[b] Sean T. Barry[a] [a]*Department of Chemistry, Carleton University, Ottawa, Ont. K1S 5B6.* [b]*Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, USA 19716.* mward3@connect.carleton.ca, sbarry@ccs.carleton.ca.

Tin-doped indium oxide is an important transparent conductor for photovoltaic cells and other optics applications. Deposition of ITO by ALD will enable the formation of very thin and conformal films of this material, and increase the application of ITO in photoelectric systems.

Our interest in group 13 guanidinate chemistry has recently led to the synthesis and characterization of monochloro-bis-n,n-dimethylamide-n,n’-diisopropyl indium guanidinate and tris-n,n-dimethylamide-n,n’-diisopropyl indium guanidinate, which might have potential as vapour precursors for the deposition of indium oxide, the first step in developing an ITO deposition process. The compounds also highlight the ligand exchange synthetic route that our group has exploited for aluminum and gallium. Interestingly the monochloro-bis-dimethylamide indium guanidinate exhibits a square planar geometry of its guanidinate ligands, unlike the aluminum and gallium analogues, which exhibit trigonal bipyramidal geometries.



T25, Session 2	14:20 Saturday	Lash Miller room 162

Synthesis of Trimethylsilylchalcogenolate complexes of Manganese(II) and Cobalt(II): Precursors to Ternary Nanoclusters.
Chhatra B. Khadka and John F. Corrigan*, *Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7.*

The demonstrated ability of metal-trimethylsilylchalcogenolate complexes to be used as precursors for the controlled assembly of ternary cluster and nanocluster[1] complexes has prompted us to expand this general synthetic route to include chalcogenolate complex containing paramagnetic metals that will allow for the assembly of nanoclusters with paramagnetic properties.

The precursor complexes $[Li(N,N'\text{-}tmeda)]_2$ $[(N,N'tmeda)Mn^{II}_5(ESiMe_3)_6 (E)_3]$ (E = S, **1a**; E= Se,**1b**), $[Li(N,N'\text{-}tmeda)]_2$ $[Mn^{II} (SSiMe_3)_4]$ **(2)** , $(N,N'tmeda)Co^{II} (ESiMe_3)_2$ (E=S, **3a**; E=Se, **3b**) and $(3,5\text{-}Me_2\text{-}C_5H_3N)_2$ Co^{II} $(ESiMe_3)_2$ (E=S, **4a**; E=Se, **4b**) have been synthesized and characterized by single-crystal X-ray diffraction. The utility of the manganese chalcogenolate complexes as a soluble source of "ME_n" units to access ternary MM'E nanoclustesr will be discussed.

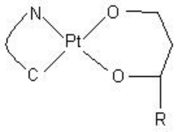
1) Degroot, M.W.; Corrigan, J. F. *Z. Anorg. Allg. Chem.* **2006**, *632*, 19-29

T26, Session 2	14:40 Saturday	Lash Miller room 162

Development of platinum(II) luminescence-based probes for the investigation of aptamer folding. Elyse D. Bernard and Maria C. DeRosa. *Department of Chemistry, Carleton University, Ottawa, Ont. K1S 5B6.*

Aptamers are single-stranded nucleic acids that act like antibodies by binding with high affinity and specificity to a target molecule. Aptamers have the advantages of being uniformly synthesized and having increased stability in comparison to antibodies making them attractive building blocks for use in sensors. The high affinity of DNA and RNA aptamers for their target molecules is related to the conformations they attain upon folding. Current methods of determining aptamer conformations include NMR spectroscopy and X-ray crystallography. The manner of their folding is not yet understood, and the development of a relatively fast and simple technique to investigate this intrinsic property of aptamers could be useful in the development of aptasensors.

When bound to aromatic ligands, square planar platinum(II) complexes (general structure shown below) have been found to exhibit excimer and monomer emission. The R group represents a functional group that will allow the complex to be attached to DNA aptamers. Through the attachment of two molecules of the complex at varying positions along an aptamer and the examination of emission spectra, information about aptamer folding could be determined. The development of such complexes for their use as aptamer structural probes will be discussed.



Talks 27-31: Solid State NMR

T27, Session 1	8:40 Sunday	Lash Miller room 159

Chlorine solid-state NMR and Computational Studies of Bioinorganic and Inorganic Systems. Rebecca. P. Chapman, Miranda Boggild, and David L. Bryce. *Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5* **bchap028@uottawa.ca**

Chlorine-35/37 solid-state nuclear magnetic resonance (SSNMR) is an underdeveloped field due to the less then ideal NMR properties of the two nuclei. However, the technique is ideal to examine the chlorine binding environment in a variety of materials as the NMR parameters are highly dependant on the local chlorine electronic and structural environment. In our research, Cl-35/37 SSNMR has been used to examine various amino acid hydrochloride salts, e.g., alanine, methionine and aspartic acid, which serve as bio-inorganic models of larger biologically relevant systems. Central transition chlorine NMR spectra of these salts acquired at two high fields, 11.75 T and 21.15 T, were used to determine the magnitude of the chlorine electric field gradient (EFG) and chemical shift (CS) tensors and their relative orientations. Analysis of the results, comparison with crystal structures and quantum chemical calculations provided insight into the effect of local electronic and structural environment at the chlorine nucleus on the chlorine NMR properties. In addition, preliminary results of Cl-35 SSNMR studies of the proposed ammine based hydrogen storage material, $MgCl_2(NH_3)_6$[1], will also be presented to further demonstrate the utility of chlorine SSNMR as means to study chlorine binding environments in a variety of inorganic and bio-inorganic materials.

1. Christensen, C.H et al. *J. Mater. Chem.* **2005**, *15*, 4106.

T28, Session 1	9:00 Sunday	Lash Miller room 159

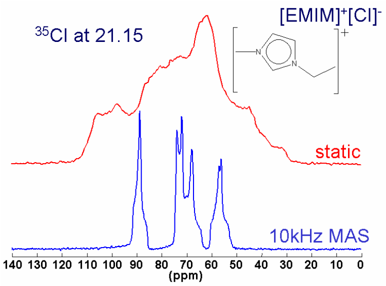
Solid-state ^{35}Cl NMR Studies of Early Transition Metal Organometallic Complexes. Aaron J. Rossini, Ryan W. Mills, Graham A. Briscoe, Erin L. Norton and Robert W. Schurko*. *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **rossini@uwindsor.ca**, *rschurko@uwindsor.ca

Metallocenes are a fascinating class of compounds with many applications in homogeneous and heterogeneous catalysis. Research in our group is focussed on the characterization of these compounds by solid-state nuclear magnetic resonance (SSNMR), quantum chemical calculations and X-ray diffraction techniques. Solid-state NMR spectra have previously been acquired for the metal nuclei that lie at the “heart” of metallocenes. Acquisition of SSNMR spectra of such nuclei can be challenging due to low natural abundance, low NMR (Larmor) frequencies, large quadrupolar interactions which give broad resonances, long acquisition times or any combination of the preceding factors. While SSNMR spectra of metal nuclei can be difficult to acquire, we have shown that they can act as very sensitive probes of molecular structure. It is well known that the ^{35}Cl SSNMR spectra of terminally bound chlorine atoms in most chemical systems are broadened to such a degree as to be spectroscopically invisible.[1] We have found that the ^{35}Cl SSNMR spectra of the terminal chloride ligands in metallocenes such as Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2 can be acquired at standard magnetic fields (9.4 T) with specialised pulse sequences. Complete ^{35}Cl NMR spectra of the complexes can be acquired in several hours at 9.4 T. The application of ultrahigh-magnetic fields (21.1 T) enables the acquisition of complete NMR spectra in several minutes. The NMR parameters obtained from ^{35}Cl SSNMR spectra are very sensitive to differences in the molecular structure of metallocene complexes. This holds much promise for the characterization of metallocene complexes that contain metal centres which are not amenable to direct observation via SSNMR. (1) Bryce, D.L; Sward, G.D.; *Magn.Reson. Chem.*,2006, *44*, 409.

T29, Session 1	9:20 Sunday	Lash Miller room 159

Probing the Local Structure of Ionic Liquid Salts with ^{35}Cl, ^{79}Br and ^{127}I Solid State NMR. Peter G. Gordon,[a] Darren H. Brouwer, [b] John A. Ripmeester.[b] [a]*Department of Chemistry, Carleton University, Ottawa, Ont. K1S 5B6.* [b]*Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ont. K1A 0R6.* **pgordon@connect.carleton.ca**, Darren.Brouwer@nrc.ca, John.Ripmeester@nrc.ca

Room Temperature Ionic liquids (RTILs) are organic salts with melting points under 100 °C. The organic cation lends itself to customization and as such RTILs are being designed to perform as solvents, reactants and catalysts. Applications are varied and increasing in number, including materials synthesis, biocatalysis, electrochemistry, and extraction. We propose to investigate the possibility of structure in the liquid state using quadrupolar nuclei as probes. Many RTILs have halide counterions (Cl, Br, I) as well as tetrafluoroborate, nitrate, perchlorate, etc. Several salts have been examined, indicating that spectra can indeed be obtained for bromide, iodide and chloride salts although at the lower fields it remains a challenge. Both quadrupolar and chemical shift parameters can be obtained. By correlating solid state and liquid spectra, we expect to be able to establish whether quadrupolar nuclei will be able to probe structure in RTILs, and if so, establish a knowledge base that will lead to an understanding of the local structure which may help inform the design of ionic liquids.



[1] H. Hamaguchi and R. Ozawa, *Adv. Chem. Phys.,* **2005**, 131, 85
[2] Bagno et al, *J. Phys. Chem. B*, **2006**, 110, 23004
[3] J. F. Huang, P-Y. Chen, I-W. Sun, S. P, Wang, *Spectr. Lett.* **2001**, 34 p. 591
[4] M. Deetlefs, C. Hardacre, M. Nieuwenhuizen, A. Padua, O. Sheppard and A. K. Soper, *J. Phys. Chem. B,* **2006**, 110, 12055

T30, Session 1	9:40 Sunday	Lash Miller room 159

Solid State NMR Studies with Fast Magic Angle Spinning of $LiFePO_4$. Linda J.M. Davis, Gillian R. Goward, *Department of Chemistry, McMaster University, Hamilton, Ont. L8S 4M1.*
goward@mcmaster.ca

The use of lithium ion batteries in portable electronic devices has been successful due to the higher energy density obtained relative to other energy sources. $LiFePO_4$ is an inexpensive, environmentally benign alternative to the widely used $LiCoO_2$. Despite the high Li mobility seen in $LiFePO_4$, the insulating effect of the phosphate groups lowers the working capacity significantly. Many attempts have been made to improve electron conductivity including carbon coating the particles before electrochemically cycling (Herle, S., Nat. Mater., 2004). This not only improves contact between the particles but under high temperature conditions leads to carbothermal reduction of the surface phosphate groups to phosphides such as FeP and Fe_2P. Although this brings the working capacity very close to the theoretical capacity, ion-electron transport becomes significantly more complex thus making solid state NMR all the more useful as an elucidation technique. To date both the lithiated and delithiated form have been characterized using high resolution solid state NMR with ultra-fast MAS. In the $LiFePO_4$, a single ^{7}Li and ^{31}P environment was observed at -11 ppm and 3076 ppm, respectively. The delithiated form, $FePO_4$, also showed a single ^{31}P resonance at 5648 ppm.

T31, Session 1	10:00 Sunday	Lash Miller room 159

^{6,7}Li 2D Exchange NMR and ^{6}Li{^{31}P} REDOR to Study Lithium Ion Dynamics in Phosphates and Fluorophosphates for Cathode Materials. Lindsay S. Cahill,[a] Gillian R. Goward, [a] Chris W. Kirby,[b] Linda F. Nazar,[c] and Yasutoshi Iriyama.[c] [a]*Department of Chemistry, McMaster University, Hamilton, Ont. L8S 4M1.* [b] *Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7.* [c] *Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1* **cahillls@mcmaster.ca**

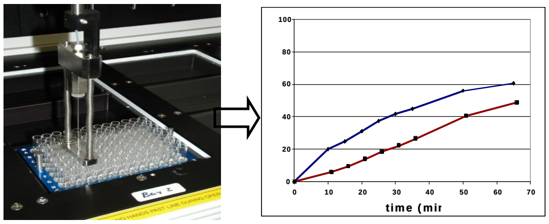
In the search for a new generation of cathode materials for lithium ion batteries, a growing family of transition metal-based phosphates and fluorophosphates has shown much promise.[1] Insight into the conduction mechanism of lithium ions within these solid-state materials is essential to the search for new materials and to make improvements to the current ones. ^{6,7}Li solid-state NMR spectroscopy was used to compare monoclinic $Li_3V_2(PO_4)_3$, $LiMPO_4$ (M = Fe, Co, Mn) and $Li_5M(PO_4)_2F_2$ (M = V, Al, Ga). $Li_3V_2(PO_4)_3$ has three well-resolved Li resonances while $Li_5V(PO_4)_2F_2$ has six crystallographic Li sites, clearly resolved by ^{6}Li NMR under MAS = 40 kHz. Using 2D Exchange Spectroscopy (EXSY), ionic mobility is probed between lithium sites and the timescale for ion hopping is determined.[2] Complementing this site-to-site dynamics, low temperature ^{6}Li{^{31}P} REDOR were performed. Strong attenuation of the Li-P dipolar coupling, relative to the value predicted from the crystallographic internuclear distances, is observed. This characterizes mobility of each lithium ion in a site-specific fashion, within the cage before Li hops to its next site. Electrochemically cycled samples from various points during the charge/discharge profile were also investigated. This allows determination of the order in which Li ions are extracted and what structural changes are observed, manifest by changes in chemical shift.

1. Nazar et al., Chem. Mater., 2006, 18, 1745.
2. Cahill et al., J. Phys. Chem. B, 2006, 110, 7171.

Talks 32 and 33: Organometallics and New Instrumentation

T32, Session 1	10:40 Sunday	Lash Miller room 159

High-throughput tools for optimization of tandem reactions and the development of reactivity profiles in olefin metathesis. Johanna M. Blacquiere and Deryn E. Fogg. *Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* **jblac042@uottawa.ca**, dfogg@uottawa.ca



In recent years, high-throughput (HT) methodologies have achieved great prominence as a tool for drug discovery in both industrial and academic programs.[1] Powerful methods for large-scale screening and data processing greatly reduced the timescale of exploratory investigations. More recently, this trend has extended into catalyst discovery and reaction optimization, initially in polyolefin catalysis.[2] Sophisticated HT tools from Symyx Technologies, recently acquired at the University of Ottawa, are opening up new opportunities in the application of HT methods to homogeneous catalyst discovery. Applications in the realm of ruthenium-catalyzed olefin metathesis will be described. HT experimentation frequently foreground issues of optimization, through exploration of a broader diversity of parameters than is realistically attainable using conventional benchtop methods. The power of these methods is showcased in the optimization of a tandem ring closing metathesis (RCM) -isomerization sequence. As well, however, we have been applying these powerful tools to “reaction profiling” to approximate in situ, real-time monitoring methods in large arrays. The demand of achieving rigorous, reproducible data introduces new challenges, a major one being the development of appropriate sampling or quenching techniques. Not only does HT optimization and reaction monitoring enable identification of the most active catalysts, but also, valuable mechanistic information can be attained.

Ref. (1) Eds. Czarnik, A.W., Ellman, J.A. *Acc. Chem. Res.* **1996**, *29*, 111-170. (2) Murphy, V. et al. *J. Am. Chem. Soc.* **2003**, *125*, 4306-4317.

T33, Session 1	11:00 Sunday	Lash Miller room 159

The First [1]Ferroceniumphane: Synthesis, Structure, and Reactivity. Georgeta Masson, [a] Alan J. Lough,[b] and Ian Manners[a,b] [a]*Department of Chemistry, University of Toronto, Toronto, Ont. M5S 3H6.* [b] *School of Chemistry, University of Bristol, Bristol BS8 1TS, England.* **gmasson@chem.utoronto.ca**, Ian.Manners@bristol.ac.uk

While the reversible one-electron oxidation of the ferrocene is well established and ferrocenium salts isolated as stable compounds,[1] very few example of strained ferrocenophanes with Fe(III) as metal center (ferroceniumphanes) have been reported to date. The only examples are [2]ferroceniumphanes with a saturated hydrocarbon *ansa* bridge.[2,3] Nevertheless, the 17-electron complex resulting upon removal of an electron from the iron center in a strained [1]ferrocenophane is still unknown. In this talk we report on the successful synthesis and characterization of the first stable [1]ferroceniumphane, $[Fe(\eta\text{-}C_5H_3R)_2SiR'_2]^+[SbF_6]^-$ obtained from oxidation of a sila-[1]ferocenophane with alkyl substituents on the Cp ligands. The reactivity and polymerization of the [1]ferroceniumphane is also described in the comparison to that of the Fe(II) ferrocenophane precursor, $[Fe(\eta\text{-}C_5H_3R)_2SiR'_2]$.

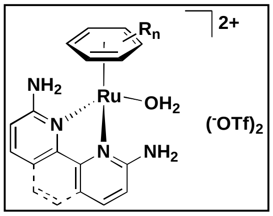
Ref. (1) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603. (2) Watanabe, M.; Sato, K; Motoyama, I.; Sano, H. *Chem. Lett.* **1983**, *11*, 1775; (3) Drewitt, M. J.; Barlow, S.; O'Hare, D.; Nelson, J. M.; Nguyen, P.; Manners, I. *Chem. Comm.* **1996**, *18*, 2153.

Talks 34-38: Transition Metal Catalysis

T34, Session 2	8:40 Sunday	Lash Miller

Development of Ruthenium Based Ionic Hydrogenation Catalysts for the Selective Deoxygenation of Sugar Polyalcohols. Kylie L. Luska [a] and Marcel Schlaf.[b] [a]*Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, QC, H3A 2K6.* [b]*Department of Chemistry, University of Guelph, 50 Stone Rd. E., Guelph, ON, N1G 2W1.* kylie.luska@mail.mcgill.ca, mschlaf@uoguelph.ca.

The syntheses of novel ruthenium based ionic hydrogenation procatalysts of the type [Ru(η^6-arene)(N∩N)(H_2O)](OTf)$_2$ have been achieved, where arene = p-MeC_6H_4Pr^i, C_6Me_6; N∩N = 2,9-diamino-1,10-phenanthroline, 6,6’-diamino-2,2’-bipyridine; and $^-$OTf = $^-OSO_2CF_3$. These complexes were synthesized to be employed as ionic hydrogenation catalysts for the selective deoxygenation of biomass derived sugar polyols. An attractive sugar polyol is glycerol, $HOCH_2CH(OH)CH_2OH$; a by-product created during the production of bio-Diesel. The selective deoxygenation of the secondary alcohol moiety of glycerol would form 1,3-propanediol; a useful value-added substrate employed in the production of the industrial plastic poly(propylene terephthalate).[1] The conversion of glycerol can be carried out in a single-pot through an acid-catalyzed dehydration to form 3-hydroxypropanal, followed by a metal-catalyzed hydrogenation of the resulting carbonyl moiety to form the desired 1,3-propanediol.[1] Catalysts employing 2,9-diamino-1,10-phenanthroline or 6,6’-diamino-2,2’-bipyridine as bidentate coordination ligands were postulated to be well-suited for the selective deoxygenation of sugar polyols as these complexes have the potential of performing hydrogenations through a ligand-metal bifunctional mechanism. Results on the catalytic deoxygenation of a model substrate, 1,2-hexanediol, the ultimate target substrate, glycerol, as well as on the capabilities and limitations of the catalyst system will be discussed .

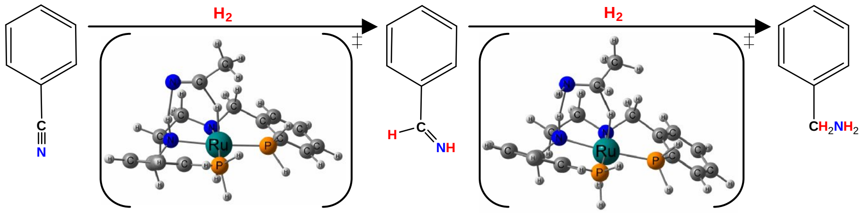


Ref. (1) Schlaf, M. *Dalton Trans.* **2006**, 4645, (2) Dykeman, R. R., Luska, K. L., Thibault, M. E., Jones, M. D., Schlaf* M., Khanfar, M., Taylor, N. J., Britten J. F. and Harrington L. .*J. Mol. Catal. A: Chem.,* in press.

T35, Session 2	9:00 Sunday	Lash Miller room 162

Hydrogenation of Benzonitrile to Benzylamine Catalyzed by Ruthenium Hydride Complexes with P–NH–NH–P Tetradentate Ligands: Evidence for a Hydridic–Protonic Outer Sphere Mechanism. Marco Zimmer-De Iuliis, Tianshu Li, Ines Bergner, F. Nipa Haque, and Robert Morris. *Department of Chemistry, University of Toronto, Toronto, Ont. M5S 3H6.*

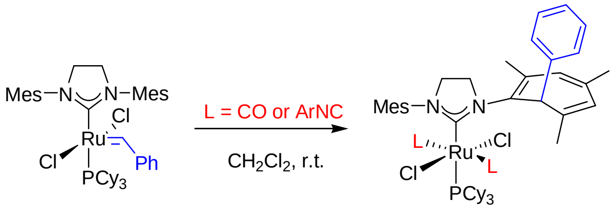
The reaction of RuHCl(PPh_3)$_3$ with the tetradentate ligand [PPh$_2$((*ortho*-C_6H_4)CH_2NHCH_2)]$_2$ {ethP$_2$(NH)$_2$} in THF produces the new complex *trans*-RuHCl{ethP2(NH)2} (**1**). Complex **1,** when activated with KOtBu/KH, is a very active catalyst for the hydrogenation of benzonitrile to benzylamine in toluene, more active than the known catalyst Ru(H_2)$_2H_2$(PCy_3)$_2$ (**2**). A mixture of **1** and **2** and base also results in efficient conversion of benzonitrile to benzylamine. The complex RuHCl{tmeP2(NH)2} (**3**) where tmeP2(NH)2 is [PPh$_2$((*ortho*-C_6H_4)CH_2NHCMe_2)]$_2$ is a less active catalyst for this reaction. These catalyst systems are air sensitive and extremely moisture sensitive. Experimental and theoretical (DFT) evidence is presented for a new mechanism for nitrile hydrogenation: the successive hydrogenation of the CN triple bond and then the CN double bond of the intermediate imine by H$^+$/H$^-$ transfer from a *trans* dihydride active catalyst. The amido complex RuH{tmeP$_2$N(NH)} (**4**) has similar activity to **3**/base for the base-free hydrogenation of benzonitrile and is moderately active for the catalytic hydration of benzonitrile.



T36, Session 2	9:20 Sunday	Lash Miller room 162

Ligand Promoted Carbene Insertion of Grubbs Ruthenium Carbene Complexes. Brandon R. Galan, Jerome B. Keister, Steven T. Diver. *Department of Chemistry, University of Buffalo, Buffalo, NY 14260*

The ruthenium based carbene catalyst **(I)** developed by Grubbs is known to catalyze alkene-alkyne metathesis to yield highly versatile and synthetically useful 1,3-dienes. Kinetic studies of alkene-alkyne metathesis have identified a new mode of reactivity of ruthenium carbenes and have led to the isolation of novel ruthenium complexes **(II)**. In attempt to quench metathesis reactions for kinetic analysis, it was found that π-acceptors such as carbon monoxide and isocyanides promote a carbene insertion into the carbon-carbon double bond of the arene substituent of the *N*-Heterocyclic carbene ligand. This insertion reaction is analogous to the Bucher reaction in which an arene undergoes cyclopropanation followed by an electrocyclic ring opening to furnish cycloheptatrienes. Studies have shown that the electronic nature of carbene and ligand influences the reactivity of the ruthenium carbene towards cyclopropanation. The synthesis of ruthenium carbene precursors, their insertion products and general trends in reactivity will be discussed.

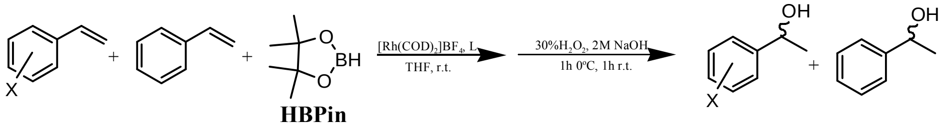


I

II

T37, Session 2	9:40 Sunday	Lash Miller room 162

Competition studies of vinyl arenes in cationic rhodium-catalyzed hydroboration systems.
Christopher J. Lata,[a] David R. Edwards[a], and Cathleen M. Crudden.[a] [a]*Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.* cruddenc@chem.queensu.ca



Since the seminal work of Mannig and Nöth[1], rhodium-catalyzed hydroborations of alkenes have come to include a myriad of chemo-, regio-, and enantioselective procedures. The reaction parameters that control these factors are dependent upon the substrate employed, the ligands bound to the active catalyst species, and even the hydroborating reagent itself [2]. Competition studies conducted on para-substituted vinyl arenes show that hydroboration catalyzed by cationic rhodium complexes a show marked linear free energy relationship correlating with the Hammett parameter, σ. The ρ-value of the linear free energy correlation is observed to change depending on both the type of ligand added as well as the hydroborating reagent employed. Additionally, in catalytic system employing diphenylphospinobutane (DPPB) ligand and pinacolborane (HBPin), a break in the Hammett plot is observed[3]. These observations suggest that small changes to the catalytic system result in a change in mechanism of this reaction for this substrate type.

Refs. (1) Mannig, D.; Noth, H. *Angew. Chem. Int. Ed.* **1985**, 24, 878. (2) Crudden, C.M.; Hleba, Y.B.; Chen, A. *J. Am. Chem. Soc.* **2004**, 126, 9200. (3) Edwards, D.R.; Hleba, Y.B.; Lata, C.J.; Calhoun, L.A.; Crudden, C.M. *Angew. Chem. Int. Ed.* **2007**, 46, 7799.

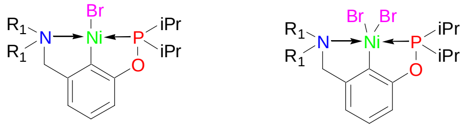
T38, Session 2	10:00 Sunday	Lash Miller room 162

Synthesis, characterization and electrochemical studies of novel POCN Pincer type complexes of Ni.
Denis M. Spasyuk, Davit Zargarian. *Département de Chimie, Université de Montréal, Montréal, QC. H3C 3J7.* ***denis.spasyuk@umontreal.ca, zargarian.davit@umontreal.ca***

Pincer type complexes have attracted much interest because of their strong activities in a wide range of catalytic processes such as olefin hydroamination, alkane dehydrogenations, Heck and Suzuki couplings, etc. Pincer complexes are, therefore, of interest for fundamental studies on the influence of pincer ligands and electronic properties of the complexes on catalytic activities.

Our group has undertaken an extensive study of pincer-type nickel complexes with a view to developing an understanding of how the catalytic reactivities of these complexes are influenced by a number of variables including the steric and electronic properties of the ligand and the oxidation state of the nickel centre.

This presentation will describe the synthesis, characterization, and electrochemical studies of the new POCN "Pincer" type complexes of Ni(II) and Ni(III), illustrated below.

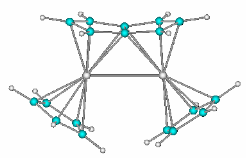


NR^{1}R^2= morpholine, NEt$_2$, N(CH$_2$Ph)H

Talks 39 and 40: Computational Organometallic Chemistry

T39, Session 2	10:40 Sunday	Lash Miller room 162

Metal-metal bonds. Believe none of what you hear and a half of what you see.
Serge I. Gorelsky, Sougandi Ilango *Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* sgorelsk@uottawa.ca



The metal-metal bonds have been a popular topic in the chemical literature for several decades. Double, triple, quadruple or even five-fold bonds between metal atoms have been reported.[1-3] Yet, the things are not as they seem to appear… We use several examples of binary, low-valence copper[4] and vanadium[2,5] complexes where the metal-metal interaction is present and provide the DFT analysis of molecular orbital interactions to explain their geometries and spectroscopic properties. Such analysis allows a rigorous determination of the nature of the chemical bonding in these species and refutes some myths that populate many papers.

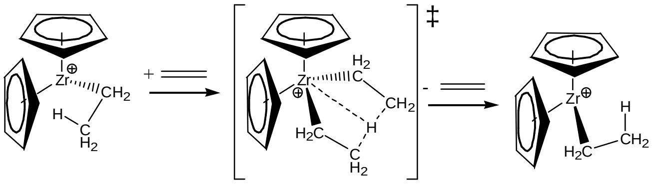
Ref. (1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, J. Wiley and Sons, New York, **1993**. (2) Jones, C. J.; O'Hare, D. *Chem. Commun.* **2003**, 2208; (3) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. L.; Power, P. P. *Science,* **2005**, *310*, 844-847. (4) Gorelsky, S. I.; Xie, X.; Chen, Y.; Fee, J. A.; Solomon, E. I. *J. Am. Chem. Soc.* **2006**, *128*, 16452-16453. (5) Ilango, S.; Vidjayacoumar, B.; Gambarotta, S.; Gorelsky, S. I. manuscript in preparation.

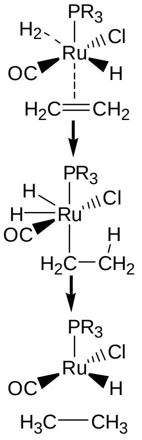
T40, Session 2	11:00 Sunday	Lash Miller room 162

Simulating the Dynamics of Catalytic Reactions: Transition Path Sampling in Organometallic Chemistry

Christopher N. Rowley, and Tom. K. Woo, *Department of Chemistry, University of Ottawa, Ottawa, ON. K1S 6N5* ***crowl055@uottawa.ca****, twoo@uottawa.ca*

In this presentation, we discuss how multiple dynamic reaction pathways can be simulated at the DFT level to get a more detailed description of a catalytic reaction. Compared to conventional "static" quantum chemical calculations, where minimum energy and transition state structures are optimized, we simulate the dynamic motion of organometallic reactions using Ab Initio Molecular Dynamics (AIMD). Moreover, we generate a large number of dynamic trajectories that link the products to reactants to get a more comprehensive picture of the process. The technique we use, known as transition path sampling, is a novel technique to focus a molecular dynamics simulation on a reactive event. We have used this technique to study the dynamics of two organometallic reactions. In the first example, we have modeled the dynamics of olefin insertion and elimination in the H_2-hydrogenation of ethylene using the catalyst $RuHCl(CO)(PH_3)$ (right). The elimination was found to proceed very rapidly after the insertion due to the localization of kinetic energy in Ru-H vibrational modes. In the second example, we have modeled the β-hydride transfer termination step of ziroconocene catalyzed ethylene polymerization (left). This study reveals that the reaction can proceed through a wide range of transition state structures and bonding modes. Several molecular dynamics animations will be presented to demonstrate these concepts.





Poster Presentations (16:30-19:30) Location: Davenport/Lash Miller

P01

Synthesis and Characterisation of a Novel Tetrathiafulvalene Complex. R. T Acha, and M. Pilkington. Department of Chemistry, Brock University, St. Catherines, Ontario, L2S 3A1 Email: ra06tu@brocku.ca

A great deal of research is currently being carried out to synthesize materials with both electrical and magnetic properties existing within the same molecule.[1]The idea involves building molecular hybrid organic/inorganic materials assembled together from a conducting organic sub lattice and a paramagnetic inorganic sub lattice. The aim of this combination is to establish coupling between the conducting electrons (π-electrons) and the localised magnetic moments (d-spins) and achieve synergistic interactions between them namely, π-d interactions.[2] With this in mind, we have prepared two tetrathiafulvalene (TTF) based ligands TTF-CH=N-2py and TTF-CH=N-4py by the Schiff base condensation of TTF-CHO with 2-aminopyridine and 4-aminopyridine respectively. Complexation to metals M(hfac)$_2$ where (M = Cu^{II}, Ni^{II}, Mn^{II}) has been carried out. Single crystal X-ray diffraction studies of the Cu(II) complex reveals the ratio between the ligand TTF-CH=N-2py and Cu^{II}(hfac)$_2$ 1:1[3]. This is due to the participation of the imine nitrogen in complexation to the metal ion. On the other hand, TTF-CH=N-4py forms a 2:1 ratio complex with Cu^{II}(hfac)$_2$. In the second case the imine nitrogen does not participate in chelation to the Cu^{II} metal, and the two TTF-C=N-4py molecules are trans to each other.

1. E. Coronado and J. R Galan-Mascaros, *J. Mater. Chem.,* **2005**, 15, 66-74.
2. N. Benbellat, Y. Le Gal, S. Golhen, A. Gouasmia, L. Ouaha and J.-M. Fabre, *Eur. J. Org.Chem.*, **2006**, 4237– 4241.
3. M. Chadma, N. Hassan, A. Alberola, H. S.- Evans, and M. Pilkington. *Inorg. Chem*., **2007**, 46, 3807- 3809.

P02

Characterization and Thermolysis of Titanium (III) Guanidinate and Amidinate Compounds. Yamile A. Wasslen and Sean Barry
Department of Chemistry, Carleton University, Ottawa, ON

Thin films of titanium nitride can be found in the semiconductor industry, used in copper-based chips as a conductive diffusion barrier between the silicon device and the metal contacts. Films of titanium nitride not only block copper from diffusing into the silicon, but it also allows an electrical connection to occur because of its conductive properties. Thus using thin film deposition techniques with a precursor that has the correct oxidation state would be very advantageous.

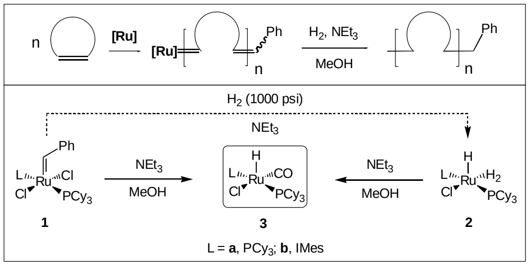
Compounds with guanidinate ligands make promising precursors due to their volatility, thermodynamic stability, and self-limiting properties. Guanidinates of the type [R$_2$NC(NR')$_2$]$^-$ (where R, R' = H or alkyl) are chelating ligands that have the ability to fulfill those favourable characteristics. Unwanted impurities can be minimized because amides and guanidinates have nitrogen directly bonded to the metal center rather than carbons or halogens.

This presentation will discuss the synthetic methods used to synthesize different paramagnetic titanium(III) complexes, their characterization techniques and their thermolysis.

P03

Hydrogenolysis *vs.* Methanolysis of Three Generations of Grubbs Catalysts: Elucidation of the Catalytic Intermediates in Tandem ROMP-Hydrogenation. Nicholas J. Beach, Kenneth D. Camm, and Deryn E. Fogg. *Center for Catalysis Innovation and Research, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5.* **nbeac038@uottawa.ca**, **dfogg@uottawa.ca**

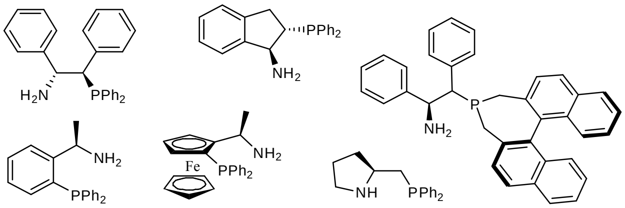
Tandem catalysis has attracted enormous interest for its power and efficiency in enabling sequential elaboration of substrates without intermediate workup stages.[1] Prominent among such processes are tandem metathesis-hydrogenation methodologies, of which ROMP-hydrogenation (ROMP = ring-opening metathesis polymerization) is particularly important in enabling routes to saturated "designer materials" inaccessible by conventional means.[2,3] The mechanistic understanding of catalyst transformations has enabled increased post-ROMP hydrogenation activity through addition of methanol and base,[4] which causes the conversion of benzylidenes **1** into hydridocarbonyl complexes **3**. Timescale NMR experiments have revealed that hydrogenolysis of **1a/b** to form **2a/b** is much more rapid than reaction of **1a/b** or **2a/b** with methanol to form **3**. Spectroscopic identification of the reaction mixture components has revealed that post-ROMP hydrogenation activity of **1c** is poor due to rapid conversion to nonhydridic species. The optimization of the **1**® **3** conversion would facilitate other post-metathesis transformations involving functionalization of the olefinic products.



1) Recent reviews: (a) Fogg, D. E.; dos Santos, E. N., *Coord. Chem. Rev.,* **2004**, *248*, 2365. (b) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.*, **2005**, *105*, 1001. 2) Camm, K.D.; Castro, N.M.; Liu, Y.; Czechura, P.; Snelgrove, J.L.; Fogg, D.E. *J. Am. Chem. Soc.* **2007**, *129*, 4168. 3) Drouin, S.D.; Zamanian, F.; Fogg, D.E. *Organometallics* **2001**, *20*, 5495. 4) Drouin, S.D.; Yap, G.P.A.; Fogg, D.E. *Inorg. Chem.* **2000**, *39*, 5412.

P04

New Aminophosphine Ligands and Catalysts for Asymmetric Hydrogenation. Kamaluddin Abdur-Rashid,[a] Rongwei Guo,[a] Wenli Jia,[a] Xuanhua Chen,[a] Chi-Wing Tsang,[a] Todd Graham,[a] Dino Amaroso[a] and Alan J. Lough.[b] [a]*Kanata Chemical Technologies Inc., MaRS Centre, Toronto, Ont. M5G 1L7.* [b]*Department of Chemistry, University of Toronto, Toronto, Ont. M5S 3H6.* **kamal@kctchem.com**



Catalytic hydrogenation of ketones, aldehydes and imines is a very valuable and fundamental process for the preparation of alcohols and amines. Since the discovery that a variety of ruthenium aminophosphine catalysts of the type $RuCl_2$(aminophosphine)$_2$ and $RuCl_2$(diphosphine)(aminophosphine) are very effective for the hydrogenation of C=O and C=N double bonds under very mild conditions we have embarked on a research program to develop and establish a broad ligand and catalyst portfolio in order to utilize this technology for high chemoselective and asymmetric hydrogenation of a wide variety of substrates. The procedures for the synthesis of the ligands will be described. Our progress in using this technology for the production of a range of commercially valuable products, such as fragrances, pharmaceuticals and agrochemicals will be discussed. The structures of the various ligands and catalysts and their manipulation for the optimization of activity and selectivity will be reviewed.

P05

Development of an aptamer-based electrochemical biosensor. David Blair, Tariq Francis and Maria C. DeRosa, Carleton University, Ottawa, Ontario

Aptamers are synthetic strands of DNA or RNA that can be selected to bind to targets with high affinity and selectivity. These characteristics make them ideal for the design of biosensors. The development of an electrochemical biosensor is desirable, as well, since there is potential to use them for *in vivo* detection. The purpose of this research is to design an aptamer-based electrochemical biosensor, and work to advance the development of *in vivo* detection as well as the use of aptasensors in medical diagnostics.

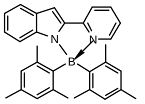
The focus of the project thus far has been the synthesis of a redox-active organometallic probe complex. The probe complex will be bound to the aptamer, and in the presence of the target will be brought close to the surface of the electrode, providing a signal. The desired complex is Co(bipy)$_2$(4-(3-Carboxypropyl)-4'-methyl)-2,2'-bipyridine, which has the advantages of being able to bind to DNA through peptide coupling and having a low redox potential, which lessens the risk of reduction/oxidation of the DNA, and decreases the chance of creating a false positive due to DNA interaction with the electrode.

Results from the synthesis and characterization (by UV-VIS spectroscopy, nuclear magnetic resonance and mass spectrometry) of the desired complex will be discussed.

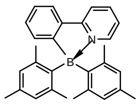
P06

Steric and Chelating Effects on Stability, Reactivity, and Luminescence of Organoboron Compounds. Hazem Y. Amarne, and Suning Wang. *Department of Chemistry, Queen's University, Kingston, ON K7L 3N6.* **hazem.amarne@chem.queensu.ca**, suning.wang@chem.queensu.ca

Two new organoboron compounds, B(mesityl)$_2$(2-pyridyl-indolyl)(**I**) and B(mesityl)$_2$(2-pyridyl-phenyl)(**II**), have been prepared in order to study the impact of the bulky mesityl group on the coordination geometry and stability of this type of organoborons. The structures of these compounds have been determined by single crystal X- ray diffraction, which show that the boron center has a four coordinate geometry. The stabilities of (**I**) and (**II**) along with the previously prepared compound B(phenyl)$_2$(2-pyridyl-indolyl)(**III**) towards moisture and fluoride anions were monitored using ^{1}H- and ^{19}F-NMR. The consequences of the structural impact due to the presence of the bulky mesityl groups were established. In contrast to the fact that such bulky groups provide stability to the boron center, especially three coordinate compounds, we found that they appear to have opposite effect in relatively crowded compounds. Compounds (**II**) and (**III**) were found to be very stable in the presence or absence of fluoride, while compound (**I**) was not stable in both cases. Based on the bond lengths and angels in compounds (**I**), (**II**), and (**III**), the unfavorable interaction of mesityl groups with the indole ring in (**I**) appears to be responsible for the poor stability of (**I**).



(I)



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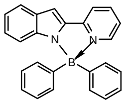


(III)

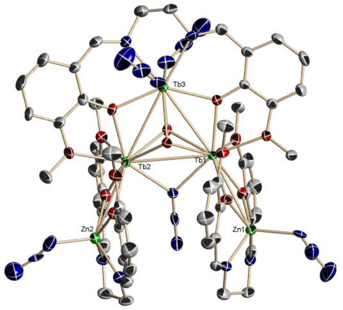
All three molecules are strongly luminescent when exposed to UV light, either as solids or in solution. The difference in luminescence properties of compounds (**I**) and (**II**) is attributed to the difference of the chelate ligand. The emission maxima of these compounds are at λ_{max}= 503, 477, and 499 nm respectively.

P07

Development of a zinc/lanthanide pentamer.

Carolyn E. Burrow,[a] Rodolphe Clérac, [b] Tara Kell,[a] and Muralee Murugesu.[a] [a]*Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* [b] *Centre de Recherche Paul Pascal, UPR CNRS 8641, Pessac, France.* **cburr043@uottawa.ca**, mmurugesu@uottawa.ca

The development of new isolated paramagnetic substances is an interesting field, with the potential for the discovery of single molecule magnets. There are many different ways to attempt to form paramagnetic substances, such as using polyoxometallates or using a ligand to "trap" a metal ion. Once formed, these paramagnetic substances can be joined by linking units, such as azide, to form chains. By the second method of utilizing a ligand to "trap" a metal ion, we have created two analogous complexes, $[Tb_3Zn_2N_{24}O_{14}C_{60}H_{65}]$ and $[Eu_3Zn_2N_{24}O_{14}C_{60}H_{65}]$. These complexes been characterized using x-ray diffraction, magnetic measurements taken, and fluorescence studies performed.

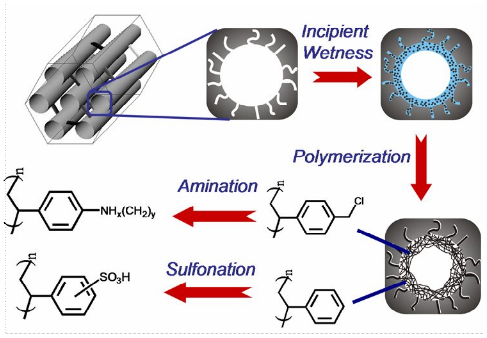


P08

Synthesis of Functionalized Mesoporous Composites Through Pore Surface-Restricted Polymerization.

Simon Bilodeau, Louis Marcoux, Tae-Wan Kim and Freddy Kleitz, *Department of Chemistry, Université Laval, Québec, Qc. G1K 7P4, freddy.kleitz@chm.ulaval.ca.*

The synthesis of mesoporous acid-base-functionalized polymer/silica composites has been realized via a two-step *pore surface-restricted* polymerization technique[1]. Reactive polymers, poly(styrene) (PS) or poly(chloromethylstyrene), (CMS) were first introduced as uniform coating inside the pores of various mesoporous silicas by using the incipient wetness technique. In a second step, functionalization of the polymer has been carried out. PS was sulfonated using H_2SO_4, leading to sulfonic acid-PS/mesoporous silica composites. In a different manner, ethylenediamine, EDA, was grafted on PCMS by nucleophilic substitution, leading to amino-polymer-silica composite materials[2]. An important feature of this approach is the possibility to tailor the quantity of functional groups by adjusting the polymer loading, the functionalization conditions or by copolymerizing with non-reactive monomers. Using this methodology, functionalized mesoporous composites with acid and basic sites ranging from 0.4 to 1.5 mmol/g and 0.3 to 2.1 mmol/g, respectively, have been synthesized, while conserving an accessible mesoporous network. The resulting materials are tested as acid-base catalysts for organic conversions.



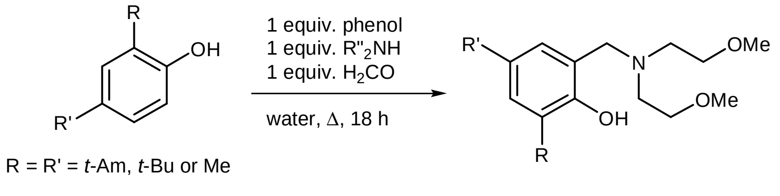
Refs. 1) M. Choi, F. Kleitz, D. Liu, Y.L. Hee, W.S. Ahn, Ryoo, R., *J. Am. Chem. Soc*. **2005**, *127,* 1924. 2) L. Marcoux, T. W. Kim, S. Bilodeau, F. Kleitz, *Stud. Surf. Sci. Catal.*, **2007**, *170*, 1836.

P09

Implementing the principles of green chemistry in coordination chemistry.

Kayla L. Collins, Nduka Ikpo, Lacey J. Corbett, Samantha M. Butt and Francesca M. Kerton. *Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X7. kayc_2@hotmail.com, fkerton@mun.ca*

The use of catalysts rather than stoichiometric reagents in synthesis is one of the twelve principles of green chemistry,[1] and probably the one which inorganic chemists are most aware of and possibly involved with. However, there are many ways that coordination chemists can make their research more environmentally benign, starting with their ligand syntheses. In this poster, the synthesis 'on water' of a series of amine-phenol ligands derived from formaldehyde, 2,4-disubstituted phenols and amines will be presented.[2,3] Yields were generally greater than reactions performed in methanol and were much improved for hydrophobic phenols. We have also used MALDI-ToF MS as an analytical tool to study the coordination chemistry of these ligands. MS has several benefits for inorganic chemists and these will be described: (a) Initial studies can be performed on a mg scale and therefore, fewer chemicals and smaller amounts of solvent are used. (b) Paramagnetic metal centres that are not amenable to study by NMR spectroscopy can be investigated. (c) Characteristic isotopic patterns are displayed by many metal complexes and can provide unequivocal confirmation of complex formation.



Yields:
R = R' = *t*-Am, 86%
R = R' = *t*-Bu, 93%
R = *t*-Bu, R' = Me, 73%
R = R' = Me, 58%

Ref. (1) Anastas, P. T.; Warner, J.C. *Green Chemistry: Theory and Practice,* **1998**, Oxford University Press; (2) Collins, K.L.; Corbett, L.J.; Butt, S.M.; Kerton, F.M. *Tetrahedron Lett.,* submitted TETL-D-07-03021; (3) Kerton, F. M.; Holloway, S.; Power, A.; Soper, R. G.; Sheridan, K. *Green Chem.,* submitted B713098H

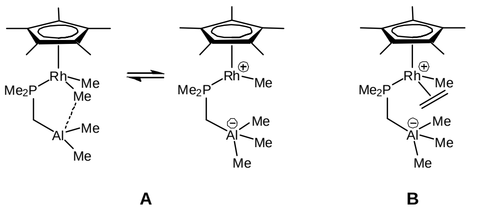
P10

Synthesis and reactivity of a Rh(III) complex featuring the ambiphilic bifunctional ligand $PMe_2CH_2AlMe_2$.

Josée Boudreau, Frédéric-Georges Fontaine. *Département de chimie, Université Laval, Québec, Qc, G1K 7P4.* josee.boudreau.3@ulaval.ca

It is well known that the addition of Lewis acids can drastically enhance many transition metal-catalyzed transformations. In order to have more reactive and efficient catalysts for a variety of reactions, our research group is looking for ways to tether Lewis acid fragments to some organometallic fragments of interest.

We studied the coordination of an ambiphilic bifunctionnal ligand, $PMe_2CH_2AlMe_2$, to a Rh(III) metal center of interest in organometallic alkane C–H activation. We have shown that the tethered Lewis acid promotes the ionisation of the Rh(III) metal center by forming zwitterionic species (**A**) and therefore opening up a coordination site.[1] We will discuss the evidences showing the formation of a π-complex when reacting with various unsaturated substrates (**B**) as well as further reactivity of these complexes.



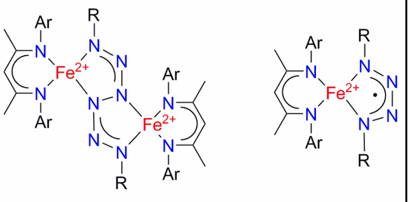
Ref. (1) Thibault, M.-H.; Boudreau, J.; Mathiotte, S.; Drouin, F.; Sigouin, O.; Michaud, A.; Fontaine, F.-G. *Organometallics,* **2007**, *26*, 3807-3815.

P11

Poly-Nitrogen Ligands: Hexazene and Tetrazene Complexes of Iron.

Ryan E. Cowley,[a] Nathan A. Eckert,[a] Eckhard Bill,[b] and Patrick L. Holland.[a] [a] *Department of Chemistry, University of Rochester, Rochester, NY 14627.* [b] *Max-Planck Institute für Bioanorganische Chemie, Mülheim an der Ruhr, Germany.*

We have characterized several examples of iron(II) complexes containing ligands with chains of four and six nitrogens. These complexes are remarkably stable with respect to dinitrogen loss, both thermal and photochemical. Full characterization of these complexes is presented, including X-ray crystallography. Mössbauer spectroscopy indicates that the tetrazene complex LFe(AdNNNNAd) (L = β-diketiminate; Ad = 1-adamantyl) contains the first example of a monoanionic $RN_4R^{\bullet}$ ligand. We also present an unusual bimetallic "hexazene" complex LFe(AdNNNNNNAd)FeL, which is the result of a reductive coupling of 1-adamantyl azide.



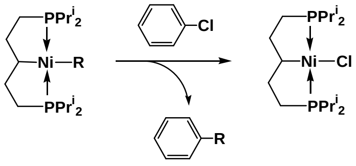
Ar = 2,6-diisopropylphenyl R = 1-adamantyl

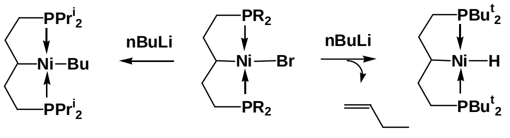
P12

New $PC_{sp3}P$-type Pincer Complexes of Nickel; Influence of Modifying the Ligand Framework.

Annie Castonguay, André Beauchamp, and Davit Zargarian. *Département de Chimie, Université de Montréal, Montréal, QC. H3C 3J7.* a.castonguay@umontreal.ca, andre.beauchamp@umontreal.ca, zargarian.davit@umontreal.ca.

PCP pincer complexes are found to be powerful catalysts for many important organic reactions and we can now find a variety of these complexes in the literature. One useful advantage of PCP ligands is that they can be modified easily at many sites, allowing the design of the electronic and steric properties of the complexes formed, in order to improve particular catalytic reactions. Our long-standing interest in organonickel chemistry complexes and the fairly unexplored chemistry of PCP-type pincer complexes of 3d transition metals, in general, and of nickel, in particular, have prompted us to investigate the preparation of PCP-Ni complexes and their reactivities. The objective of our research is the study of new pincer complexes of nickel bearing $PC_{sp3}P$ pincer-type ligands, such as $R_2P(CH_2)_5PR_2$ (R = *t*-Bu, *i*-Pr). We have focused our research on the study of the differences of reactivities of the complexes formed arising from specific modifications of the ligand framework, as for example the change of the nature of the phosphorus substituents or the nature of the cyclometallated carbon.



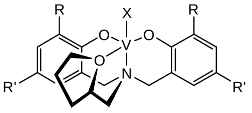


This presentation will describe synthetic routes leading to some of these complexes, their characterization and some of our preliminary results on their reactivities.

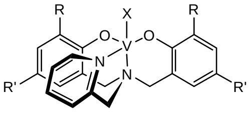
P13

Small molecule activation by vanadium complexes of amine-bis(phenolate) ligands. Angela K. Crane,[a] and Christopher M. Kozak.[a]
[a]*Department of Chemistry, Memorial University of Nfld., St. John's, NL. A1B 3X7.* angelacrane@nl.rogers.com, ckozak@mun.ca

Small molecule activation remains an important focus in organometallic chemistry. In particular, the investigation of processes that involve abundant, renewable and cheap molecules such as CO_2 and simple esters as feedstocks for fine chemical synthesis have far reaching potential. We have recently begun studies of vanadium complexes supported by amine-bis(phenolate) ligands with the general formulae $VX[O_2NO]^{RR'}$ and $VX[O_2NN']^{RR'}$ where R, R' = ^{t}Bu or Me, X = Cl or Br, see below. They can be used as precursors for the preparation of organometallic derivatives, which will be employed for small molecule activation. A goal of these compounds will be for use as catalysts toward the copolymerization of CO_2 with simple epoxides such as propylene oxide and cyclohexene oxide to generate polycarbonates. Our recent results concerning the synthesis and characterization of these complexes, and future targeted reactions, will be presented.



$VX[O_2NO]^{RR'Furf}$

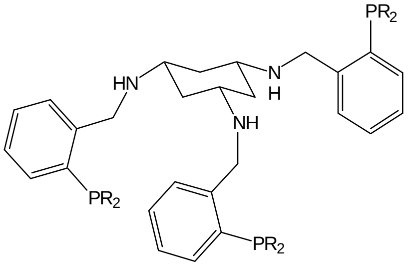


$VX[O_2NN']^{RR'Pyr}$

P14

Reactivity of a hexadentate bifonctionnal ligand with Ga, Zr, Y, Ta and V. Guillaume B. Chabot, Marie-Hélène Thibault, Nadège Boccon, Frédéric-Georges Fontaine, *Département de chimie, Université Laval, Québec, Qc, G1K 7P4.*

Few bifunctional complexes with Lewis acidic and basic moieties have been synthesized over the last few years. Although these complexes might show unusual activity, little reactivity studies have been done. A novel organic framework (**P3**) has been synthesized for the purpose of stabilizing Lewis acid-nucleophilic transition metal interactions in the form of an ancillary ligand. While Al substituted complexes show interesting results (see poster by M.-H. Thibault), the reaction observed with other acidic metals is significantly different. This paper will describe the reactivity of P3 with gallium, zirconium, yttrium, tantalum and vanadium.

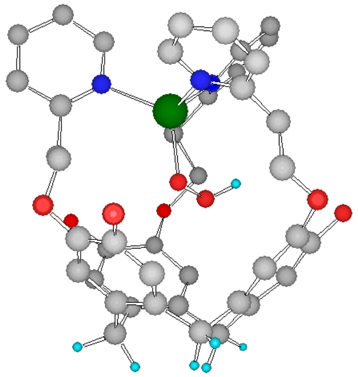


P3

P15

Design and synthesis of supramolecular ligands to stabilize reactive mononuclear metal complexes. François G. David, Steven Horvath, Daniel Rosenberg, Laura Chaloner, Xavier Ottenwaelder* *Department of Chemistry and Biochemistry, Concordia University, Montréal, QC, H4B 1R6.* fg_david@alcor.concordia.ca, xotten@alcor.concordia.ca

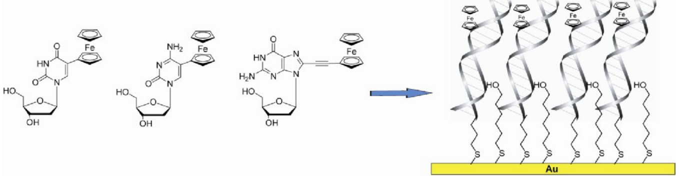
Several non-heme metalloenzymes performing difficult oxygen-atom transfer reactions, such as the direct hydroxylation of a C–H bond, contain a single metal ion in their active site: non-heme mono-oxygenases (Fe), dopamine-b-hydroxylase (Cu), etc. In the active site of these enzymes the metal ion is in a reduced coordination environment, frequently made of three histidine donors. Our goals are to prepare synthetic analogues of these active sites and to elucidate the nature of the intermediates forming along the reaction from the activation of O_2 to the hydroxylation of the substrate. This requires ligands that can stabilize reactive species while maintaining the mononuclear integrity of the complex. In this poster, we present our design, based on a rigid supramolecular platform that would entropically favour mononuclear configuration. Computational chemistry was employed in the design of tridentate ligands based on a cyclotriveratrylene (CTV) scaffold (see picture) with either aliphatic or aromatic nitrogen donors. The cavity size of these complexes was evaluated against the size of potential substrates prior to synthesis. In addition, we prepared cryptand-type ligands in which the donor atoms are tethered as part of a multi-chelating ligand (e.g. tren). Such preorganized cryptands shall prevent oligomerization reactions and ensure mononuclear configuration. Our main targets are mononuclear Zn-hydroxo species, superoxo, peroxo and hydroperoxo species of Cu and Fe, as well as the highly reactive Fe(IV)=O species that is believed to be a strong hydroxylating agent.



P16

Synthesis and electrochemical properties of ferrocene-nucleic acid conjugates. Haifeng Song and Heinz-Bernhard Kraatz
Department of Chemistry, University of Western Ontario, London, ON. N6A 5B7. **hsong42@uwo.ca**, hkraatz@uwo.ca

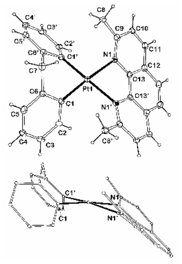
Nucleosides site-specifically modified with redox probes have attracted great deal of interest recently[1,2]. Modified nucleosides can be incorporated into oligonucleotides by solid phase synthesis or enzyme method in order to investigate electron transfer through DNA and molecular recognition of DNA. Ferrocene (Fc) is one of the most used redox probes due to its stability during the synthesis and analytical processes. In our group, we are exploring the synthesis of novel Fc-modified nucleosides, including modified deoxyuridine, deoxycytidine and deoxyguanosine. Fc-modified deoxyuridine has been used to prepare the designed sequences for the study of electron transfer in DNA. Here, the results of our synthetic and electrochemical study of the novel Fc-modified nucleosides will be presented.



Ref. (1) Pike, A. R.; Ryder, L. C.; Horrocks, B. R.; Clegg, W.; Connolly, B. A.; Houlton, A. *Chem.Eur. J.* **2005**, *11*, 344-353. (2) Song, H.; Li, X.; Long, Y.; Schatte, G.; Kraatz, H.-B. *Dalton Trans.* **2006**, 4696 – 4701

P17

9,10-Dihydroplatinaanthracenes with Aromatic Diimine Ligands: Syntheses, Spectroscopic and Computational Studies of New Luminescent Materials Antonio G. De Crisci,[a] Alan J. Lough[b], Kanwarpal Multani [a], and Ulrich Fekl.[a*] [a]*Department of Chemical and Physical Sciences, University of Toronto Mississauga, 3359 Mississauga Road N, Mississauga, ON, Canada L5L 1C6; and* [b]*X-ray Crystallography Lab, University of Toronto, 80 St. George St., Toronto, ON, Canada M5S 3H6* * ulrich.fekl@utoronto.ca



Platinum-based luminescent compounds are extremely promising as dopants for high-quantum-yield OLEDs, and synthetic organometallic chemistry is currently making an important contribution to developing new tunable luminescent materials. We just discovered that 9,10-dihydroplatinaanthracenes with nitrogen-based ligands are strongly luminescent, and that both absorbance and emission properties can be straightforwardly tuned by changing the substituents on the diimine. 9,10-Dihydroplatinaanthracenes with aromatic nitrogen ligands were synthesized, derived from 2,2'-bipyridine, 4,4'-dichloro-2,2'-bipyridine, 4,4'-dimethoxy-2,2'-bipyridine, 4,4'-bis(dimethylamino)-2,2'-bipyridine, 4,4'-di-*tert*butyl-2,2'-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (insert), 3,4,7,8-tetramethyl-1,10-phenanthroline, and 2,2'-biquinoline. For comparison purposes, the *N,N,N',N'*-tetramethylethylenediamine-derived compound was also obtained. The diimine-derived compounds are highly luminescent in the solid state at room temperature, as well as in frozen solution. The luminescent complexes are easily prepared by ligand substitution from the new organometallic platinum precursor $\{[H_2C(C_6H_4)_2]Pt(SEt_2)\}_n$ (n = 2, 3). In order to obtain insight into orbital energies and the tunability of the optical properties, absorbance, electrochemical data, as well as DFT and TD-DFT data were obtained and show us that the lowest-energy absorbances are due to charge transfer from orbitals located largely on the electron-rich metallacyclic ligand with some coefficient on Pt into π^* orbitals of the diimine. Computations suggest that the low energy bands mostly originate from charge transfer from the HOMO-2, HOMO-1, and HOMO into to the LUMO (rarely LUMO+1 and LUMO+2) molecular orbitals. Emission maxima range from 536 to 690 nm.

Ref. (1) De Crisci, A. G.; Lough, A.J.; Multani, K.; Fekl, U. *manuscript submitted*.

P18

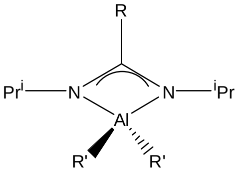
Chromium Amidate and Amidinate Complexes as Catalysts for Ethylene Oligomerization. Terri Clarke, Sandro Gambarotta,
Department of Chemistry, University of Ottawa, Ottawa, ON. K1N 6N5. **tclar084@uottawa.ca**, **sandro.gambarotta@science.uottawa.ca**

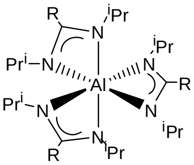
The catalytic oligomerization of ethylene is being explored as a route to selectively synthesize linear α-olefins. A number of chromium-based complexes have been developed to date. The most desirable catalysts are highly active, and also selective towards one or more desirable linear α-olefin. The oligomerization results will be presented for both Cr(II) and Cr(III) complexes with amidate and amidinate ligands. The systems tested proved to be highly active in ethylene oligomerization, but tend to produce a statistical distribution of oligomers.

P19

A Thermolysis Study of Aluminum Amidinates, Guanidinates, and Formamidinates. Julie R. Delahunt,[a] Paul A. Johnson, [a] and Sean T. Barry.[a] [a]*Department of Chemistry, Carleton University, Ottawa, Ont. K1S 5B6.*

In designing precursors for atomic layer deposition (ALD), thermal stability is important to ensure that the precursor does not decompose in the gas phase. Amidinates, guanidinates and formamidinates are of particular interest as they exhibit several favourable characteristics of ALD precursors. By sealing our samples in thick-walled NMR tubes, we were able to perform step-wise thermolysis experiments and analyze the results by ^{1}H NMR. We were able to determine the relative thermal stabilities of the compounds as well as identify certain by-products, such as carbodiimide which can deinsert when the exocyclic position, R, is occupied by a reactive species. The effect on thermolysis by the nature of the exocyclic R group will be examined.





$R = H, CH_3, N(CH_3)_2$

$R' = CH_2CH_3, N(CH_3)_2$

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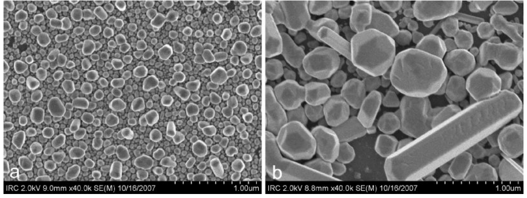
P20

Synthesis and thermal chemistry of copper (I) guanidinates and their use as precursors in chemical vapour metal deposition. Jason P. Coyle,[a] and Seán T. Barry.[a] [a]*Department of Chemistry, Carleton University, Ottawa, Ont, K1S 5B6*. jcoyle@connect.carleton.ca, sbarry@ccs.carleton.ca

Copper (I) guanidinate dimers were generated by a salt metathesis route. Their potential as chemical vapour metal deposition precursors was investigated by several methods, including a novel temperature-resolved, gas-phase method that was monitored by mass spectrometry. The copper guanidinates underwent carbodiimide deinsertion to produce copper metal at temperatures of 125°C in solution and between 225 – 250°C in the gas phase. This decomposition pathway is unique to copper (I) guanidinates as other copper metal precursors undergo a well known disproportionation pathway[1]. The guanidinate compounds deposited crystalline copper at 225°C in a simple CVD experiment and between 170-200°C in an ALD experiment using dihydrogen as the second precursor.



Ref. (1) a) Shimokawa, C.; Tachi, Y.; Nishiwaki, N.; Ariga, M.; Itoh, S. Bull. Chem. Soc. Jpn. 2006, 79, 118. b)Chen, T.-Y.; Vaissermann, J.; Ruiz, E.; Sénateur, J. P.; Doppelt, P. Chem. Mater. 2001, 13, 3993. c) Chi, K. M.; Shin, H.-K.; Hampden-Smith, M. J.; Duesler, E. N. Polyhedron 1991, 19, 2293.

P21

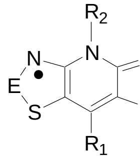
Search for the stannous in non-stoichiometric $M_{1-x}Sn_xCl_{1+y}F_{1-y}$ (M = Sr and Ba) and in Ba_2SnCl_6. Georges Dénès[a], Abdualhafeed Muntasar[a], Maria Kaltcheva[a] , Sihem Boufas[b] and Hocine Merazig[b] [a] *Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Department of Chemistry and Biochemistry, Concordia University, Montreal, Qc. H4B 1R6,* [b,] *Laboratoire de Chimie Moléculaire, du Contrôle de l'Environnement et de Mesures Physico-Chimiques, Département de Chimie, Université Mentouri, Constantine, Algeria. h.merazig@caramail.com, gdenes@alcor.concordia.ca . h.merazig@caramail.com, gdenes@alcor.concordia.ca*

Lone pair stereoactivity of tin(II) halides is expected to be maximal for the fluorides, and to decrease down the halogen group. This is due to the relative energies of the valence p orbitals of the halogens compared to the 5s and 5p orbital energy of tin. Since the higher the lone pair stereoactivity, the more covalent the Sn-X bond, and the more *p* character in the lone pair, the higher the electric field gradient (e.f.g.) it generates at tin, and the larger the quadrupole splitting Δ. In addition, the higher the *p* character of the lone pair, the lower its *s* character, and therefore le lower the isomer shift δ. It results that high Δ and low δ are always observed for fluorides and chlorides (large lone pair stereoactivity, with covalent bonding and hybridized tin orbitals), while low Δ and large δ are found in iodides and some bromides (small lone pair stereoactivity, with ionic bonding and unhybridized tin orbitals). In the case of high symmetry crystals, such as in $CsSnBr_3$, a totally non-stereoactive lone pair (spherical, i.e. purely $5s^2$ lone pair) has been observed], and bonding can be assumed to be ionic (Sn^{2+} stannous ion). Anhydrous $SnCl_2$ is a unique case for chlorides, and it gives a single Mössbauer line. However, $SnCl_2$ has an orthorhombic structure and therefore the tin site is distorted, although not enough to generate an e.f.g. from the lone pair (Vzz_{val}) sufficiently large to give a resolved Δ. In the present work, a solid solution that is doubly disordered, $M_{1-x}Sn_xCl_{1+y}F_{1-y}$ (M = Sr & Ba) has been prepared and characterized. For M = Ba, depending on the method of preparation and on the stoichiometry, it contains either a mixture of ionic Sn^{2+} and covalently bonded tin (Mössbauer doublet and a singlet) or pure ionic Sn^{2+} (singlet only) (fig. 1). We have prepared crystals of another new tin(II) compound, Ba_2SnCl_6, that the first case of a tin(II) chloride where the tin lone pair is spherical due to crystal symmetry.

P22

Ferromagnetic Ordering in a Heavy Atom Heterocyclic Radical Conductor. Kristina Cvrkalj, Craig M. Robertson and Richard T. Oakley. *Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1.* **kcvrkalj@uwaterloo.ca**, oakley@uwaterloo.ca

The use of neutral *p*-radicals as building blocks for single component molecular conductors requires materials with a low on-site Coulomb repulsion *U* and a high solid-state bandwidth *W*. Good conductivity is achieved with a high *W*/*U* ratio. Resonance stabilized bisdithiazolyl systems (*e.g.* **1,** E = S)[1] fulfill these criteria, but the formation of slipped *p*-stacks in the solid state limit their bandwidth. In order to improve bandwidth, the incorporation of the more spatially extensive chalcogen selenium was investigated.[2] This poster describes the synthetic challenges encountered in the preparation of one of these compounds (**1**, E = Se, R_1 = Me, R_2 = Et). The compound has been characterized in the solid state by X-ray crystallography (Figure 1). Its conductivity and magnetic properties have also been probed. The conductivity of the radical is two orders of magnitude greater than other all-sulfur containing analogues. In addition, we have discovered that the incorporation of selenium gives rise to ferromagnetic ordering below 12 K, and the material exhibits hysteretic behavior with an exceptionally large coercivity.



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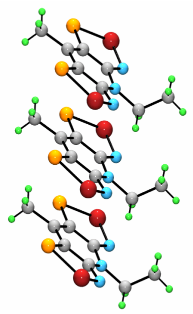


Figure 1.

Ref. (1) Beer, L. *et al. J. Am. Chem. Soc.,* **2002**, *124*, 9498-9509; (2) Robertson, C. M. *et al. J. Am. Chem. Soc.,* **2007**, *129*, 12688-12689

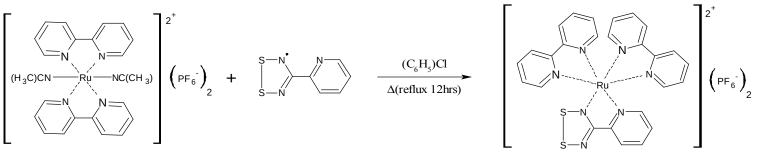
P23

Effect of ball-milling on the structure and texture of materials the structure of which is derived from the fluorite type: stoichiometric $MSnF_4$(M = Ba and Pb) and non-stoichiometric $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$. Abdualhafed Muntasar**,** Georges Dénès, and M. Cecilia Madamba *Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Department of Chemistry and Biochemistry, Concordia University, Montreal, Qc. H4B 1R6***.** gdenes@alcor.concordia.ca

Ball-Milling provides solid materials with a large amount of mechanical energy that usually results in a reduction of particle size, and eventually amorphization. Ball-milling times required to get a significant decrease of particle dimensions of oxides are hours or even days. Ball-milling of $MSnF_4$ (M = Ba and Pb) and of the doubly disordered $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution was carried out in an attempt to reduce preferred orientation in thee materials. However, for $PbSnF_4$, a drastic change of X-ray diffraction pattern was observed to start within seconds, and was completed in about one minute. In one minute ball-milling, a phase transition had taken place, to give a nanocrystalline disordered fluorite-type structure. Additional ball-milling for 30 minutes resulted in no further transformation. Similar ball-milling of isotypic $BaSnF_4$ gives a similar structural transformation, with however two major differences: (i) it takes much longer (ca. 20 minutes) and it is occurs in two distinct steps, namely first a “positional order-disorder transition”, and in a second step after substantial additional ball-milling, an “orientational order-disorder transition” to give a fully disordered structure. Tin-119 Mössbauer spectroscopy showed that tin(II) does not occupy the center of the fluoride ions in the disordered structures, the way the metal ion does in the fluorite-type structure, thereby proving that local order is still present. No such phase transition was observed in the $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution, which is a disordered form of the BaClF structure, which is itself derived from fluorite-type BaF_2.

P24

Coordination of 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl radical to Ruthenium(II) complexes. Domenic V. Di Mondo,[a] Kathryn E. Preuss,[a] and Nigel G.R. Hearns .[a] [a]*Department of Chemistry, University of Guelph, Guelph, Ont. N1G 2W1.*



Coordination of the 4-(2’-pyridyl)-1,2,3,5-dithiadiazolyl (pyDTDA) radical has been previously reported for copper(II), manganese(II), and cobalt(II) complexes containing bis(hexafluoro-acetylacetonato) spectator ligands, generating neutral complexes. We are now attempting to coordinate the pyDTDA radical to a bis(bipyridine)-Ru(II) metal fragment. Early experiments have shown success in coordination of the charged ruthenium complex. The synthesis of the desired complex is confirmed by ESI mass spectrometry in CH_2Cl_2. Peaks for the $[Ru(bipy)_2(pyDTDA)]2+[PF_6-]$ (*m/e* = 741) and for the $[Ru(bipy)_2(pyDTDA)]2+$ (*m/e* =298) include appropriate isotope patterns for ruthenium. We have also achieved a more efficient synthetic method for the preparation of ruthenium(II)bis(benzonitrile)bis(bipyridine). The bulkier benzonitrile ligand present on this fragment should be easily displaced by the pyDTDA radical, increasing the success and thereby the yield of the coordinated Ru(II) complex.

P25

Synthesis and characterization by X-ray diffraction of bis(adeninium) hexacholorostannate(IV) dichloride tetrahydrate.

Hocine Merazig,[a,] S. Bouacida ,[a, b], M.A. Benseguini,[a] A. Beghidja, [a] C. Beghidja, [a] and Georges Dénès.[# a,] *Laboratoire de Chimie Moléculaire, du Contrôle de l'Environnement et de Mesures Physico-Chimiques, Département de Chimie, Université Mentouri, Constantine, Algeria,* [b] *Département de Chimie, Université A. Mira de Béjiaia, Béjiaia, Algeria,* [#] *Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Department of Chemistry and Biochemistry, Concordia University, Montreal, Qc. H4B 1R6*. **h.merazig@caramail.com**, **gdenes@alcor.concordia.ca**

Studies of organic inorganic hybrid materials have received a great attention recently, because of their ionic, electrical, magnetic and optical properties. Adenine is one of the precursors of DNA and RNA nucleotides, the adeninium cation (1+ or 2+) is known to form a variety of inorganic salts, e.g. chloride, bromide, bistriiodide, sulfate , phosphate or nitrate. In the present study, a new organic-inorganic hybrid compound has been ptrepared and its crystal structure determined. It is based on tin with adeninium, and it combines the superior carrier mobility of inorganic semiconductors with the processability of organic materials. The title compound, $[SnCl6]^{2-}$ $2[C5H6N5]^{+}$ $2Cl^{-}$ 4H2O crystallized in the orthorhombic crystal system, with Fdd2 space group, it was prepared by slow evaporation of an aqueous solution of adenine, tin(II) oxalate and hydrochloric acid in a molar ratio of 10:5:1. The structure can be described as alternating layers of $[SnCl6]^{2-}$ and $[C5H6N5]^{+}$ ions along the b axis of the unit-cell, with $[SnCl6]^{2-}$ lying on a two-fold axis. The adenine base is protonated at positions N1 and N7 and the C—N—C angle at the protonation of N atom is larger by 4°and 3°, respectively, than the corresponding angle in the neutral adenine molecule. Layers of adeninium cations and hexachlorostannate anions are linked by strong anion-cation, cation-water and water-water hydrogen bonds, in the crystallographic [101] direction. This three-dimensional complex network of hydrogen bonds ensures the cohesion of the ionic structure.

P26

Highly Efficient Iron Catalysts with Tetradentate P-N-N-P Donor Ligand for the Asymmetric Hydrogenation of Polar Bonds.

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The asymmetric transfer of hydrogen from 2-propanol to prochiral, unsaturated molecules catalyzed by certain transition metal complexes is a powerful method for the synthesis of enantiopure alcohols and amines.[1] To date, the most efficient and enantioselective transition metal catalysts for this reaction are based on ruthenium and rhodium. Iron-based catalysts of comparable activity would be desirable due to their potentially lower cost, toxicity and environmental impact. Given the high activity and enantioselectivity for acetophenone transfer hydrogenation[2-3] and H_2-hydrogenation[3] displayed by the ruthenium complexes with tetradentate diaminediphosphine P-NH-NH-P or diiminodiphosphine P-N-N-P ligands we wondered whether similar iron catalysts could be developed. Here we report the discovery of the complex $[Fe(NCMe)_2((R,R)\text{-cy}P_2N_2)](BF_4)_2$ ((R,R)-cyP_2N_2 = (R,R)-(PPh_2(*ortho*-C_6H_4)CH=NHC_6H_{10}N=CH(*ortho*-C_6H_4)PPh_2)), which constitutes the first well-defined iron catalyst for the asymmetric H_2-hydrogenation of acetophenone. Its modification by reaction with CO or CN*t*Bu gives the precatalysts $[Fe(CO)(NCMe)((R,R)\text{-cy}P_2N_2)](BF_4)_2$ and Fe(CN*t*Bu)(NCMe)((R,R)-cyP_2N_2)]$(BF_4)_2$ which promote the first asymmetric transfer hydrogenation of polar bonds at RT, such as ketones, aldehydes and imines, with an excellent TOF (907 h^{-1}) that out-performs many of the most active ruthenium and rhodium transfer hydrogenation catalysts.

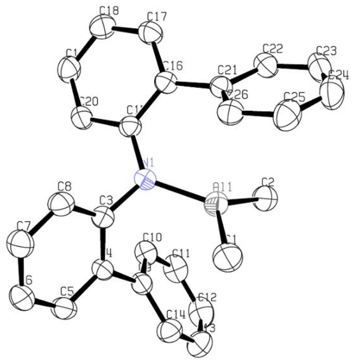
Ref. (1) Gladiali, S.; Alberico, E.*Chem. Soc. Rev.* **2006**, *35*, 226. (2) Gao, J.X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087. (3) Rautenstrauch, V.; Hoang-Cong, X.; Churlaud, R.; Abdur-Rashid, K.; Morris, R. H. *Chem. Eur. J.* **2003**, *9*, 4954.

P27

Hemilabile-amido-arene complexes of aluminum.

Meghan A. Dureen,[a] Douglas W.Stephan.[b] [a]*Department of Chemistry, University of Toronto, Toronto, Ont. M5S 3H6.* [b]*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **mdureen@chem.utoronto.ca**, stephan@uwindsor.ca

We are now engaged in an examination of hemilabile ligands based on amido-biphenyl systems. The rationale behind using this type of ligand is to facilitate a fine balance between reactivity and stability. Specifically, we have targeted cationic aluminum complexes. Structural data have confirmed that amido-biphenyl ligands stabilize monomeric, three-coordinate aluminum alkyls from which cationic complexes have been generated *in situ*. These species have been characterized and the reactivity assessed. The nature of the arene-aluminum interaction has been probed spectroscopically and computationally and these data will be presented.

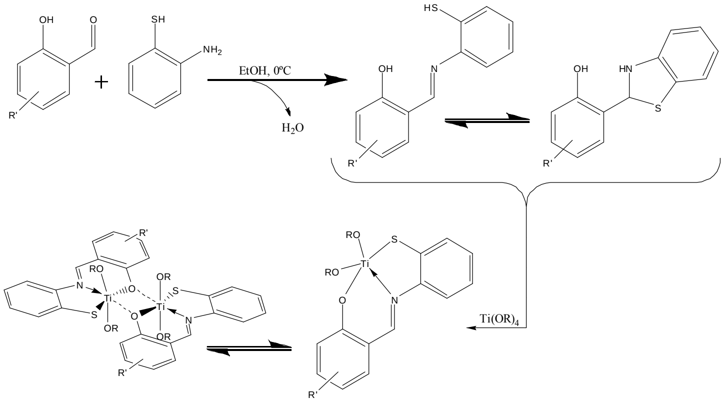


P28

Synthesis and electrochemistry of Ti(IV) complexes of dithiocarbamates, thiophenol and thiophenol-derived Schiff bases.

Alberto Donzelli[a] and Pierre G. Potvin*[b]. *Department of Chemistry, York University, 4700 Keele Street, Toronto, ON M3J 1P3.*
[a]donz@yorku.ca [b]pgpotvin@yorku.ca

The chemistry of titanium has been widely explored over the years; however the investigation of the electrochemical properties of its complexes has been almost completely neglected. Our interest in electron-rich Ti^{IV} compounds originates from their possible use as electrocatalysts of methanol oxidation in Direct Methanol Fuel Cells, where they could overcome the kinetic limitations of the Pt-based electrodes currently used. Our designs take advantage of some favourable characteristics of Ti^{IV} complexes, namely fast alcohol-alkoxide exchanges, anchoring to the surface metals of nano-crystalline TiO_2-coated electrodes through strong Ti-O-Ti linkages, and the possibility of enabling two-electron oxidation. During the past few years, several classes of electron-rich ligands have been investigated, their complexes with Ti^{IV} isolated and characterized, and an initial investigation into their electrochemical properties has been conducted.



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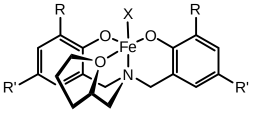
P29

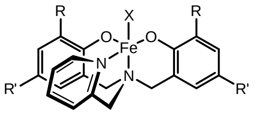
Cross-coupling catalysis by Fe(III) amine-bis(phenolate) complexes.

Candace Fowler,[a] Philip Kwong,[b] Julie Collins,[c] and Christopher M. Kozak.[a] [a]*Department of Chemistry, Memorial University of Nfld., St. John's, NL. A1B 3X7.* [b]*Department of Chemistry, Queen's University, Kingston, Ont. K3K 0K7.* [c]*C-CART X-Ray Crystallograpic Service, Memorial University of Nfld.* e66cif@mun.ca, ckozak@mun.ca

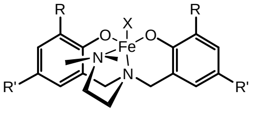
Amine-bis(phenolate) ligands have been used extensively with the early transition metals and the lanthanides. However, their use with late transition metals is still in its infancy. We have prepared a series of Fe(III) complexes supported by tetradentate amine-bis(phenolate)-donor ligands of the general formulae $FeX[O_2NO]^{RR'}$, $FeX[N_2NN']^{RR'}$ and $FeX[ONNO]^{RR'}$, where R, R' = ^{t}Bu or Me, X = Cl or Br (see right). We have used these complexes as precatalysts for C-C cross-coupling reactions of aryl Grignard reagents with primary and secondary alkyl halides. Typically, these "Kumada"-type reactions use expensive Pd or toxic Ni catalysts, so our systems represent cheap, easily prepared, environmentally non-toxic catalysts. These iron precatalysts give high conversions to cross-coupled products in very good yields. Herein we discuss our results concerning the cross coupling of substituted aryl Grignard reagents with several primary and secondary alkyl halides.[1] The physical properties of these complexes will also be presented.



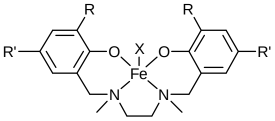
$FeX[O_2NO]^{RR'Furf}$



$FeX[O_2NN']^{RR'Pyr}$



$FeX[O_2NN']^{RR'NMe2}$



$FeX[ONNO]^{RR'}$

Ref. (1) Roy Chowdhury, R.; Crane, A. K.; Fowler, C.; Kwong, P. and Kozak, C. M.. *Chem. Commun.*, **2007**, Submitted B713647A.

P30

Computational Insights into the Mechanism of an Aluminum Amide Catalyzed Cyclo-Trimerization of Dimethylcyanamide

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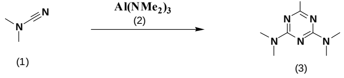
Hexamethylmelamine (3) is an important pharmaceutical agent that has been used for the treatment of ovarian cancer.[1] Recently, we have identified an efficient one-step synthesis of this compound by treating dimethylcyanamide (1) with aluminum amide catalyst (2). In an effort to elucidate the mechanism of this interesting transformation, we have performed modeling using density functional theory (DFT). It has been shown that insertion of the nitrile into the aluminum amide bond has a very low energetic barrier. Two subsequent insertions yields a linear trimer which can undergo a 6π-electron electrocyclization, followed by de-insertion to give the aromatic product. Alternative mechanisms will be discussed as well as the preference for cyclotrimerization as opposed to dimerization or polymerization. Implications for expansion of the synthetic scope will also be presented.



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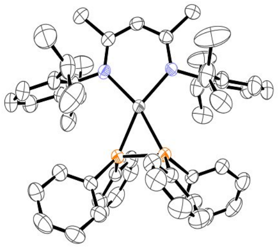
P31

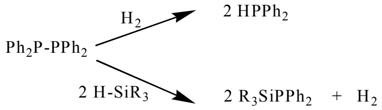
Rh-catalyzed P-P and P-H Bond Activation.

Stephen J. Geier and Douglas W. Stephan. *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.*



RhNacNac(P_2Ph_4)

The field of "inorganometallics" has drawn much recent attention.[1] One area of study has been the catalytic activation of main group-hydrogen bonds, such as P-H, Si-H and B-H bonds. One type which has been explored is the dehydrocoupling reaction, which can be used to form new bonds between main group elements. In some cases these reactions can even produce polymeric material. An area that has not received significant attention has been the reverse reaction, hydrogenative decoupling. We have recently shown that a RhNacNac {NacNac=HC(CMeN(*i*$Pr_2C_6H_2$))$_2$} catalyst precursor can hydrogenate the P-P bond in Ph_2PPPh_2 to form two equivalents of $HPPh_2$.[2] In an analogous reaction, the P-P bond can be cleaved by hydrosilylation, the use of excess silane results in the formation of a second equivalent of silyl phosphine through dehydrocoupling of the generated secondary phosphine and a second equivalent of silane. The scope and mechanism of this reaction have been explored, including the characterization of possible intermediates (for example, RhNacNac(P_2Ph_4), ORTEP depiction shown at right) and related Rh-polyphosphine complexes.



Ref. (1) Fehlner, T.P. Inorganometallics. Plenum Press, New York, **1992**. (2) Geier, S. J.; Stephan, D.W. *Chem Comm.* In Press

P32

Unprecedented Cyclotrimerization of Di-substituted Alkynes with Nickel Complexes with Zwitterionic Amido Donor Ligands.

Meghan E. Doster and Samuel A. Johnson; *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* ***doster1@uwindsor.ca*** *,* **sjohnson@uwindsor.ca**.

A new zwitterionic amido ligand allows for the stabilization of a wide variety of metals, due to resonance structures where the nitrogen donor can be anionic or neutral. The neutral imine minimizes charge separation whereas the zwitterionic amide, despite a separation of charge, has the benefit of aromatic stabilization. The complexes formed and promising applications such as cyclotrimerization will be discussed.

P33

Stability of Mesoporous Materials used in Pd Catalysis.

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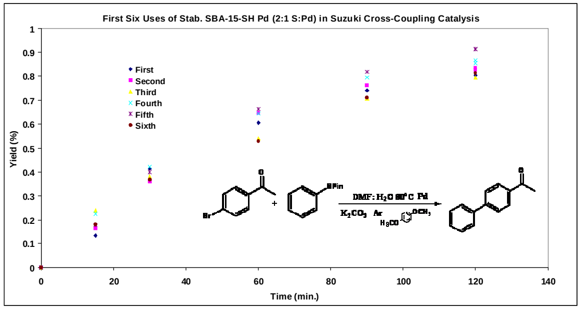
Palladium-loaded mesoporous silica materials (SBA-15, MCM-41) are effective catalysts for the Suzuki, Heck and other Pd-catalyzed cross-coupling reactions. The catalysts can be isolated and reused, remaining functionally heterogeneous and maintaining their high catalytic activity.[1,2] However, before these catalysts find more wide-spread use and application, the issue of material degradation under reaction conditions must first be addressed. With this in mind, the stabilities of three materials, MCM-41-SH Pd, SBA-15 –SH Pd and salt stabilized SBA-15-SH Pd, were examined over the course of a series of Suzuki reactions. Drops in catalytic activity after two uses of the thin-walled MCM-41 type material coincided with a significant loss of order and porosity. Conversely, the SBA-15 type materials maintained order for upwards of six uses, actually outlasting the activity of the catalyst. Surface protection methods and the effect of thiol loading were also examined.



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P34

Characterization of heme binding and spectroscopy in Isd proteins in *Staphylococcus aureus*. Michael T. Tiedemann, Martin J. Stillman, *Department of Chemistry, The University of Western Ontario, London, Ont. M5S 3H6.*
mtiedema@uwo.ca, martin.stillman@uwo.ca

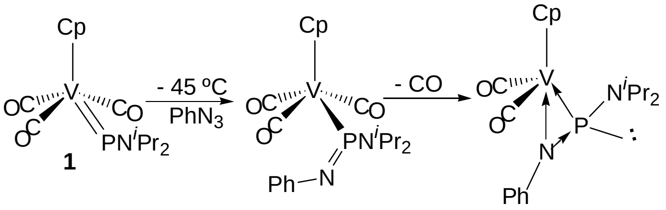
Staphylococcus aureus, an antibiotic resistant bacterium, is a substantial problem in hospitals and communities worldwide. Infections caused by Staphylococcus aureus range from superficial wound lesions, pneumonia, osteomyelitis bacteremia and death.

Bacterial survival is largely dependant on iron scavenging. *Staphylococcus aureus* has adopted a number of specialized mechanisms for scavenging iron from the host. The recently identified cell wall and membrane-associated iron regulated surface determinant (Isd) protein system is one such pathway. The Isd proteins allow the bacterium to scavenge iron from the heme in hemoglobin. Spectroscopic properties of the recombinant Isd proteins IsdA, IsdC and IsdE have been reported[1,2] and show that the heme is bound to the protein through the iron. The electronic structure of the heme and its amino acid ligands have yet to be characterized. Utilizing recent crystal structures of IsdA, IsdC and IsdE, the ground state geometry and excited states of the heme PPIX-DME were calculated in order to determine the electronic contribution of the amino acid axial ligands to heme binding stability. From the electronic spectrum calculations, the effects of the axial ligands and their contribution to the spectroscopy can be explained and potentially predicted. Overall, this leads to an understanding of the heme binding mechanism in the Isd pathway.

Ref. (1) Pluym, M.; Vermeiren, C. L.; Mack, J.; Heinrichs, D. E.; Stillman, M. J., Journal of Porphyrins and Phthalocyanines, **2007**, 11(3-4), 165-171.
Red (2) Pluym, M.; Vermeiren, C. L.; Mack, J.; Heinrichs, D. E.; Stillman, M. J., Biochemistry ACS ASAP. CODEN: BICHAW ISSN:0006-2960. AN 2007:1148158

P35

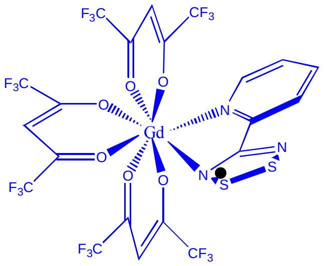
Low Coordinate, Metal Stabilized Phosphorus (I) Ligands: Synthesis and Remarkable Reactivity of the First Thermally Stable, Neutral, Electrophilic Phosphinidene Complexes of Vanadium [CpV(CO)$_3$(h^1-PNR$_2$)]. Todd W. Graham, Konstantin A. Udachin, Arthur J. Carty*, Steacie Institute for Molecular Sciences, 100 Sussex Drive, National Research Council of Canada, Ottawa, ON K1A 0R6*
tgraham@kctchem.com; carty.arthur@ic.gc.ca.



We have extensively investigated the remarkable reactivity of *cationic* complexes containing terminal electrophilic phosphinidene ligands (e.g. [Re(CO)$_5${η^1-P(N^{i}Pr$_2$)}]$^+$ and [CpFe(CO)$_2${η^1-P(N^{i}Pr$_2$)}]$^+$) which are analogues of Fischer carbene (L$_n$M=C(OR)R') complexes. We now report the synthesis of the first thermally stable *neutral* terminal electrophilic phosphinidene complexes [CpV(CO)$_3$(η^1-PNR$_2$)] (R = ^{i}Pr (**1**), Cy (**2**)); comparisons of the stability and reactivity of the new molecules to the well known transient species M(CO)$_5$(η^1-PR) (M = Mo, W) provides important insights into the bonding of these complexes. Compounds **1** and **2** are also the first electrophilic phosphinidene complexes of vanadium. The chemistry of **1** towards unsaturated substrates such as PhC≡CPh, bis-^{t}Bu-imidazol-2-ylidene, PhN$_3$ and Ph$_2$C=N=N has been investigated in order to probe the electrophilic (or nucleophilic) character of the P(I) ligand. These produce complexes containing P-coordinated phosphirenes [CpV(CO)$_3${P(N^{i}Pr$_2$)PhC=CPh}], 'abnormal' NCN carbene adducts [CpV(CO)$_3${P(N^{i}Pr$_2$)(4-cyclo-C$_3$H$_2$-1,3-(N^{t}Bu)$_2$)}], P-coordinated phosphaimine [CpV(CO)$_3${P(N^{i}Pr$_2$)=NPh}] and diazaphosphaimine [CpV(CO)$_3${P(N^{i}Pr$_2$)=N-N=CPh$_2$}] complexes, respectively. The complex [CpV(CO)$_3${P(N^{i}Pr$_2$)=NPh}] readily loses a CO ligand to afford the complex [CpV(CO)$_2${η^2-P(NiPr2)-NPh}], which contains a 4-electron donor η^2-(PN) ligand. The X-ray structures and bonding of the new complexes will be described.

P36

Lanthanide Coordination Complexes of a Neutral Radical Thiazyl Ligand Elisabeth M. Fatila and Kathryn E. Preuss. *Department of Chemistry, University of Guelph, Guelph, Ont. N1G 2W1.* efatila@uoguelph.ca, kpreuss@uoguelph.ca.



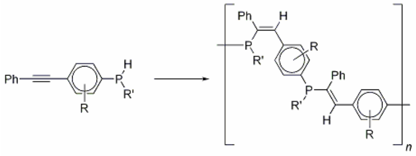
The magnetic properties of the neutral radical ligand 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl (pyDTDA) have been previously studied with paramagnetic 3d transition metals (1). The lanthanides are another group of metals which may coordinate to the pyDTDA ligand. The lanthanide 4f electrons, unlike the 3d electrons, penetrate the xenon core and therefore weakly overlap with ligand valence orbitals (2). The difference in electronic structure between the lanthanides and transition metals may yield interesting differences in their magnetic properties. Our research aims to coordinate the neutral radical ligand 4-(2'-pyridyl)-DTDA to lanthanide ions in order to determine the magnetic properties of these complexes.

Ref. (1) N.G.R. Hearns, K.E. Preuss, J.F. Richardson, S.Bin-Salamon. J.Am. Chem. Soc., **126**, 9942, (2004).
Ref. (2) S. Cotton. Lanthanide and Actinide Chemistry. Wiley, New York, 2006.

P37

Hydrophosphination as a Route to Phosphorus-Containing Polymers. Sharonna Greenberg,[a,b] Gregory L. Gibson,[a] and Douglas W. Stephan.[a,b] [a]*Department of Chemistry and Biochemistry, University of Windsor, Windsor ON, N9B 3P4.* [b]*Department of Chemistry, University of Toronto, Toronto ON, M5S 3H6.* **sgreenbe@chem.utoronto.ca**

The development of polymers containing inorganic elements remains a challenge compared to the well-developed field of carbon-based polymers. Polymers incorporating phosphorus in the main chain could have applications in catalysis or materials science. Our research has focused on hydrophosphination of alkynes as a new route to phosphorus-based polymers. To this end, various monomers incorporating both P−H and C≡C functionalities were synthesized and characterized, and their polymerization behavior was studied.



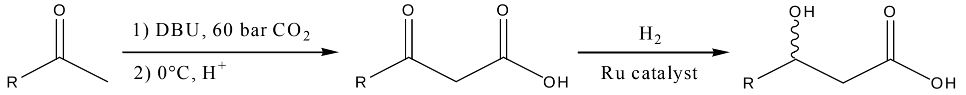
P38

CO_2 as a Reagent for the Catalytic Synthesis of β-Hydroxycarboxylic acids. Brendan J. Flowers, Robyn Service-Gatreau, Philip G. Jessop. *Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, K7L 3N6.* ***brendan.flowers@chem.queensu.ca***, *jessop@chem.queensu.ca*

Although carbon dioxide as a greenhouse gas is a serious environmental concern, it remains a valuable C1 source if viable methods are available for its conversion into useful products. Herein, we present recent progress in the synthesis of numerous β-keto carboxylic acids and the preliminary results from subsequent asymmetric hydrogenation to give β-hydroxy carboxylic acids.

These β-hydroxy carboxylic acids are valuable building blocks for asymmetric synthesis and medicinal chemistry; however, current synthetic methods, such as aldol-type and Reformansky-type reactions, are not stereoselective, and therefore are not ideal for industry. Noyori's pioneering work with β-keto esters has received a great deal of attention, but research into the asymmetric hydrogenation of α,β-unsaturated carboxylic acids and α-keto carboxylic acids is also significant. However, due to the inherent instability of β-keto carboxylic acids, caused by their facile decarboxylation, research using these substrates is almost non-existent.

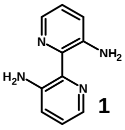
For the synthesis of the β-keto carboxylic acids, we investigated the effects of temperature, reaction length, and stoichiometry of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), which we found previously to promote carbon-carbon bond formation with CO_2. We then determined the effect of solvent choice and H_2 pressure on the asymmetric hydrogenation of such β-keto carboxylic acids. This reaction system is industrially advantageous due to the limited number of reactants required, their low-cost, and the potential for recycling unused materials.



P39

Synthesis, Reactivity and Coordination Chemistry of Novel 2,2'-Bipyridine Schiff-Base Ligands. Gumbau Brisa R.[a], Lin Z. H.[a], Wang J.[a], and Pilkington M.[a]. [a]*Department of Chemistry, Brock University, St. Catharines, Ont. L2S 3A1. mpilkington@brocku.ca*

Although 2,2'-bipyridines are widely used ligands in the field of supramolecular chemistry, reports of 3,3'-disubstituted-2,2'-bipyridines are surprisingly scarce.[1] Our group has recently targeted the preparation and study of 3,3'-disubstituted-2,2'-bipyridine ligands via the Schiff-base condensation of 3,3'-diamino-2,2'-bipyridine **1** together with suitable arylaldehydes. In this respect, condensation with salicylaldehyde and 2-formyl pyridine has afforded two new Schiff base *bis* imine ligands **2** and **3** respectively. The reactivity of both ligands is influenced by their susceptibility to nucleophilic attack at their imine functionalities, assisted via chelation to Lewis acidic metal ions. The intervention of these metal cations adds a surprising extra dimension to their reactivity.[2] The synthesis, reactivity and coordination chemistry of these two ligands will be presented.



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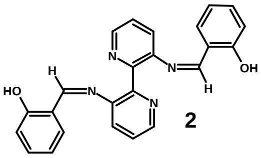

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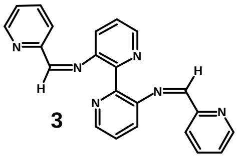

3

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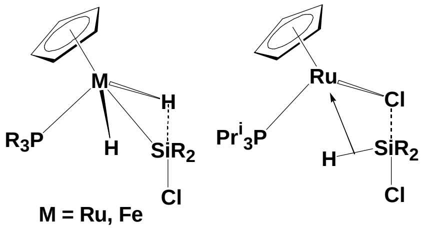
P40

Syntheses and X-ray diffraction studies of half-sandwich hydridosilyl complexes of ruthenium and iron. Dmitry V. Gutsulyak and Georgii I. Nikonov. *Department of chemistry, Brock University, 500 Glenridge Ave., St. Catharines, Ont. L2S 3A1.* **dg06to@brocku.ca**, **gnikonov@brocku.ca**

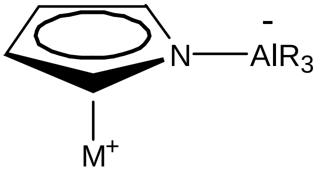


We investigated the effect of Cp-ring on the extent of nonclassical Interligand interactions Si-H in half-sandwich hydridosilyl complexes of ruthenium and iron. The reactions of novel trihydride complexes $CpRu(PR_3)H_3$ ($R_3 = Ph_3$ (**1a**), Ph_2Pr^i (**1b**), $PhPr^i_2$ (**1c**), Pr^i_3 (**1d**))[1] with $HSiMe_2Cl$ give hydridosilyl complexes $CpRu(PR_3)H_2SiMe_2Cl$ ($R_3 = Ph_3$ (**2a**), Ph_2Pr^i (**2b**), $PhPr^i_2$ (**2c**), Pr^i_3 (**2d**)) with Interligand Hypervalent Interactions (IHI).[2,3] Comparison of the X-ray structures of complexes **2a**, **2c** and **2d** shows that the strength of IHI decreases with the decreasing basicity of the supporting phosphines. Comparison of the X-ray structure of **2a** with its Cp* analogue shows stronger IHI in the former. The first examples of analogous iron complexes $CpFe(PPr^i_2Me)H_2SiR_3$ ($R_3 = Cl_3$ (**3e**), Cl_2Me (**3f**), $ClMe_2$ (**3g**), H_2Ph (**3h**)) were also prepared. Silane σ-complexes $CpRu(PPr^i_3)(Cl)(\eta^2\text{-H-}SiR_3)$ ($R_3 = Cl_3$ (**4e**), Cl_2Me (**4f**), $ClMe_2$ (**4g**), H_2Ph (**4h**)) were synthesized by the reaction of a new 16-electron complex $CpRu(PPr^i_3)Cl$ with silanes. According to X-ray analysis and NMR data (*J*(Si-H) = 33 Hz(**4e**), 41 Hz(**4f**), 50 Hz(**4g**), 37 Hz(**4h**)), complexes **4f** and **4g** exhibit simultaneous Si-H and RuCl◦◦◦SiCl interactions, which were previously observed in analogous complex $(C_5Me_5)Ru(PPr^i_3)(Cl)(\eta^2\text{-H-}SiClMe_2)$.[4] The strength of Si-H bonding is stronger in the Cp-series due to the weaker donor ability of Cp ring.

Ref. (1) D.V. Gutsulayk, G.I. Nikonov et al., *J. Organomet. Chem.*, **2007**, *692*, 5081; (2) G.I. Nikonov et al., *J. Am. Chem. Soc.*, **2003,** *125*, 642; (3) G.I. Nikonov, *Adv. Organomet. Chem.* **2005**, *53*, 217; (4) G.I. Nikonov et al., *Chem. Commun.*, **2005**, 3349.

P41

Ziegler-Natta Catalysis by Well-Defined Single-Site/Single-Component Zwitterionic Transition Metal Pyrrolide Complexes. Amir Jabri,[a] Sandro Gambarotta,[a] Robbert Duchateau.[b] [a]*Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N6.* [b] *Department of Chemistry, Technical University of Eindhoven, Eindhoven, Netherlands.* **ajabr076@uottawa.ca**

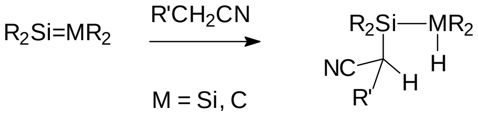


Since the discovery of highly active and selective olefin polymerization catalysis with transition metal salts activated by aluminum alkyls (Ziegler), the polyolefins industry has grown tremendously to the point of producing many hundreds of millions of metric tons of polyolefins annually. The accompanied progress in mechanistic understanding of this process in universities has led to new important commercial applications in catalysis. Recently, the fastest growing market segment is in engineered polymers like ethylene-hexene copolymer (LLDPE), and thus the demand for 1-hexene and 1-octene has soared. In response, industry has developed a new class of selective commercial catalysts for the production of these two alpha olefins. The most famous of these, a chromium-pyrrole-aluminum alkyl catalyst, is the subject our mechanistic investigation. We have isolated reactive catalytic intermediates in this previously misunderstood catalyst, giving us direct experimental evidence for a proposed “metallacyclic mechanism” which could account for the high selectivity observed, as well as guiding new catalyst design for this and other related catalytic processes. We present for the fist time the synthesis, characterization, mechanistic and catalytic studies of single-site/single-component zwitterionic pyrrolide complexes for both selective trimerization and polymerization, as well as some unanticipated new catalytic applications that have emerged in the course of this investigation.

P42

The Addition of Nitriles Containing an a-CH Bond to a Disilene and Two Silenes. Julie A. Hardwick and Kim M. Baines. *Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7.* jclatten@uwo.ca; kbaines2@uwo.ca

(Di)silenes, $R_2Si{=}SiR_2$ and $R_2Si{=}CR_2$, respectively, react with a variety of reagents including carbonyls, alcohols, and alkenes. However, the addition of nitriles to (di)silenes has not been thoroughly examined and therefore these reactions are of fundamental interest. As well, the addition products may be further functionalized if the CN triple bond remains intact.

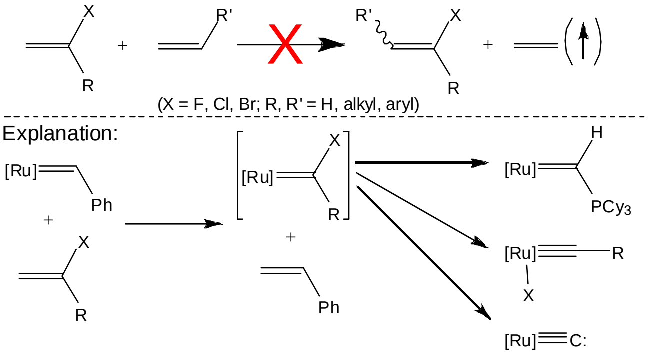


During a recent solvent effects study, acetonitrile adducts of tetramesityldisilene and a Brook silene were prepared. In both cases, the nitrile adds to the (di)silene through the CH bond rather than the CN triple bond. Further investigation into the addition of nitriles to (di)silenes has lead to the room temperature preparation and isolation of the acetonitrile adduct of dimesitylneopentylsilene as well as the observation of the phenylacetonitrile adduct of $Mes_2Si{=}SiMes_2$. The latter product was found to undergo an unprecedented hydrolysis and rearrangement. As previously observed for $Mes_2Si{=}SiMes_2$ and the Brook silene, the nitriles initially add through the α-CH bond rather than the CN triple bond. Since the nitrile group remains intact after addition to the (di)silene, the addition products may be further functionalized to form more complex silicon-containing compounds which would be inaccessible by other synthetic routes.

P43

Reactions of ruthenium alkylidene complexes with alkenyl halides. Marisa L. Macnaughtan, Jeff W. Kampf, J. Brannon Gary, and Marc J. A. Johnson. *Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.* mjaj@umich.edu

The failure of Ru-based complexes to effect cross-metathesis of vinyl halides is a long-standing limitation to the olefin metathesis method, given the importance of alkenyl halides as substrates for cross-coupling reactions. These reactions fail for two reasons. First, the ruthenium-halocarbene intermediates in the metathesis cycle are thermodynamically stable relative to the corresponding alkylidene intermediates. More importantly, the former complexes are susceptible to facile carbon-halogen bond scission. Formation of terminal carbide, carbine (alkylidyne), and phosphonioalkylidene complexes is discussed along with strategies to permit the desired cross-metathesis reactions.



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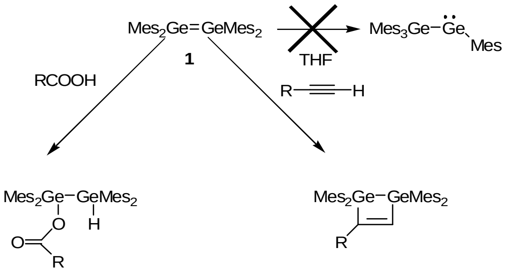
P44

Tetramesityldigermene: Synthesis, Reactivity and Structural Characterization Krysten L. Hurni, Paul A. Rupar, Nicholas C. Payne, Kim M. Baines *Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7* kbaines2@uwo.ca

Our group has had a long-standing interest in the chemistry of digermenes, typically employing tetramesityldigermene **(1)** as a prototypical substrate. The mesityl substituents are bulky enough to kinetically stabilize digermene **1**, but not too bulky to facilitate dissociation of digermene **1** to dimesitylgermylene. Previously, **1** was generated *in situ* because of its tendency to rearrange at room temperature. We recently reported the preparation of digermene **1** in THF. Under these conditions, digermene **1** does not rearrange, which has allowed the isolation and structural characterization of **1** for the first time. The reactivity of **1** with carboxylic acids alkynes will be discussed.

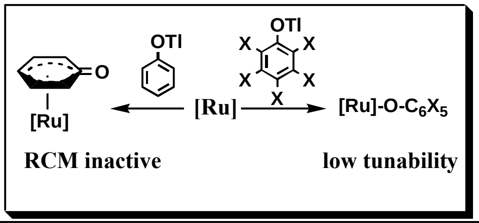


Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* DOI 10.1021/ef030044

P45

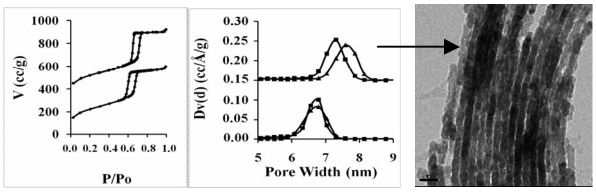
Ruthenium Aryloxide Catalysts: Balance Between Activity, Tunability, and Stability. Titel Jurca, Sebastien Monfette, Jay C. Conrad, and Deryn E Fogg. *Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* tjurc079@uottawa.ca, dfogg@uottawa.ca

Due to their versatility, robustness and ease of handling, Grubbs catalysts are now widely used by synthetic chemists. The importance of this type of catalyst stimulates research centered around improving their efficiency, as exemplified by the incorporation of NHC and labile ligands. Another way of improving the efficiency of catalysts is by the determination of their deactivation pathways in order to circumvent them. Our group and others have shown that Cl-bridged dimers are implicated in the deactivation of Grubbs catalyst. We therefore decided to investigate alternative anionic ligands. Phenoxide were first investigated, but their kinetic instability toward formation of catalytically inactive piano-stool structures led us to incorporate electron-deficient perhalophenoxides, which show impressive performance in RCM applications, in particular. However, the requirement of five halide substituents limits the tunability of the aryloxide ligands. We therefore undertook a study directed at establishing the minimum electron-deficiency required to prevent sigma-pi isomerization of the phenoxide ligand. As well, recent DFT studies in our group suggest that secondary interactions between o-Br groups on perbromoaryloxide ligands could affect catalytic activity. A synthetic target is therefore a 3,4,5-tribromophenoxide derivative, the activity and lifetime of which will shed light on the this issue. Implementation of catalysts bearing this new ligand in ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) processes will be presented.



P46

Tailoring mesoporosity and intrawall porosity in large pore silicas: Material synthesis and sorption behavior. François Bérubé, Rémy Guillet-Nicolas, Tae-Wan Kim, and Freddy Kleitz* *Department of Chemistry, Université Laval, Quebec G1K 7P4, Canada.* *freddy.kleitz@chm.ulaval.ca*



Ordered mesoporous SBA-15[1] & KIT-6[2] materials attract more and more the attention of scientists because of their interesting physicochemical characteristics and wide potential of applications.[3] Moreover, it was shown that these organized silicas could themselves be used as hard templates to create new ordered nonsiliceous materials;[4] this is possible because of their complementary intrawall porosity.[5,6] With regard to the development of SBA-15 materials, substantial efforts are being deployed to understand the effects of synthesis parameters (*e.g.* silica/block copolymer molar ratio, synthesis acidity, aging temperature and time) on the structural and textural properties of the material. We initiated therefore a systematic study to rationalize the effects of the different synthesis parameters on the sorption hysteresis behavior. All materials were characterized by N_2 sorption, low-angle XRD and TEM imaging with nanocasted cobalt oxide replicas[4] of the silica pore structures. A detailed analysis of the adsorption results demonstrates a correlation between porous network topology and sorption hysteresis behavior. Furthermore, the effects of synthesis parameters on pore size, pore connectivity and wall thickness of SBA-15 materials have been subtantiated. Modification of interconnections size is demonstrated and it represents a step forward in the tailoring and design of mesoporous silicas.

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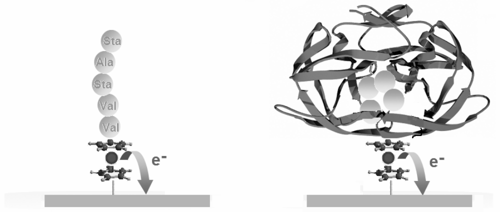
P47

Bioorganometallic approach for the electrochemical detection of HIV-1 protease Kagan Kerman,[a] Khaled A. Mahmoud,[b] Heinz-Bernhard Kraatz,[a] [a]*Department of Chemistry, University of Western Ontario, 115 Richmond St., London, ON N6A 5B7,* [b]*Biotechnology Research Institute, 6100 Royalmount Ave., Montreal, Quebec H4P 2R2* *kkerman@uwo.ca*, *hkraatz@uwo.ca*

This report demonstrates the proof-of-concept study of a new bioorganometallic approach showing that Ferrocene (Fc)-peptide bioconjugates bound to a transducer surface, hold promise for the electrochemical detection of clinically important proteins that have no redox-active centers, such as HIV-1 protease. The binding affinity of HIV-1 protease to a short peptide inhibitor, pepstatin, was elucidated for our method. As the enzyme concentration increased, the formal potential for the surface-bound Fc-pepstatin bioconjugate shifted to higher potentials, indicating that HIV-1 PR was binding to pepstatin and encapsulating the Fc redox center on the surface. The possibility of detecting HIV-1 PR in biological fluids was investigated as well as in the presence of other interfering proteins. This general procedure can be readily applied in the future to the detection of other biomolecules in complex matrixes.



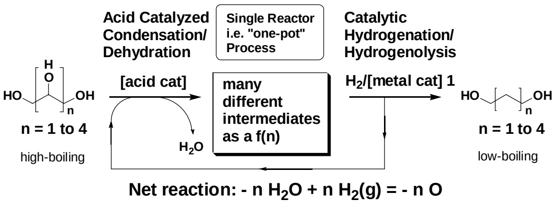
Ref. (1) Kerman, K., Mahmoud, K. A., Kraatz, H.-B. *Chem. Commun.,* **2007**, 3829-3831.

P48

Ruthenium Carbonyl Catalysts for the Selective Deoxygenation of Polyols. Eike Kunst,[a] Marcel Schlaf, [a] *Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1.* ekunst@uoguelph.ca, mschlaf@uoguelph.ca

Glycerol is produced at ~ 1 MMt/year from the manufacturing of biodiesel as a potentially valuable by-product.[1] Due to this abundance of glycerol, processes which transfer polyols into comparably more valuable feedstocks are worth exploring. For example, 1,3 propanediol serves as a monomer unit for the polymers Sorona^{TM} and Corterra^{TM}.

For this project ruthenium carbonyl complexes with the thermal robustness required for the deoxygenation of glycerol are being developed.[2] A diverse class of ruthenium carbonyl aqua complexes have been prepared and their activity in the deoxygenation of diol model systems is being investigated. Complexes bearing ligands with proton-donating groups in close proximity to the ruthenium centre, potentially enabling a metal-ligand bifuntional hydrogenation mechanism,[3] will be compared to the corresponding parent systems.



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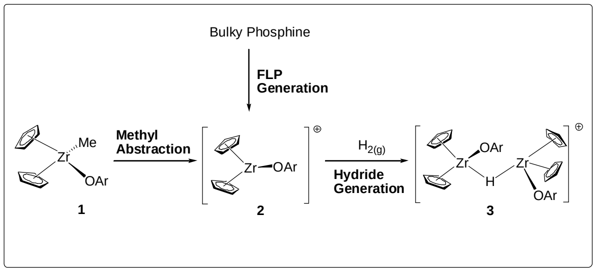
P49

Synthesis of Group (IV) Metal Hydrides via Frustrated Lewis Pair Interactions. Ojisamola A. Labeodan,[a] Douglas W. Stephan.[a]
[a].*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **labeoda@uwindsor.ca**, stephan@uwindsor.ca

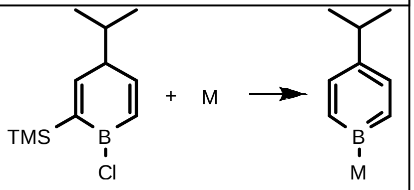
Our research group recently introduced the new concept of "Frustrated Lewis Pairs" (FLP) wherein sterically demanding Lewis acids and bases do not interact in the expected donor-acceptor fashion, but rather exhibit unique reactivity. To date this concept of FLPs has been limited to main group systems. In this presentation we demonstrate that Lewis acidic early metal cations can also react with sterically demanding donors to exhibit unique reactivity. In this initial report we describe the reactions of early metal cations, sterically hindered phosphines and hydrogen. This affords a unique route to early metal hydride species.



P50

Coordination of borabenzene with rich platinum(0) complexes, André Languérand and Frédéric-Georges Fontaine, *Department of Chemistry, Université Laval, Québec, Qc G1K 7P4.*

Since the discovery of borabenzene by Herberich[1] in 1970, several borabenzene and boratabenzene transition metal complexes have been synthesized and characterized. To our knowledge, all of these complexes feature a η^6 coordination *via* the aromatic ring and none exploit the Lewis acidic nature of boron to coordinate nucleophilic transition metal. We will discuss the different experiments conducted with a borabenzene precursor in order to investigate its behaviour as a Lewis-acid in the presence of electron rich platinum(0) complexes.



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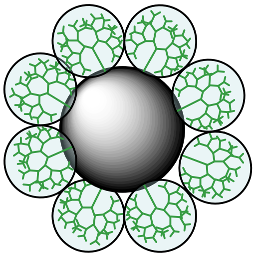
P51

Nano-structural assembly of dendreimer. Anas Lataifeh,[a] and Heinz-Bernhard Kraatz.[a] [a]*Department of Chemistry, University of Westren Ontario, London, Ont. N6A 5B7.* alataife@uwo.ca

Dendritic ligands have been shown to control both size and stability of encapsulated metal nanoparticles[1], mainly due to inherent branched architectures of the dentritic ligand. However, none of the previously reported dendritic metal nanoparticles has used large nano-sized dendrimer to modify nanoparicles to build up inorganic-organic hydrid 2D/3D nanoscale arrays.

This poster describes the synthesis and use of 2.4 nm sized glutamic acid based dendrimer surface modified with disulfide ligand that is covalently attached to the surface of 5.0 nm gold nanoparticles.



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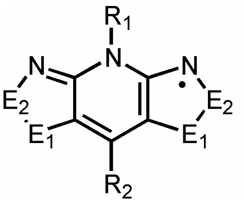
P52

Polymorphism in Heavy Atom Heterocyclic Radicals.

Alicea A. Leitch, Kristina Cvrkalj, Craig M. Robertson, Robert W. Reed, and Richard T. Oakley. *Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1.* **aaleitch@sciborg.uwaterloo.ca**, oakley@sciborg.uwaterloo.ca



	E_1	E_2
1	S	S
2	S	Se
3	Se	S
4	Se	Se

Recent studies on heavy atom heterocyclic radicals have demonstrated their potential for applications in magnetic and conductive materials. The Oakley group has studied compound **1**, as it meets the necessary energetic criteria for good conductivity. Unfortunately, the bandwidth *W* in these systems is insufficient to overcome the onsite Coulomb repulsion *U*, and they are Mott insulators. In order to increase the intermolecular interactions in system **1**, and hence the bandwidth and conductivity, selenium, a more spatially disperse chalcogen, has been incorporated to obtain compounds **2**, **3** and **4**.[1] Depending on the selenium content and choice of R_1 and R_2 groups, these heterocyclic radicals crystallize in a variety of packing arrangements. What appears to be a minor molecular modification can make a dramatic difference to the space group, and hence the transport properties.

We hoped that the incorporation of selenium into **1** would give an isostructural set of compounds (**1**, **2**, **3** and **4**), and allow for the observation of improved *W* on the transport properties. This was possible in the case of R_1 = Et, R_2 = Cl, where a complete family of compounds was found to crystallize in the same space group. However, the R_1 = Me, R_2 = Cl series was complicated by the presence of polymorphism, and this poster describes the successes and challenges associated with the multiple phase issue.

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P53

Synthesis of Rhenium Molecular Magnetic Materials with the bis(bipyridyl) ligand.

Brian Li Tai Tsat,[a] Tara Burchell,[a] and Muralee Murugesu,[a] [a]*Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* ***blita094@uottawa.ca,*** *m.murugesu@uottawa.ca*

Molecular nano-magnetism is an up and coming field in material science, which involves the synthesis and study of nanoscale magnetic molecules. In recent years, this field has generated a large amount of interest due to the possible application of these materials in molecular electronics such as memory storage devices. Two particularly interesting areas in molecular magnetism are single-molecule magnets (SMMs) and single chain magnets (SCMs). Such molecules derive their properties from a combination of a large ground state spin (S) value and an Ising (or easy-axis) type of magnetoanisotropy (negative zero-field splitting parameter, D).

The overall aim is to develop novel synthesis methodologies to produce new SMMs and SCMs in order to improve our understanding of these interesting phenomenons. For this reason, transition metal chemistry is being exploited as their complexes exhibit properties which are comparable to the nanoparticles. Due to their orbital size and the presence of spin orbital angular momentum, 4d and 5d transition metals represent an even more interesting class. Complexes with these metal ions are more likely to exhibit a large magnetoanisotropy thus yielding novel SMMs and SCMs.

In this respect, synthesis of rhenium bis(bipyridyl) complexes are being explored. Furthermore, the planar bis(bipyridyl) ligand is also an ideal candidate for making mononuclear building block which subsequently be employed for the isolation of novel SCMs using building block approach.

P54

Experimental and Theoretical Examination of C-CN and C-H Bond Activations of Acetonitrile Using Zerovalent Nickel.

Ting Li,† Tulay A. Atesin,† Sebastien Lachaize,† William W. Brennessel,† Juventino J. Garcia,‡ and William D. Jones*,† *Contribution from the †Department of Chemistry, University of Rochester, Rochester,New York 14627, and ‡Facultad de Quimica, Universidad Nacional Autonoma de Mexico,Mexico City, Mexico, D.F. 04510*

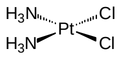
Experimental and density functional theory show that the reaction of acetonitrile with a zerovalent nickel bis(dialkylphosphino)ethane fragment (alkyl) methyl, isopropyl) proceeds via initial exothermic formation of an h^2-nitrile complex. Three well-defined transition states have been found on the potential energy surface between the h^2-nitrile complex and the activation products. The lowest energy transition state is an h^3-acetonitrile complex, which connects the h^2-nitrile to a higher energy h^3-acetonitrile intermediate with an agostic C-H bond, while the other two lead to cleavage of either the C-H or the C-CN bonds. Gas-phase calculations show C-CN bond activation to be endothermic, which contradicts the observation of thermal C-CN activation in THF. Therefore, the effect of solvent was taken into consideration by using the polarizable continuum model (PCM), whereupon the activation of the C-CN bond was found to be exothermic. Furthermore the C-CN bond activation was found to be favored exclusively over C-H bond activation due to the strong thermodynamic driving force and slightly lower kinetic barrier.

Ref. Atesin, T. A.; Li, T.; Lachaize, S.; Brennessel, W. W.; Garcia, J. J.; Jones, W. D. *J. AM. CHEM. SOC.* **2007**, *129*, 7562-7569.

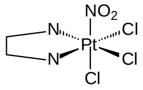
P55

Synthesis, Characterization and Properties as a Stat3 Inhibitor of the Prototypical Platinum(IV) Anticancer Drug, CPA-7. Littlefield, S.L. Presenter and Baird, M.C. Professor. *Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.* Shalyn.littlefield@chem.queensu.ca, bairdmc@chem.queensu.ca

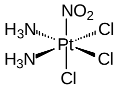
Although the prototype platinum-based anti-tumor drug is *cis*-$PtCl_2(NH_3)_2$ (cisplatin), a series of platinum(IV) compounds such as $PtCl_4$ and the nitro compounds CPA-1 and CPA-7 have also recently been found[1] to be promising inhibitors of the signal transducer and activator of transcription-3 (Stat3), a protein frequently up-regulated in a variety of human cancers.[2]



cisplatin



CPA-1



CPA-7

While this novel drug CPA-7 has the potential to be very useful in modern medicine, there is no accepted synthesis or any previous reports of its characterization. We have therefore assessed and modified a rather generic, patented procedure describing the synthesis of a family of Pt(IV) nitro complexes,[3] and have successfully synthesized several batches of a yellow substance which is found to behave appropriately as a Stat3 inhibitor and which we therefore believe is representative of Stat3 inhibitors used elsewhere. In an effort to identify the products obtained as containing the compound $PtCl_3(NO_2)(NH_3)_2$, with the structure shown above, and to establish criteria by which this compound can be identified, we have also characterized the products obtained by IR spectroscopy, ^{195}Pt, ^{14}N, ^{15}N and ^{1}H NMR spectroscopy, and single crystal X-ray crystallography.

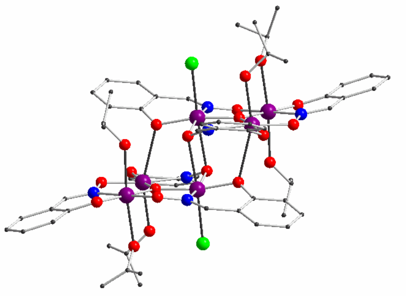
1. Rosenberg, B.; VanCamp, L.; Trosko, J. E.; Mansour, V. H. *Nature (London)* **1969**, *222*, 385.
2. Yu, H.; Jove, R. *Nat. Rev. Cancer* **2004**, *4*, 97.
3. Kay, H.; Palmer, J. W.; Stanko, J. A.; Sebti, S. M. U.S. Pat. Appl. Publ. (2005), US 2005288365.

P56

Synthesis of New Manganese Single Molecule Magnets. Po-Heng Lin,[a] Tara Burchell, [a] Ilia Korobkov ,[a] Rodolphe Clerac[b] and Muralee Murugesu.[a] [a]*Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.* [b] *CRPP-CNRS 8641, 115 Ave. du Dr. A. Schweitzer, 33600 Pessac, France.* **plin033@uottawa.ca**, m.murugesu@uottawa.ca

Single Molecule Magnets (SMMs) represent a molecular approach to nanoscale magnetic materials. Such molecules derive their properties from a combination of a large ground state spin (S) value and an Ising (or easy-axis) type of magnetoanisotropy (negative zero-field splitting parameter, D). They also display quantum properties such as quantum tunneling of magnetization (QTM) and quantum phase interference. Our aim is to develop novel synthesis methodologies to produce new SMMs in order to improve our understanding of these interesting phenomenons.

With this in mind, we are currently investigating the use of a tridentate oximate ligand (salicyaldoxime ($saeH_2$)) in the synthesis of new metal cluster complexes. Reaction of $MnCl_2$, $saeH_2$ in presence of Et_3N in isopropanol yielded in a hexanuclear manganese cluster, $[Mn^{III}_6(\mu_3\text{-}O)_2(sae)_6(OC_3H_7)Cl_2]$ (**1**). Variable-temperature solid-state magnetic susceptibility studies reveal that complex (**1**) has a S = 4 spin ground state and the slow relaxation of magnetization reveal it's SMM nature.



$[Mn^{III}_6(\mu_3\text{-}O)_2(sae)_6(OC_3H_7)Cl_2]$ (**1**)

P57

Synthesis of ferrocenoyl functionalized copper and silver chalcogenolate cluster complexes
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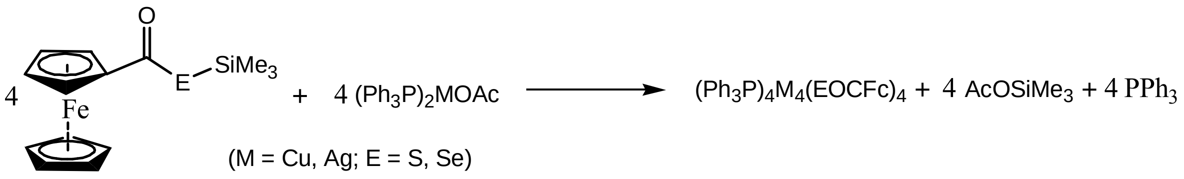
dmacdo9@uwo.ca, *jfcorrig@uwo.ca*

A novel series of silylated ferrocenoyl chalcogenide reagents, $FcCOESiMe_3$ (E=S,Se,Te; Fc=ferrocene), can be prepared in very good yield from FcCOCl and $LiESiMe_3$. These reagents are used in the preparation of triphenylphosphine-ligated copper and silver ferrocenoyl chalcogenolate complexes, $(Ph_3P)_4M_4(EOCFc)_4$, (M=Cu,Ag; E=S,Se) and $(Ph_3P)_2Cu_2(SeOCFc)_2$ from solublilized copper and silver acetate. The structures of these complexes have been determined via single-crystal X-ray diffraction. The driving force guiding these reactions is the thermodynamically favorable formation and elimination of $AcOSiMe_3$. The synthesis and characterization of both starting reagents and cluster complexes will be presented.



(M = Cu, Ag; E = S, Se)

P58

Synthetic Routes to 1,2,3-Dithiazyl Radicals as Potential Spin-Bearing Ligands

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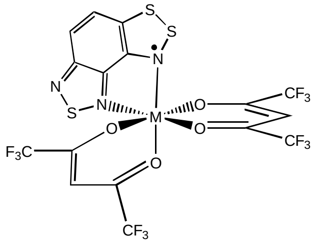
This poster presents preliminary synthetic strategies toward 1,2,3-dithiazyl radical ligands and their transition metal coordination complexes. While thiazyl radical chemistry is well-established, the coordination of radicals which incorporate nitrogen and sulfur based heterocycles into their molecular framework has only come under investigation in the last twenty years. To date, the use of a 1,2,3-dithiazyl (DTA) fragment as a building block for radical ligands has not been reported. These ligands could provide systems with remarkably different chemical and physical properties compared with the 1,2,3,5-DTDA and 1,3,2-DTA ligands currently known[1]. Calculations presented herein provide evidence that the incorporation of a 1,2,3-DTA fragment into a ligand structure will result in a greater delocalization of the singly occupied molecular orbital (SOMO) spin densities over a larger molecular area. This could have repercussions with respect to how these ligands interact in the solid state, and by extension, on the conductivity and magnetism of the coordination complexes in the solid state.



Ref. (1) Preuss, K.E. *J. Chem. Soc. Dalton Trans.*, **2007**, 2357.

P59

Detection of Chemical Warfare Agents by Electrochemical Means.

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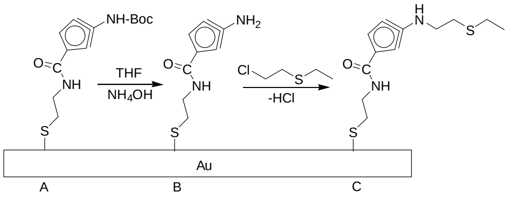
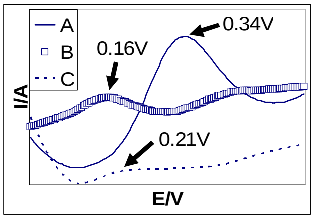
Misuse of chemical warfare agents (CWA) is of growing concern; thus, their detection is of increasing importance. Current onsite detection methods require high concentrations for detection. Our objective is to detect CWAs at low concentrations (ppm scale) via an electrochemical system. This system consists of [Boc-HN-Fc-CO-CSA]$_2$ - a ferrocene (Fc) derivative conjugated to a cystamine linker[1]. This sulfur-containing linker allows for self-assembled monolayers on gold surfaces [A]. CWAs react with the Boc-deprotected form [B] at the amino group producing electrochemical changes on the Fc probe. The product molecule [C] allows for detection by potentiometric methods such as differential pulse voltammetry.

Ref. (1) Khan, MAK; Long, Y-T; Schatte, G; Kraatz, H-B. Anal. Chem. **2007**, 79, 2877-2884.





P60

Octomeric Zr(III) Cluster Supported by Hemilabile Dipyrrole Ligand System.

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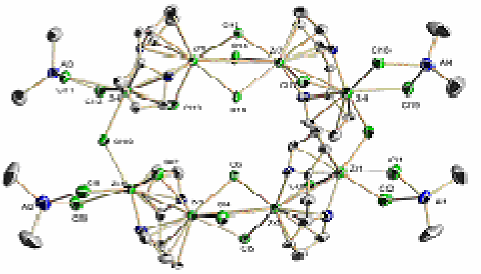

The Cyclopentadiene(Cp) ligand system has been widely explored and studied on a variety of different metals. A hemilabile ligand system which is analogous to the Cp ligand could change the reactivity and stability significantly. The use of the pyrrolide anion(analogous to Cp) has the ability to form σ or π bonded complexes. Although the σ case may be preferential, the use of a strong lewis acid such as AlX_3 (X=halogen,alkyl), can lock the N sp^2 orbital and force π bonding to the metal. This resulting complex could have its bonding mode and hemilability tuned, based on Lewis acid selection. Previous work in our research lab produced single component catalysts from metals not notoriously known for catalysis (ie. V). Following similar strategies, the group IV metals were explored, as low valent Ti or Zr would be expected to be single component catalysts. Successful Zr(IV) structures have been obtained containing a π-bonded pyrrolide anion, and reduction of them has appeared to be successful. Dipyrrole ligands have appeared to be capable ligands to stabilize the Zr(III) oxidation state, as the formation of an octomeric Zr(III) complex was observed and structurally characterized making use of the above strategies. Preliminary results about the chemical behavior of this species will be presented.

P61

Substituted Crown Ethers for Building [2]Rotaxanes, and Metal Organic Rotaxane Framework (MORF)s

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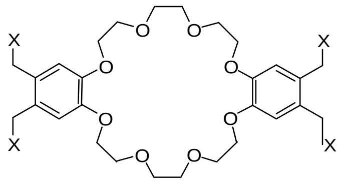
We have previously employed pseudrotaxanes containing 1,2-bis(4,4'-bypyridinum) ethane or its bis N-oxide derivatives as axles in building MORFs. As the metal-ligand framework and wheel component are completely separate entitles, it should be possible to retain the basic framework while turning the physical properties of the material by introducing substitutions on the 24-membered ring. Here in, we present the synthesis of new crown ethers as components for building functionalized MORFs, and [2]Rotaxanes. The synthesis and characterization of the new crown ethers and the physical properties of these crown ethers in pseudrotaxanes formation, and [2]Rotaxanes will be presented. A new 1,2-bis(4,4'-bypyridinum) ethane hybrid axle will also be introduced.



X = Br, O-Ph, O-Ph(COOEt)

P62

Synthesis of new spin bearing ligands which have potential to be single molecule magnets when coordinated to high spin d-block metals.

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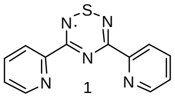
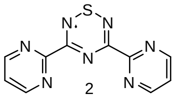
imorgan@uoguelph.ca, kpreuss@uoguelph.ca



1



2

The sulphur-nitrogen radical ligands, 3,4-di(pyrid-2-yl)-1,2,4,6-thiatriazine (TTA), **1,** and 3,5-di(pyrimidin-2-yl)-1,2,4,6-thiatriazine,**2**, have been designed to be spin bearing ligands and when coordinated to a variety of high spin transition metals, will effectively mediate magnetic coupling between them. The synthesis route to develop ligand **1** is modelled after a similar known route[1] and once fully characterized, the process to develop ligand **2** should be comparable. Ligand **2** is designed to chelate three high spin transition metals. It is anticipated that the coordination of two Mn^{2+} (in the bidentate sites) along with one Mn^{3+} (in the tridentate site) will produce a magnetic complex. The two Mn^{2+} ions (hs-d^5) generate a large spin quantum number (S) and Mn^{3+} is known to give rise to large axial magnetoanisotropy ($D < 0$). The combination of both the large spin quantum number and the negative magnetoanisotropy is the perfect mechanism for generation of a single molecule magnet. This poster will present recent findings of the synthesis of ligand **1**.

[1] Oakley, R. T.; Reed, R. W., Cordes, W. A., Craig, S. L., Graham, J.B. *J. Am. Chem. Soc.,* **1987**, 109, 7745-7749.

P63

Iron(II) Complexes with New Tetradentate PNNP and Tridentate PNN Ligands

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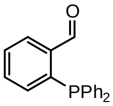
Second and third row transition metals complexes with tetradentate PNNP ligands showed high catalytic activity in the enantioselective transfer and H_2-hydrogenations of polar unsaturated bonds[1]. They have been obtained mostly from condensation of different diamines with 2-(diphenylphosphino)benzaldehyde (**1**). The uniqueness of (**1**) in PNNP ligand formation arises from its unusual stability, compared to other amphoteric phosphinoaldehydes, which can polymerize and are air sensitive. The benzene ring in this core structure gives rigidity to the catalyst, and stability to the ligand and its amphoteric precursor. On the other hand, the benzene ring restricts ligand optimization. Here we report the preparation of the stable precursor **2**,[2] which we use for the formation of PNNP and PNN ligands. The advantage of (**2**) is that electronic and steric properties of corresponding ligands can be adjusted by varying R-groups. Template synthesis of iron(II) complexes using various diamines and the dimer was studied in different conditions to give bis-tridentate (**3**) and tetradentate (**4**) complexes.



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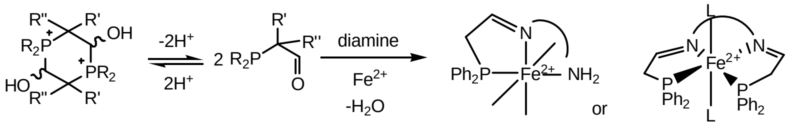


2 **3** **4**

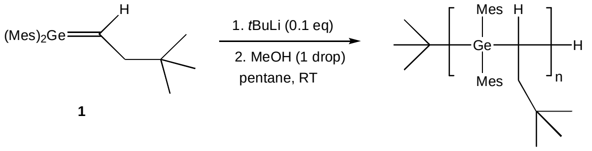
Ref (1). Gao, J. X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087. (2). D. Matt *New Journal of Chemistry* **1996**, 20, 1258.

P64

Germene Reactivity: Alkyne Addition and Polymerization.

Laura C. Pavelka,[a] Simon J. Holder,[b] Kim M. Baines.[a] [a]*Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7.* [b]*School of Physical Sciences, University of Kent, Canterbury, UK CT2 7NH.* lcpavelk@uwo.ca, kbaines2@uwo.ca

Germenes (Ge=C) are highly reactive species relative to their all carbon analogues, alkenes. As a result, germenes can be versatile starting materials to synthesize a variety of new organogermanium compounds. Cycloaddition, involving heavy main group element alkene analogues, is a common method to synthesis new heterocycles and in this study the cycloaddition reactivity of dimesitylneopentylgermene (**1**) with alkynes was examined and the results will be presented. Also, the potential of germene **1** to function as a polymer precursor was investigated. Recently, phosphaalkenes (P=C) have been shown to undergo addition polymerization in a similar manner as alkenes (using anionic and radical initiators) to form polymethylenephosphines.[1] Addition polymerization is a common method for organic polymer preparation and the expansion of this chemistry to inorganic systems has the potential for many new and exciting inorganic polymers. Germene **1** is a good candidate as a polymer precursor since it is readily prepared in large quantities and in high purity. A description of the initial work into the polymerization of germene **1** will be discussed.



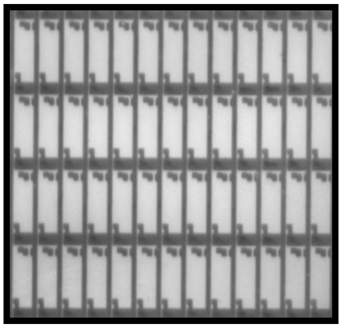
Ref. (1) Tsang, C.-W.; Yam, M.; Gates, D. P. *J. Am. Chem. Soc.* **2003**, *125*, 1480.

P65

New, Low-Cost Fabrication Methods for Polymer-Based Electronic Devices.

Michael S Miller,[a] Gregory J.E. Davidson,[a] and Tricia Breen Carmichael.[a] [a]*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* mille2h@uwindsor.ca

We present an unconventional, low-cost fabrication method to deposit patterned metal films–an integral part of any electronic device – on polymeric substrates. We use microcontact printing of Aluminum (III) tetraphenylporphyrin (Al-TPP) onto polymeric surfaces which have been chemically oxidized or plasma treated to generate carboxylic acid groups. The patterned Al-TPP layer can then bind Pd/Sn colloids, which catalyze the electroless deposition of copper cleanly within the printed pattern. This general fabrication method can be applied to many polymers of technological importance and will be demonstrated with flexible poly(ethylene terephthalate) and mechanically rigid epoxy-based photoresist SU-8.



P66

Synthesis and catalytic reactivity of molybdenum imido hydrides.

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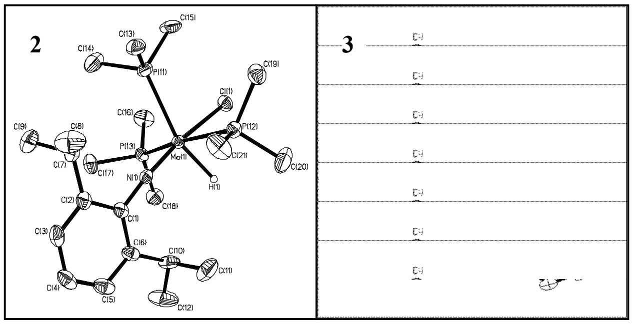
Treatment of (ArN=)Mo$(PMe_3)_3(Cl)_2$[1] with two equivalents of $LiBH_4$ allows for preparation of new bis(borohydride) complex, (ArN=)Mo$(PMe_3)_2(\eta^2\text{-}BH_4)_2$ (**1**). Complex **1** reacts with Me_2SiHCl and $PhSiH_3$ to give hydride derivatives (ArN=)Mo(H)(Cl)$(PMe_3)_3$ (**2**) and (ArN=)Mo(H)$(SiH_2Ph)(PMe_3)_3$ (**3**), respectively. Alternatively and more efficiently, compound **2** can be prepared by the reaction of (ArN=)Mo$(PMe_3)_3(Cl)_2$ with one equivalent of L-Selectride. These novel derivatives were characterised by spectroscopic methods and X-ray analysis. The structure of **3** is unusual in that the hydride is placed trans to the imido group. Although these compounds (RN=)Mo$(PMe_3)_3$(H)(X) are isoelectronic and isolobal with metallocene hydrides Cp_2M(H)(X) (X = H, Cl, SiR_3), their reactivity is different. The less bulky imido ligand allows for more space around the metal atom, and studies show that **2** and **3** are active catalysts for hydrosilation of aldehydes and ketones and show moderate activity towards alkenes and alkynes.



Ref. (1) Ignatov S.K., Rees N.H., Dubberley S.R., Razuvaev A.G., Mountford P., Nikonov G.I. *Chem. Commun.,* **2004**, 952-953.

P67

New bioinorganic macrocyles and their use in synthesizing of topologically linked catanes and rotaxanes.

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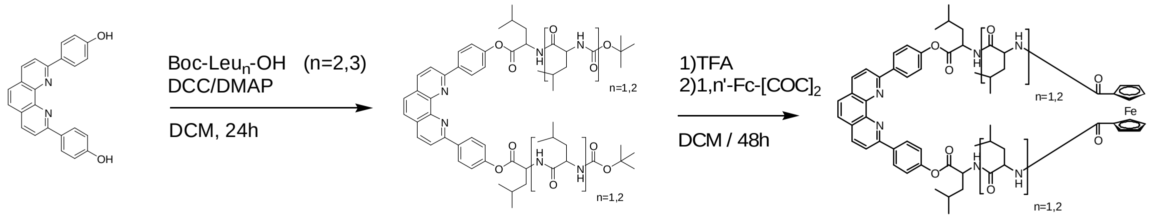
The synthesis of bioinorganic cyclic molecules has been studied by our group for a number of years[1]. We have now expanded our study to include the study of peptide rotaxanes and catenanes. Both rotaxanes and catenanes have been reported in a number of protein structures[2]. The compounds to be synthesized are to act as models for this new secondary structural element found in proteins. In addition, we gain a better understanding of the synthetic approach of topologically linked molecules.

Here we will report the results of our studies in which diphenol phenanthroline (Dpp) was chosen as a turn inducer and also as a complexing site for catenane synthesis which is linked to a redox active ferrocene group (Fc) via a peptide spacer.



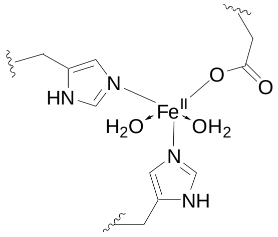
(1) S. Chowdrury, et al. Dalton Trans. **2004**. 1726-1730.
(2) W. R. Wikoff, *et al.* Science. 289. **2000**. 2129-2133.

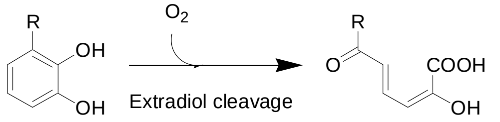
P68

Investigation of the Determinants of Suicide Inactivation in Extradiol Dioxygenases

Sara S. Rocks[a], Timothy E. Machonkin[b] and Patrick L. Holland[a] [a]*Department of Chemistry, University of Rochester, Rochester, NY 14627* [b]*Department of Chemistry, Whitman College, Walla Walla, WA 99362* **srocks@mail.rochester.edu**

Extradiol catechol dioxygenases (EDOs) use molecular oxygen to regiospecifically cleave catechols. The active site of the enzyme contains an Fe(II) ion ligated to two histidine residues and a glutamate residue, and situated in a pocket with a complex second-coordination sphere hydrogen bonding network. These enzymes are of interest for the bioremediation of polychlorinated biphenyls (PCBs). However, not all PCBs can be cleaved successfully by dihydroxybiphenyl dioxygenase. Certain substrates lead to suicide inactivation of the enzyme, which creates a roadblock in the bioremediation of PCBs, therefore making EDOs an important target for study. The high-spin Fe^{II} active site is not amenable to electronic absorption or EPR spectroscopies, but paramagnetic NMR spectroscopy can be used to investigate the electronic structure of the active site of the enzyme as well as synthetic models. This contribution reports NMR studies of enzyme-substrate adducts and of synthetic model complexes that mimic the coordination environment of the enzyme.



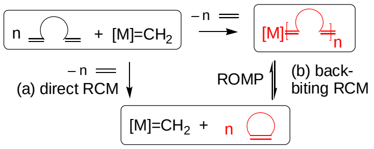


P69

Effective Molarities in Ring-Closing Metathesis, Guidelines for a Successful Reaction.

Sebastien Monfette,
Maureen E. Robinson, Philippa R. Payne, Jay C. Conrad and Deryn E. Fogg* *Department of Chemistry, University of Ottawa, Ottawa ON, Canada K1N 6N5.* smonf065@uottawa.ca, dfogg@uottawa.ca

Cyclization reactions are of fundamental importance in organic chemistry.[1] Optimization of reaction conditions and choice of catalyst, however, remain largely a matter of trial and error. In order to efficiently plan synthetic routes incorporating RCM, there is a growing need to improve our understanding of factors that affect the probability of success. Substrate concentration has long been known to play a crucial role in determining the bias toward intramolecular cyclization vs. intermolecular oligomerization reactions.[2] Classic studies by Illuminati and Mandolini applied the concept of effective molarity (EM) to elucidating these relationships.[3] However, the correlation between concentration, ring strain, and the probability of cyclization has been little explored in context of RCM. We recently described the operation of concentration-dependent, oligomerization-backbiting equilibria in RCM of conformationally flexible α,ω-dienes via the Grubbs second-generation catalyst.[4] We wished to establish, first, whether other catalysts share the kinetic bias of the second generation catalyst toward oligomerization of all but high-EM substrates, and secondly, whether they likewise participate in backbiting. Here we describe the very different behaviour characteristic of different catalysts, which partition into those operating by direct (kinetic) and by indirect (thermodynamic) RCM.



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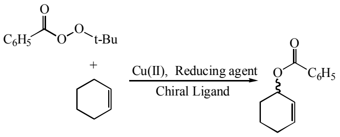
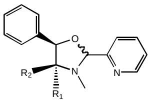
P70

Pyridyloxazolidine-stabilized Copper Colloid in The Asymmetric Kharasch-Sosnovsky Reaction. Elizabeth T. J. Strong and Nathan D. Jones. *Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7*

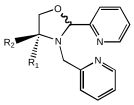
Pyridyloxazolidines **1-5**[1] were made via condensation reactions in high yields and good diastereoselectivity. These compounds have been applied as stereodirecting ligands in the asymmetric Kharasch-Sosnovsky reaction. No clear relationship between ligand structure and reactivity has yet been established either in our work or in existing literature reports.[2-6] Perhaps the most interesting aspect of the reaction is that *in situ* generation of the catalyst by reduction of a Cu(II) precursor has exhibited improved reactivity over direct catalyst formation using a Cu(I) salt.[3] Using dynamic light scattering (DLS) and transition electron microscopy (TEM) we have shown that this reaction pathway involves the formation of Cu nanoparticles that decay in size to <1 nm as the reaction proceeds. Preliminary work has shown that the diameter of the particles is heavily dependent on factors such as temperature, concentration and solvent. This behavior may go towards explaining the variable literature reports concerning this important asymmetric C-H bond activation.



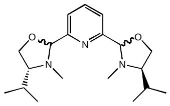
The Asymmetric Kharasch-Sosnovsky Reaction



1: $R_1 = CH_3$ $R_2 = H$
2: $R_1 = H$ $R_2 = CH_3$



3: $R_1 = Bn$ $R_2 = H$
4: $R_1 = H$ $R_2 = Bn$



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P71

Homo- and copolymerization studies of ethylene and polar comonomers initiated by a Brookhart-type nickel (II) α- diimine precatalyst. Heidi Murray,[a] and Dr. M. C. Baird.[b] [a, b]*Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.*
heidi.murray@chem.queensu.ca, bairdmc@chem.queensu.ca

Investigations into the homopolymerization of ethylene and the copolymerization of ethylene with (allyloxy)trimethylsilane as a polar comonomer are reported. Polymerization was initiated using the MAO activated 1, 4-bis(2, 6-diisopropylphenyl) acenaphtene diimine nickel (II) dibromide precatalyst. The polyethylene obtained was highly branched with turnover frequency comparable to that obtained by Brookhart et al. and the polar comonomer was successfully incorporated into the polymer backbone with a 3% rate of incorporation.

References: (1) Gibson, V.; Spitzmesser, S.; *Chem. Rev*. **2003**, 103, 283-315;
(2) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, 117, 6414- 6415;
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P72

New Development in the Field of Nickel Complexes Supported by Novel Bis-iminopyridine Ligand.
Indira Thapa**,** Sandro Gambarotta, *Department of Chemistry, University of Ottawa, Ottawa, Ontario*

In natural processes, the enzyme nitrogenase catalyzes the process of dinitrogen fixation and its transformation into the most useful biological form, ammonia. This process occurs in ambient environment at the metal-sulfur centre in the centre of the Mo-Fe protein. However, the mechanism of this process is largely unknown. Dinitrogen chemistry involving late transition metal is less developed compared to early and f-block systems. Research is thus focused on the metal complexes that bind dinitrogen and facilitate reduction or oxidation under mild conditions. Novel bis-iminopyridine ligand is established for its ability to stabilize nickel complexes. We are thereby, describing the synthesis and characterization of novel nickel dinitrogen complex supported by bis-iminopyridine ligand system. Further reduction of this complex resulted in a novel nickel-hydrido complex. Mechanistic insight and application of these novel nickel complexes will be presented.

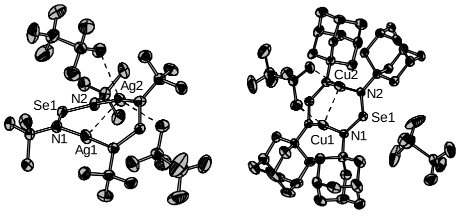
P73

Selenium Diimides as Ligands in Transition Metal Complexes.

Maarit Risto,[a] Teemu T. Takaluoma,[a] Tom Bajorek,[a] Raija Oilunkaniemi,[a] Risto S. Laitinen,[a] and Tristram Chivers.[b] [a]*Department of Chemistry, P.O. Box 3000, FI-90014 University of Oulu, Finland.* [b]*Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta T2N 1N4, Canada.* **maarit.risto@oulu.fi**

Selenium diimides have been known for over 30 years.[1] Unlike monomeric sulfur diimides and dimeric tellurium diimides, which are thermally stable and have proven to be versatile precursors for the preparation of metal complexes,[2,3] selenium diimides have a low thermal stability and their ligand chemistry is virtually nonexistent. The only hitherto known structurally characterized complexes of selenium diimides are [$SnCl_4${*N*,*N*'-Se(N^tBu)$_2$}][4] and [Sn_2{*μ*-*N*,*N*'-Se(N^tBu)$_2$}{$SiMe_2$(*N*,*N*'-N^tBu)$_2$}$_2$](*Sn*-*Sn*).[5]

In the present contribution, we report the preparation and structural characterization of the coinage metal complexes of *tert*-butyl and adamantyl selenium diimides. In both silver and copper selenium diimide metallacycles, the geometrical arrangement suggests d^{10}-d^{10} metallophilic interactions. Computational results clearly support these metallophilic interactions.



[Ag_2{*μ*-Se(N^tBu)$_2$}][CF_3SO_3]$_2$ *d*(Ag···Ag) = 2.738(1) Å

[Cu_2{*μ*-Se(NAd)$_2$}][CF_3SO_3]$_2$ *d*(Cu···Cu) = 2.532(3) Å

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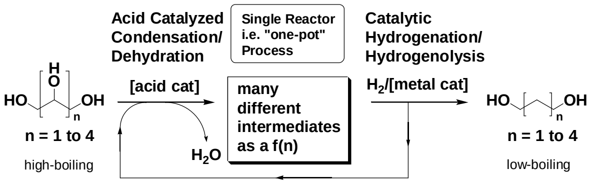
P74

Development of Homogenous Ruthenium-based Ionic Hydrogenation Catalysts for the Selective Deoxygenation of Glycerol.

Michelle E. Thibault, Marcel Schlaf. *Department of Chemistry, University of Guelph, Guelph ON N1G 2W1.* mthibaul@uoguelph.ca, mschlaf@uoguelph.ca.

Glycerol is an abundant by-product of fatty acid methyl ester (FAME) biodiesel production. The current oversupply is > 1 MMt/a[1], resulting in a search for alternative applications and uses. We propose to convert glycerol to 1,3-propanediol, the cost-controlling component in the production of the polyester Sorona/Corterra (poly(propylene terephthalate), PPT), through an acid-catalyzed dehydration and a metal-catalyzed hydrogenation in a single pot.

Previous work in our group has shown that the metal catalyst must be thermally stable, i.e., withstand T > 150 °C in order to effect deoxygenation of glycerol.[2] We have developed homogenous ruthenium-based catalysts that are stable to at least 200 °C. Preliminary studies with the model substrate, 1,2-hexanediol, and with glycerol itself will be discussed.



Net reaction: - n H_2O + n H_2(g) = - n O

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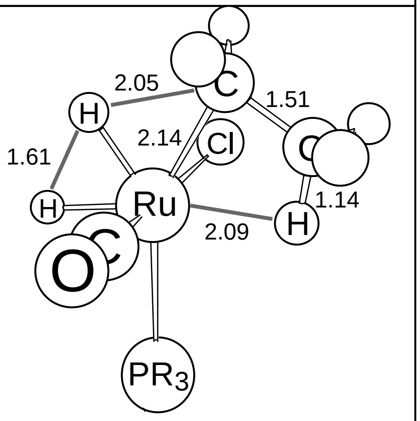
P75

Surprising Mechanistic Insights from DFT Modeling of Ruthenium Hydride Catalysts for Olefin Hydrogenation

Christopher N. Rowley, Heather M. Foucault, Deryn E. Fogg, Tom. K. Woo, *Department of Chemistry, University of Ottawa, Ottawa, ON. K1S 6N5* ***crowl055@uottawa.ca***, ***dfogg@uottawa.ca***, *twoo@uottawa.ca*

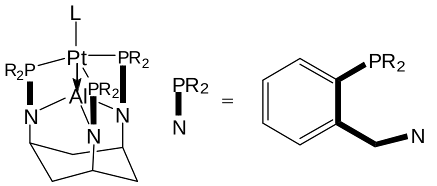
Transition metal catalyzed olefin hydrogenation is of major importance to industry and synthetic organic chemistry. In particular, ruthenium hydrides, such as RuHCl(CO)(PCy_3)$_2$ and RuHCl(PPh_3)$_3$ are efficient catalysts that can be used with a range of substrates. We have used DFT calculations to model the full catalytic cycle to better understand the mechanisms. Our results clarity several important aspects of the reaction mechanism. Firstly, although hydride catalysts are frequently thought to operate most favourably via the unsaturate route, we find that the H2 must coordinate to the catalyst prior to the olefin insertion step Secondly, alkane elimination proceeds via a Ru(IV) dihydride insermediate (right), which had previously been considered too unstable to play a role in this catalytic cycle, at least for arylphosphine catalysts. We have used transition path sampling to simulate the molecular dynamics of this catalytic cycle and have found that the reaction proceeds irreversibly after the olefin insertion. Also, the molecular dynamics indicate that the lifetime of the Ru(IV) dihydride intermediate is extremely short and is expected to exist only transiently.



P76

Synthesis of a sigma-acid ligand and its interactions with platinum(0). Marie-Hélène Thibault,[a] . Frédéric G. Fontaine[a] *Département de chimie, Université Laval, Québec, Qc. G1K 7P4.* **marie-helene.thibault.3@ulaval.ca**, Frederic.fontaine@chm.ulaval.ca

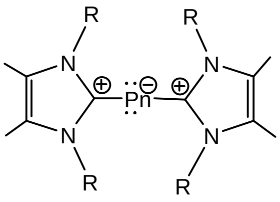
The synthesis of a sigma-acid metalloligand is discussed. The new ambiphilic ligand (AlP_3) would present a trivalent aluminum atom linked to a triaminocyclohexane (tach) template on which three phosphine arms are grafted. These form a cage overlaying and protecting the Lewis acid moiety. The phosphines can be later used as chelating agents for electron rich transition metals such as Pt (0) and Rh(I). We propose to use that strong affinity to force an interaction between the Al(III) and Pt(0). Thus far, the syntheses attempts yield compounds having two aluminum atoms which are still bearing alkyl group moieties (Al_2P_3). The aluminum bearing compound were reacted with tris(norbornene)platinum(0) to afford an intriguing complex. To assess the effect of aluminum in the coordination chemistry of Al_2P_3, the ligand without aluminum was reacted with platinum(0) and platinum(II) compounds. The latter reactions afford totally different platinum complexes than when aluminum is present.



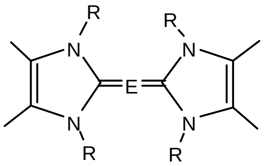
P77

Coordination of low-valent main group elements with N-heterocyclic carbenes. Rajoshree RoyChowdhury, Charles L.B.Macdonald. *Department of Chemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **roychow@uwindsor.ca** , **cmacd@uwindsor.ca**

Simple synthetic approaches to compounds containing cations such as **1**, consisting of various *N*-heterocyclic carbenes ligated to some low-valent group 15 centers (Pn = P, As), have been successfully developed in our group [Ellis *et al*., *Chem. Commun.* **2005**, 1965]. Computational studies of the electronic structures of heavier group 14 allene analogues **2** suggest that such compounds will have similar structural and electronic properties as the group 15 species. Currently we are investigating the various synthetic routes to prepare such compounds, including the parent allene (E = C), which is also predicted to have very unusual features. Some of our currents results and future directions will be presented.



1



E = Si,Ge,Sn

2

P78

The bis-iminopyridinato ligand as a non-innocent supporting ligand of highly active polymerization catalysts.
Indu Vidyaratne[a] Ilia Korobkov, [a] Tara Kell, [a] and Professor Sandro Gambarotta. [a] [a]*Department of Chemistry, University of Ottawa, Ottawa, Ont. K19 6N5.* [b] **Induvidyaratne@yahoo.com**, sgambaro@uottawa.ca

In 1998, the groups of Brookhart and Gibson simultaneously discovered highly active late transition metal ethylene polymerization catalysts supported by the bis-iminopyridine ligand. Prior to this publication, single-site olefin polymerization involved mainly early metal Group 4 systems. Since then, numerous studies involving this ligand system with various transition metals have been undertaken and shown that it can support a high level of catalytic activity when coordinated to early as well as late metals. However, throughout these studies it became apparent that the ligand is anything but ancillary, becoming involved in the reactivity of the metal center through various transformations, such as nucleophilic attack at any position of the backbone, deprotonation, dimerization, and even redox processes with the metal center. We will discuss the reactivity of the Cr catalyst with regards to alkylation and activation/deactivation with aluminum alkyl co-catalysts and the importance of the electron-accepting ability of the ligand in sustaining the high degree of catalytic activity for ethylene polymerization as well as dinitrogen fixation and activation..

P79

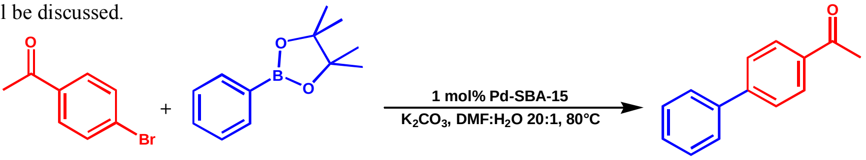
The Formation of Self-Assembled Monolayers (SAMs) on Gold and the Formation of Gold Nanoparticles with Dithiophosphonic Acids. Ronan R. San Juan, Holger S. Eichhorn, Tricia B. Carmichael. *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.* **tbcarmic@uwindsor.ca**

We present the preparation of dithiophosphonic acids ($R_2P(S)SH$, R = $C_{10}H_{21}$, Ph) and their use in the fabrication of self-assembled monolayers (SAMs) on gold and as stabilizing ligands for gold nanoparticles. The self-assembly of dialkyldithiophosphonic acids on gold substrates results in SAMs in which the alkyl chains are loosely packed, as evidenced by reflection-absorption infrared spectroscopy (RAIRS) and contact angle measurements. Loosely-packed SAMs are interesting because of their potential use as stimuli-responsive surfaces. Dithiophosphonic acids also undergo exchange reactions with amine-stabilized gold nanoparticles to form highly stable gold nanoparticles. Preliminary characterization of the new nanoparticles by UV-vis spectroscopy and solution NMR spectroscopic studies will be presented.

P80

Palladium Loaded onto SBA-15: Another Look Webb, Jonathan D.; MacQuarrie, Stephanie; McEleney, Kevin; Crudden, Cathleen M. *Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.*

Palladium is a privileged metal, as it is capable of facilitating a variety of C-C bond forming reactions. These processes proceed with high selectivity even in the presence of a variety of functional groups, and as such Pd catalyzed reactions are of interest in the production of industrially relevant compounds. However, the difficulty of separating products from waste Pd has prevented widespread application in industry. One solution to this problem is immobilization of the metal on a solid support, allowing the catalyst to be filtered after reaction with minimal metal leaching. In that vein we loaded Pd onto SBA-15, an ordered mesoporous silicate.[1,2] The resulting material was a recyclable catalyst for a variety of Cross-Coupling reactions leaching < 1 ppm Pd (See Below). Here we report a reexamination of this material with regard to stability and catalyst heterogeneity.[3] Even though only a small amount of Pd is leached, the active catalyst is homogeneous; this was indicated by careful interpretation of the three-phase test and selective catalyst poisoning studies. Moreover, recycling of the catalyst was found to be coincident with loss of order. Current research is focused on increasing support stability, preliminary results will be discussed.



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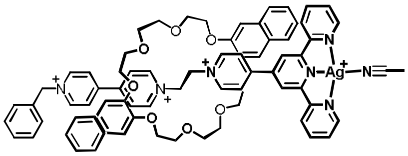
P81

Controlling the ON/OFF threading of a terpyridine containing [2]pseudorotaxane ligand via changes in coordination geometry.
Sapna Sharma, Gregory J. E. Davidson and Stephen J. Loeb.* *Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada*

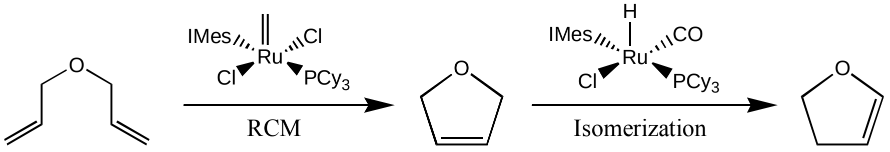
The incorporation of metal centres into rotaxanes has proven to be a valuable tool in the construction of interlocked molecules. Our current research focus is on controlling [2]pseudorotaxane formation by the coordination of different transition metals. The idea is that different metal ions will require different geometries and this variation will affect the [2]pseudortoaxane association constant. We used a tridentate ligand, 2,2':6',2"-terpyridine (terpy) to study the metal coordination controlled threading and unthreading of [2]pseudorotaxane. [2]Pseudorotaxanes were synthesized by incorporating terpy into cationic 1,2-bis(pyridinium)ethane axles. The 24-membered crown-8 ethers: 24-crown-8, dibenzo-24-crown-8 and dinaptho-24-crown-8 were used as the wheel component. The resulting interpenetrated molecules were characterized be ^{1}H NMR spectroscopy and mass spectrometry.



P82

An enabling transformation in tandem catalysis: Efficient hydridocarbonylation of Ru alkylidenes. Joseph W.E. Weiss, Johanna M. Blacquiere, Jay C. Conrad, and Deryn E. Fogg. *Centre for Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ont. K1N 6N5.*

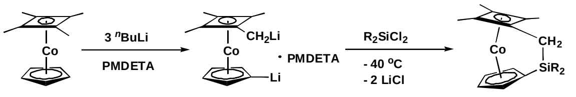
Ruthenium-catalyzed metathesis is an efficient, versatile, and reliable method of achieving new C-C bonds. Recent advances have included the development of tandem catalysis reactions in which the metathesis catalyst is transformed, and can carry out two different catalytic processes. A clear advantage of tandem catalysis processes is the ability to carry out both transformations in a single vessel. Less obvious perhaps, is the ability to access target compounds that you cannot achieve by direct metathesis routes. Two such reactions are tandem ROMP-hydrogenation and RCM-isomerization, both of which involve transforming the ruthenium methylidene into a ruthenium hydride complex. Our research involves the *in-situ* transformation of a ruthenium methylidene metathesis catalyst to a carbonylated ruthenium hydride hydrogenation catalyst, which displays superior catalytic activity as compared to more traditional hydrides. Not only does this complex serve as an effective hydrogenation catalyst, but it also acts as an excellent isomerization catalyst. We are currently looking into alternative, highly efficient synthetic methods to optimize the transformation of ruthenium methylidene to hydride.



P83

Synthesis of neutral mixed sandwich CH_2-SiR_2 bridged [2]cobaltoarenophanes from the dilithiation of Cb*CoCp [Co(h^4-C_4Me_4)(h^5-C_5H_5)]. Preeti Chadha, Jason L. Dutton, Michael J. Sgro and Paul J. Ragogna* *Department of Chemistry, The University of Western Ontario, 1151 Richmond St. London, Ontario, N6A 5B7, CANADA.* pchadha@uwo.ca

A wide range of strained *ansa*-bridged metallocene complexes composed of a variety of transition metals (Group 4 to 8) with different π-hydrocarbon ligands and bridging elements have been developed.[1] Such strained species have the potential to undergo ring-opening reactions to form metallopolymers with diverse properties and applications.[2,3] However, there are no reported examples of neutral, 18 electron metallorenophanes featuring late transition metals. Specifically, *ansa*-metallocene complexes with Group 9 metals have remained unreported, even though they have been identified as desirable synthetic targets. In this context, we have developed the synthesis of new, neutral, 18 electron, cobaltoarenophanes incorporating a Group 9 transition metal. The synthesis of the CH_2-SiR_2 bridged [2]cobaltoarenophanes (**3**) has been achieved *via* dilithiation of the parent cobaltoarenocene Cb*CoCp (**1**) to give **2** and subsequent salt metathesis of **2** using R_2SiCl_2 (R = ^{i}Pr, Me) to give **3**.



1 **2** **3** R = ^{i}Pr, Me

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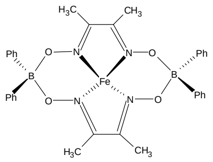
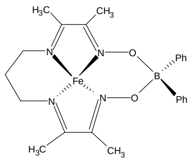
P84

ESI-MS and CID Studies of low spin Fe(II) complexes of tetradentate N4 macrocylic ligands. Alexandra Younes*, Janna Anichina, Dennis V. Stynes and D.K. Böhme, *Department of Chemistry, York University,, Toronto, Ont. M3J 1P3*, **stynes@yorku.ca**

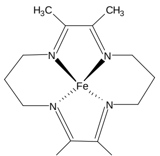
Mass spectrometric studies of FeN_4XY complexes, $FeTIMLX^{2+}$, $Fe(DOBPh_2)LX^+$, and $Fe(DMGBR_2)_2LX$ where L or X = methylimidazole, CO, benzylisocyanide, acetonitrile are reported. Stepwise collision induced dissociation leads to FeN_4L and FeN_4 ions and provides a measure of the coordinate bond energies in the gas phase. In the case of uncharged complexes, $Fe(DMGBR_2)_2$ LX, ESI leads to oxidation in the electron spray tip to $Fe(DMGBR_2)_2LX^+$ and CID studies of these ions give bond energy data for the Fe(III) derivatives. The Fe(II) results will be compared with extensive kinetic data for ligand dissociation available for these systems in solution.



1 $Fe(DMGBR_2)_2$



2 $Fe(DOBPh_2)^+$



3 $FeTIM^{2+}$

P85

The Preparation and Characterization of New Building Blocks for Molecule-Based Magnetic and/or Conducting Materials.

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Considerable efforts have been made recently in the pursuit of molecule-based materials possessing a number of cooperating physical properties. In particular, there is great interest in designing and synthesizing compounds exhibiting magnetism and/or electrical conductivity. For the preparation of magnetic materials, one of the most commonly employed strategies is to unite spin-bearing organic ligands with transition metal ions.[1] For the preparation of molecule-based conductors, exploiting the chemistry of organosulfur compounds such as tetrathiafulvalene (TTF) is a common approach.[2]

In recent years, the design and synthesis of TTF-based electron donors appended with various radical species has received much attention. Specific interest has been in the covalent attachment of metal binding sites onto these organic donor compounds. In doing so, these types of molecules are expected to exhibit interesting magnetic properties (mainly attributed to the presence of an unpaired spin), electrical conductivity (due to the highly reversible electrochemical oxidation of TTF and the uncanny stability of its radical-cation and dication) and ready chelation with transition metal ions (by virtue of the linker unit between the two aforementioned partners).

Research performed by Hicks *et al.* has developed the chemistry of oxoverdazyl radical systems.[3] In the quest for conducting magnetic materials, our research group is combining the stability and unique magnetic properties of oxoverdazyl radicals together with the electronic properties of TTF. Lately, we have been devoted to the preparation of TTF-oxoverdazyl systems possessing an imine-[4], π-ethynyl-[5] and a substituted pyridyl-bridge[6]. The latest developments in this area will be presented.

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P86

Indolylphosphines as Anion Receptors.

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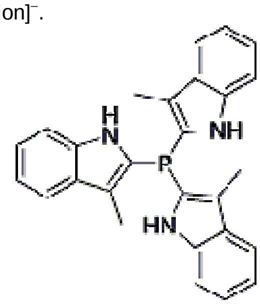
Tris(3-methylindolyl)phosphine, **1**, has demonstrated the ability to capture a wide variety of anion guests via H-bonding. Using ^{1}H NMR titration techniques, equilibrium constants were determined for a series of selected anions. Crystal structures of the [**1**·anion]$^-$ host-guest complexes exhibit how **1** sequesters the anion via hydrogen-bonding through the NH moieties of all three indolyl substituents. Coordination at the phosphorus centre of [**1**·anion]$^-$ complexes is demonstrated in the reaction of **1** with Cu(NCCH$_3$)$_4$BF$_4$. Anion binding affects the net basicity of the phosphine as determined in Ni(CO)$_3$[**1**·anion]$^-$.

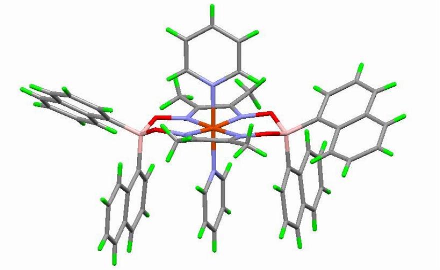


P87

Iron(II) bis-(Boryldimethylglyoximes)- The Next Generation of EE Probes.

Tran Doan and Dennis V. Stynes. *Department of Chemistry, York University, Toronto, Ont. M3J 1P3*

The title compounds, Fe(dmgBR$_2$)$_2$LL', where R = phenyl or fluoro and L or L' any monodentate ligand, have provided a versatile framework in which to explore ligand binding to low spin Fe(II).[1] The structures place boron-linked R groups in intimate contact with the axial ligands. When L is a chiral ligand the complexes have application as hi-throughput NMR probes of enantiomeric excess.
Here we will describe the new system, R = 1-naphthyl. The effects of the naphthyl groups on ligand binding to iron, the conformational dynamics of the macrocycle, and intramolecular NAP-TCNE charge transfer interaction will be reported. As an EE probe for L= R,S-methylbenzylamine the naphthyl system provides the largest chemical shift difference for the dmg methyl proton resonances ever recorded.



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P88

Kinetics of the Electron Self-Exchange and Electron-Transfer Reactions of the (Trimethylammonio)methylferrocene Host-Guest Complex with Cucurbit[7]uril in Aqueous Solution.

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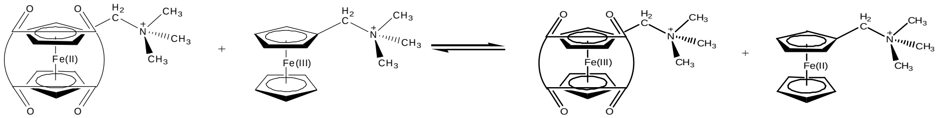
The effects of host-guest complexation of (trimethylammonio)methylferrocene(+/2+) couple ($FcTMA^{+/2+}$) with CB[7] on the kinetics of its electron self-exchange and electron transfer reactions were investigated in aqueous solution at 25 °C, using ^1H NMR line-broadening experiments and Stopped-Flow spectrophotometer. The very strong binding between ferrocene guest to CB[7] host results in slow exchange for the guest on NMR scale, which makes it possible to monitor the resonances of both free and bound forms of the reduced ferrocene $FcTMA^+$ in the presence of the $FcTMA^{2+}$ species independently, such that the rate constants for the possible self-exchange pathways involving the bound and free forms of both the oxidized and reduced forms of the guest can be determined separately. The inclusion of both $FcTMA^+$ and $FcTMA^{2+}$ by CB[7] increases the rate constant of its electron self-exchange reaction from $(2.1 \pm 0.1) \times 10^6$ M^{-1} s^{-1} (for $FcTMA^{+/2+}$) to $(6.7 \pm 0.7) \times 10^6$ M^{-1} s^{-1} (for $\{FcTMA\bullet CB[7]\}^{+/2+}$), however, the encapsulation of reduced form only decreases the rate constant to $(6 \pm 1) \times 10^5$ M^{-1} s^{-1}. The electron transfers reactions between $FcTMA^+$ and hydroxymethylene with bis(2,6-pyridinedicarboxylato)cobaltate(III) ion (which doesn't bind to CB[7]) are also investigated in the absence and the presence of CB[7] in aqueous solution at 25 °C. The encapsulation of ferrocene guests by CB[7] significantly reduces the rate constant for their oxidation as a result of reduced thermodynamic driving forces and steric hindrance to close approach of the oxidant to the encapsulated ferrocenes.



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P89

Non-cooperative binding of cadmium to the beta domain of human metallothionein.

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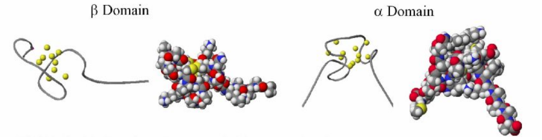
Metallothionein (MT), a ubiquitous family of metalloproteins, has been implicated in a number of physiological functions including zinc and copper homeostasis, heavy metal detoxification, and radical scavenging. The most widely studied of this protein family are the mammalian MTs, which through their 20 cysteine residues are able to bind between 7 and 18 metals, depending on the type of metal. The mode of metal binding is important in terms of possible structures protein-protein interactions. Recently, the binding of 4 Cd^{2+} to the alpha domain of human metallothionien-1a, studied using electrospray ionization mass spectrometry (ESI-MS), was determined to be non-cooperative.[1] The beta domain of human MT is able to bind 3 Cd^{2+}. Using ESI-MS, binding to the beta domain occurred in a non-cooperative manner. Intermediates of Cd_1-MT and Cd_2-MT dominate the spectra upon addition of fewer than three equivalents of cadmium. Since both of the domains of MT are thought to operate independently of each other, these results imply that Cd^{2+} and Zn^{2+} bind to the whole MT protein in a non-cooperative manner.



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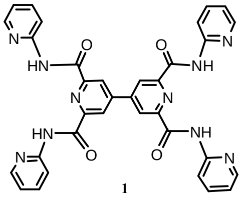
P90

Synthesis, characterization and coordination chemistry of a novel tetracarboxamide *bis* bipyridyl ligand.

Niloofar Zarrabi and Melanie Pilkington. *Department of Chemistry, Brock University, St. Catharines, Ont. L2S 3A1.* **nz07ty@brocku.ca**

One of the major challenges at the forefront of molecular magnetism is to develop new synthetic routes to suitably functionalized organic ligands and then to control/predict their assembly together with appropriate paramagnetic metal ions in the solid state for the preparation of materials with a diverse range of magnetic properties. During recent years, pyridyl carboxamide ligands have found useful applications in the fields of asymmetric catalysis.[1] dendrimer synthesis,[2] molecular receptors,[3] as well as for the preparation of platinum complexes with antitumor properties.[4] Although studied widely for their biological applications,[5] these ligands have not yet been exploited as precursors to molecule-based magnetic materials. Furthermore, carboxamide ligands containing a bipyridyl moiety are much more rare and have not yet realized their full potential as versatile ligands in the field of coordination chemistry. In this respect, we have recently targeted the tetracarboxamide *bis* bipyridyl ligand **1** and report herein its synthesis, characterization and preliminary coordination chemistry.



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P91

A Detailed Study into the Effect of Solvation on the ^{125}Te NMR Chemical Shift of Ditellurides.

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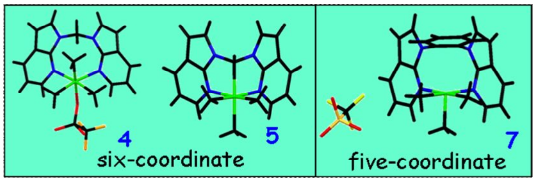
The interpretation of spectroscopic data of compounds containing tellurium atoms can often be difficult due to many factors. The strong dependence of the ^{125}Te chemical shift on temperature and the ability of tellurium to form adducts through secondary bonding interactions with strong donor solvents can often complicate the results. In order to properly interpret the spectra, it is necessary to precisely determine the effect of each solvent on the tellurium environment. A study has been undertaken to determine the influence of several solvents on the spectroscopic properties of ditellurides. Experimentally obtained ^{125}Te NMR data displays correlation of the solvent donor ability with the ^{125}Te NMR chemical shift. Concentration has also been found to affect the results. A computational study using density functional theory (DFT) has been undertaken to aid in the interpretation of the spectra. Calculated ^{125}Te NMR chemical shifts have shown a strong dependence on conformation. Solvent effects have been approximated using explicitly solvated molecules; conformational changes upon solvation may explain some of the experimental variation in the ^{125}Te NMR data.

P92

New Insights into Ligand Effects On the Chemistry of Platinum Complexes with 7-Azaindolyl Derivative Ligands.

Shu-Bin Zhao, and Suning Wang. *Department of Chemistry, Queen's University, Kingston, Ont. K7L 3N6.*



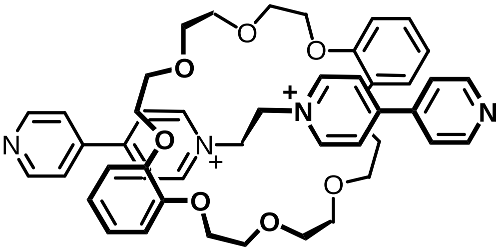
Ligands play a crucial role in controlling hydrocarbon C-H bond activation process at a Pt(II) center with a significant impact on selectivity and efficiency. Hence, a detailed investigation of the ligand effect from a mechanistic viewpoint is of great importance in understanding the "Shilov chemistry" towards the ultimate development of practical systems for direct hydrocarbon functionalization. During the course of our C-H activation study, we have obtained a series of methylated cationic Pt(II) complexes of 7-azaindolyl derivative ligands that display unusual reactivity and reaction patterns, owing to their unique structural features imposed by the ligands. For example, five-coordinate Pt^{IV} compounds are intermediates in the Shilov methane conversion process and also are highly reactive species that have not been isolated before with neutral N,N-chelating ligands. We have found recently that our 7-azaindolyl derivative ligands can effectively stabilize reactive Pt^{IV} species such as Pt^{IV}Me$_3$, as shown by compound **7**. Two related six-coordinate Pt(IV) complexes, **4** and **5** have also been isolated and structurally characterized. Their corresponding Pt(II) complexes have been found to display unique diastereoselectivity in ethylbenzene C-H bond activation as well as unprecedented intramolecular roll-over C-H activation driven self-assembly. These new insights of ligand impact on the chemistry of Pt complexes will be presented.

P93

Self-Assembly of Metal Organic *Rotaxane* Polygons and Polyhedra, MO*R*Ps.

Elizabeth Viljoen and Stephen J. Loeb. *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont. N9B 3P4.*

The linear ligand1,2-bis(4,4'-bipyridinium)ethane can be used as an axle for the formation of a [2]pseudorotaxane using dibenzo-24-crown-8-ether as the wheel. This [2]pseudorotaxane can be incorporated into molecular squares and cubes employing cis-protected and face-capped metal fragments, and transition-metal-mediated, coordination-driven self-assembly. The formation of the rotaxane allows for control of the assembly architecture and the synthesis of Metal Organic *Rotaxane* Polygons and Polyhedra (MO*R*Ps). The synthesis and characterization of several assemblies will be presented.



P94

The Reactivity Patterns of Low-Coordinate Iron Hydride Complexes. Ying Yu,[a] Azwana R. Sadique,[a] Jeremy M. Smith,[a] Thomas R. Dugan,[a] Thomas R. Cundari,[b] William W. Brennessel,[a] Christine J. Flaschenriem,[a] and Patrick L. Holland.[a] [a]*Department of Chemistry, University of Rochester, Rochester, NY 14620.* [b] *Department of Chemistry, University of North Texas, Denton, TX 76203.*

Though iron hydride complexes have long been of interest in catalysis, they have received special attention recently with the discovery that iron hydride species are present in activated forms of the paramagnetic iron-molybdenum cofactor in nitrogenase enzymes. Thus, iron hydrides are likely to play an important role in reduction of N_2 to NH_3, but there are few synthetic examples with the appropriate electronic and structural environment (high-spin electronic configuration, low coordination number) to mimic the reactivity of such potential biological iron-hydride intermediates. We report a survey of the reactivity of $[L^RFe(\mu\text{-}H)]_2$ (L^R = R-substituted bulky β-diketiminate) – the first isolable iron-hydride complexes with a coordination number less than five – with representative cyanide, isocyanide, alkyne, N_2, alkene, diazene, azide, CO_2, carbodiimide and Brønsted acid substrates. A number of the products present rare or unique structural features. The reaction outcomes fall into three categories: (1) insertion of Fe-H across a multiple bond of the substrate, (2) reductive elimination of H_2 to form iron(I) products, and (3) protonation of the hydride to form iron(II) products. These results expand the range of known bond transformations at iron complexes, and give insight into the elementary transformations that may be possible at the iron-molybdenum cofactor of nitrogenases.

Enjoy the conference banquet, following the poster session!

The conference banquet was made possible due to the generous support by Bruker Spectrospin (Canada) Ltd.

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