

46TH INORGANIC DISCUSSION WEEKEND



Y o r k U n i v e r s i t y

The Birthplace of the IDW

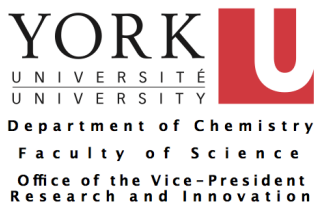
November 8–10, 2013

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INORGANIC DISCUSSION WEEKEND

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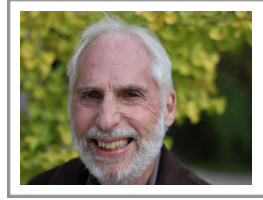
Inorganic Division
Canadian Society for Chemistry

MATERIALS DIVISION
of the Chemical Institute of Canada

Organizing Committee



Prof. Gino G. Lavoie
conference chair



Prof. Barry Lever
founding father of the IDW



Dr. Mike R. Hempstead



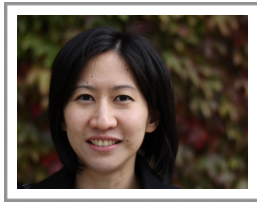
Prof. Bill J. Pietro



Prof. Dennis V. Stynes



Prof. Sylvie Morin



Prof. Jennifer Chen



Prof. Pierre G. Potvin

Ms. Nicole Chevannes-McGregor (administrative assistant)
and many volunteers

Agenda

Friday, November 8th, 2013

19:30 – 22:30 Registration and **GreenCentre Canada** mixer
Student Centre, the Underground

Saturday, November 9th, 2013

8:30 – 8:50 Opening Remarks – Lassonde Bldg, Lecture Hall C

9:00 – 10:20 Oral Presentations – Lassonde Bldg, Lecture Halls B & C

10:20 – 10:40 Session Break – Lassonde Bldg, Lobby

10:40 – 12:00 Oral Presentations – Lassonde Bldg, Lecture Halls B & C

12:00 – 13:40 Lunch (many eateries available on campus, see p.5)

13:40 – 15:00 Oral Presentations – Lassonde Bldg, Lecture Halls B & C

15:00 – 15:20 Session Break – Lassonde Bldg, Lobby

15:20 – 16:10 Plenary Lecture (Professor Jonas C. Peters)
Lassonde Bldg, Lecture Hall C

16:30 – 18:30 **Bruker–Gaussian–New Journal of Chemistry**
Poster Session
Accolade East Bldg, Hallway and CIBC Lounge

19:00 **York University** Banquet – Schulich Executive Dining Room

Sunday, November 10th, 2013

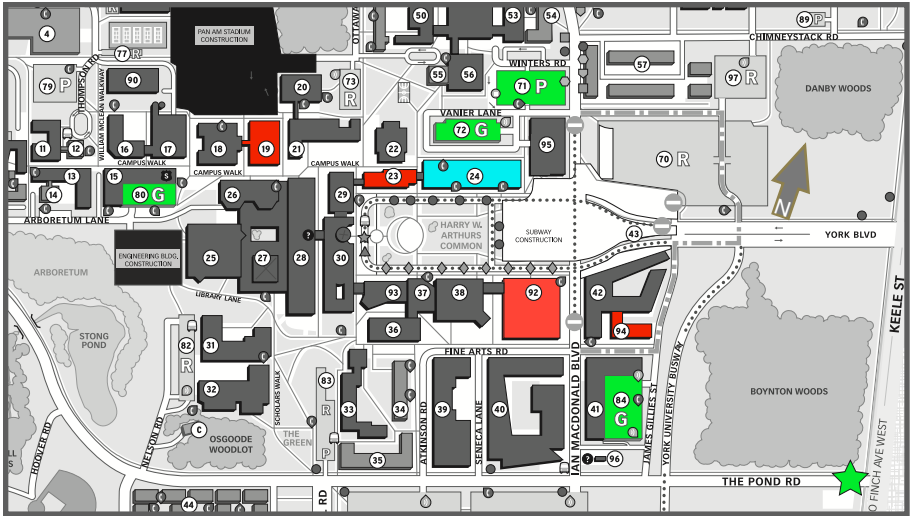
9:00 – 10:20 Oral Presentations – Lassonde Bldg, Lecture Halls B & C

10:20 – 10:40 Session Break – Lassonde Bldg, Lobby

10:40 – 11:30 Plenary Lecture (Professor Richard R. Schrock)
Lassonde Bldg, Lecture Hall C

11:30 – 12:00 Awards Presentation and Closing Remarks
Lassonde Bldg, Lecture Hall C

Campus Map



Talks: Lassonde Building (#19)

Posters: Accolade East Building (#92)

Mixer: the Underground in the Student Centre (#23)

Lunch: many options available in the Student Centre (#23) and in York Lanes (#24)

Banquet: Dining Room in the Executive Learning Centre (#94)

Parking: preferred garage due to construction on campus #84;
other options: #71, #72, #80

★ preferred access to campus by car (Keele St. and The Pond Rd.)

Internet: stay connected through the IDW by using credentials from your home institution on the “**eduroam**” wireless network;

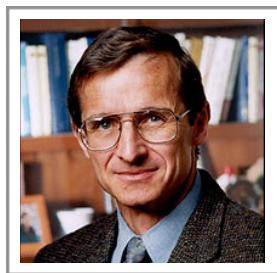
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Professor Richard R. Schrock

Nobel Prize Laureate in Chemistry Massachusetts Institute of Technology

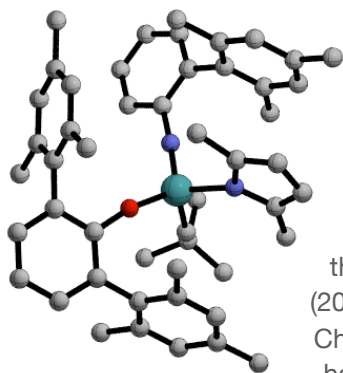
Richard R. Schrock received his Ph. D. degree in inorganic chemistry from Harvard in 1971 under the tutelage of John Osborn. After spending one year as an NSF postdoctoral fellow at Cambridge University working for Lord Jack Lewis, and three years at the Central Research and Development Department of E. I. duPont de Nemours and Company in Wilmington Delaware, he moved to



MIT in 1975. He became full professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the inorganic and organometallic chemistry of high oxidation state, early metal complexes (especially those that contain an alkylidene or alkylidyne ligand), catalysis and mechanisms, catalytic reactions that involve alkylidene complexes, and the catalytic reduction of dinitrogen. Among his awards are the ACS Award in Organometallic Chemistry (1985), the Harrison Howe Award of the Rochester ACS section (1990), the ACS Award in Inorganic Chemistry (1996), the Bailar Medal from the University of Illinois (1998), an ACS Cope

Scholar Award (2001), the RSC Centenary Medal (1991), the Sir Geoffrey Wilkinson Medal (2002), the Sir Edward Frankland Prize (2004), the August Wilhelm von Hofmann Medal of the German Chemical Society (2005, with R. H. Grubbs), the Theodore Richards Medal (2006), the ACS F. Albert Cotton Award in Synthetic Inorganic Chemistry (2006), and the Basolo Medal from Chicago ACS Section (2007). In 2005, he shared the Nobel Prize in Chemistry with R. H. Grubbs and Y. Chauvin. He has been elected to the American Academy of Arts and Sciences and the National Academy of

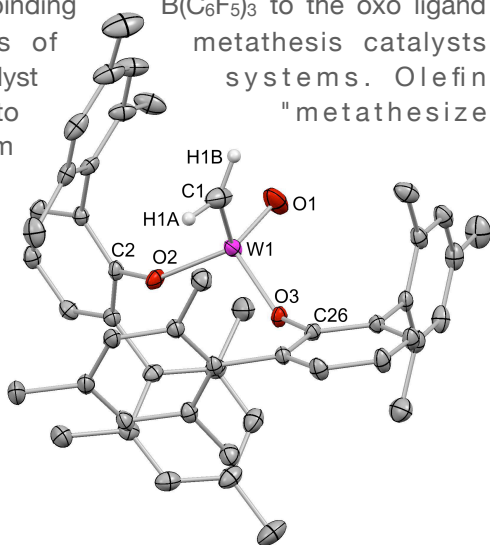
Sciences and is a Foreign Member of the Royal Society. He was Associate Editor of *Organometallics* for eight years, has published more than 550 research papers, and has supervised over 170 PhD students and postdocs.



Advances in olefin metathesis by molybdenum and tungsten catalysts

Abstract

The most important development in the last five years in olefin metathesis chemistry employing Mo or W catalysts has been $M(NR)(CHCMe_2R')(OR)$ (Pyrrolide) (MonoAlkoxidePyrrolide or MAP) species, especially those in which OR is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT). MAP species of this type under the right circumstances have proven to be Z-selective in a variety of olefin metathesis reactions, among them enantioselective ring-opening/cross-metatheses, ROMP to give highly stereoregular polymers, ethenolysis of internal olefins such as oleates, coupling of terminal olefins, cross coupling of terminal olefins, and synthesis of macrocyclic natural products. The most recent development has been the synthesis of a variety of tungsten oxoalkylidene complexes, among them complexes that contain two sterically demanding terphenoxides, e.g., $W(O)(CH_2)(OHMT)_2$ (see Figure). Oxo complexes are "activated" by binding $B(C_6F_5)_3$ to the oxo ligand and are likely to be analogs of metathesis catalyst systems. Olefin metathesis has been employed to "metathesize" alkanes" employing a tandem catalyst in which Ir is the metal employed to make alkenes *in situ* from alkanes. Other recent applications will be discussed as time allows.



The structure of $W(O)(CH_2)(OHMT)_2$.

Professor Jonas C. Peters

Bren Professor of Chemistry
California Institute of Technology

Academic History: B.S., 1993, University of Chicago; Graduate Research, 1993-1994, University of Nottingham with James J. Turner; Ph.D., 1998, MIT with Christopher C. Cummins; Postdoctoral Associate, 1998-1999, UC Berkeley with T. Don Tilley.

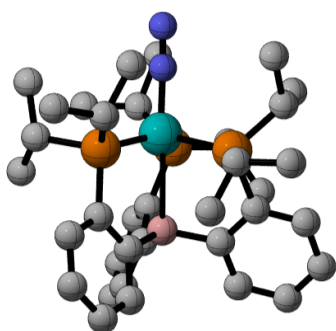
Current Position: Bren Professor of Chemistry, Caltech.

Past Positions: Assistant Professor, 1999-2004; Associate Professor, 2004-2006; Professor, 2006-2007; Keck Professor of Energy and Chemistry, 2007-2009, MIT.

Awards and Recognitions: Marshall Scholar, University of Nottingham, 1993; NSF Graduate Fellowship, 1995; Department of Defense Graduate Research Fellow, MIT, 1995; MIT's Davison Prize, Inorganic Thesis Award, 1998; Miller Fellow, UC Berkeley, 1998; Camille and Henry Dreyfus Teacher-Scholar Award, 1999 and 2002; Department of Energy Defense Program's Early Career Scientist and Engineer Award, 1999; Presidential Early Career Award for Scientists and Engineers, 2000; Alfred P. Sloan Research Fellow, 2003; Senior Research Fellow, St. John's College, Oxford, 2011.



Professional Activities: Executive Officer, Division of Chemistry and Chemical Engineering, Caltech, 2012-present; Faculty Board and Faculty



Board Steering Committee Member, Caltech, 2012-present; Co-investigator of an NSF-sponsored center: "Powering the Planet: A Chemical Bonding Center for the Direct Conversion of Sunlight into Chemical Fuel," 2006-present; Co-investigator, Joint Center for Artificial Photosynthesis and Project Lead for Benchmarking Task, 2010-present; Advisory Board, Resnick Institute for Science, Energy, and Sustainability, 2010-present; International Advisory Committee, Institute of Molecular Functional Materials, 2010-present.

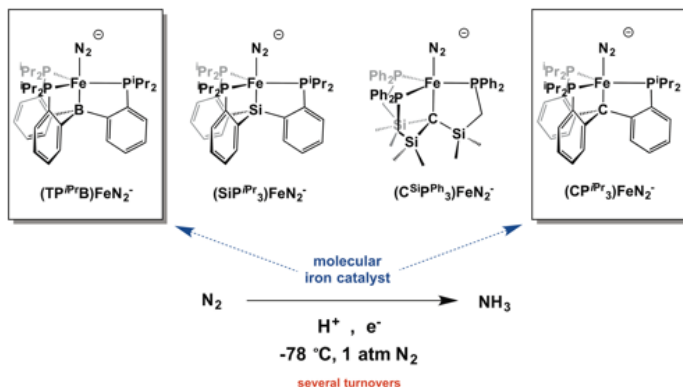
Research Interests: Synthetic approaches to metal-mediated small molecule activation chemistry with a particular focus in exploring reductive transformations that couple protons and electrons to catalytically evolve hydrogen, or direct their flow to challenging substrates including N_2 and CO_2 .

Catalytic reduction of nitrogen to ammonia by mononuclear iron complexes

Abstract

Nitrogen reduction to NH_3 is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of debate has been the site(s) of dinitrogen coordination and reduction. The synthetic inorganic community placed an early emphasis on Mo because Mo was thought to be an essential element of nitrogenases, and because pioneering work by Chatt and his co-workers established that well-defined Mo model complexes could mediate the stoichiometric conversion of coordinated N_2 to NH_3 . Such a transformation was first demonstrated catalytically using a molecular Mo system by Schrock and coworkers, and Nishibayashi and coworkers have more recently discovered another catalytically active Mo system.

It is known, however, that Fe is the only transition metal essential to all nitrogenases, and recent biochemical and spectroscopic data have implicated Fe as the likely site of N_2 binding in FeMo-co. These observations motivate a search for functional Fe catalysts. In this talk, I will discuss a tris(phosphine)borane supported Fe complex that catalyzes the reduction of N_2 to NH_3 , wherein $>40\%$ of the H^+/e^- equivalents are delivered to N_2 . This catalytically functional model system establishes that a single Fe site may be capable of stabilizing the various N_xH_y ligands generated en route to NH_3 formation. Geometric flexibility at Fe imparted by a hemi-labile axial donor may be critical for catalysis, and the interstitial C-atom recently assigned in the nitrogenase cofactor may serve a similar hemi-labile role. To further build on this idea, I will discuss more recent data for Fe complexes wherein a C-atom anchor is positioned trans to an Fe- N_2 binding site.



Programme

Abstracts for all talks and posters are available at idw.info.yorku.ca/programme.

Saturday	Lassonde, Lecture Hall B	Lassonde, Lecture Hall C
8:30 – 8:50	Opening Remarks (Lassonde, Lecture Hall C)	
9:00 – 9:20	<p>OB1 <i>Pressure Induced Phase Transitions and Metallization of a Neutral Radical Conductor</i> <u>Joanne W. L. Wong</u>, Aaron Mailman, Kristina Lekin, Stephen M. Winter and Richard T. Oakley* University of Waterloo, Waterloo.</p>	<p>OC1 <i>Effective Iron Catalysts for the Asymmetric Reduction of Ketones and Imines</i> <u>Weiwei Zuo</u>, Alan J. Lough, Young Li and Robert H. Morris* University of Toronto, Toronto.</p>
9:20 – 9:40	<p>OB2 <i>Sensitization of Rare Earth Metals with Boron Functionalized β-diketones</i> <u>Larissa F. Smith</u>, Hee-Jun Park, Barry A. Blight and Suning Wang* Queen's University, Kingston.</p>	<p>OC2 <i>4,5-Diazafluorenone Derivatives: Binucleating Ligands for the Synthesis of Heterobimetallic Compounds</i> <u>Rhys Batcup</u>, Vincent T. Annibale, and Datong Song* University of Toronto, Toronto.</p>
9:40 – 10:00	<p>OB3 <i>Preliminary Surface Mechanisms and In situ Optical Monitoring for Metal Deposition from Group 11 Iminopyrrolidines by CVD</i> <u>David J. Mandia</u>, Matthew. B.E. Griffiths, Peter J. Pallister, Jason P. Coyle, Wenjun Zhou, Jacques Albert, Seán T. Barry* Carleton University, Ottawa.</p>	<p>OC3 <i>Ligand Formation and Open Site Creation Through Nucleophilic Addition to the Ligand on a Molybdenum Tris(dithiolene) Complex</i> <u>N. Nguyen</u>, D. Armstrong and U. Fekl* University of Toronto, Mississauga.</p>
10:00 – 10:20	<p>OB4 <i>Property-based evolutionary design and optimisation of functionalised metal organic frameworks</i> <u>Thomas D. Daff</u>, Sean Collins, and Tom K. Woo* University of Ottawa, Ottawa.</p>	<p>OC4 <i>Transition Metal Complexes of a Ferrocene-Based Bisphosphine-Borane Ligand</i> <u>Bradley E. Cowie</u>, David J. H. Emslie* McMaster University, Hamilton.</p>
10:20 – 10:40	Session Break (Lassonde, Lobby)	

Saturday Lassonde, Lecture Hall B

10:40 – 11:00 **OB5** *New Families of 4f- and 3d/4f-Metal Complexes Exhibiting Single-Molecule Magnetism, Magnetic Refrigeration and Photoluminescence Properties*
Dimitris I. Alexandropoulos, Luís Cunha-Silva, Jinkui Tang, and Theocharis C. Stamatatos*
 Brock University, St. Catharines.

11:00 – 11:20 **OB6** *Magnetically Interesting Lanthanide Complexes of Schiff-Base Macrocycles and Crown Ethers*
Emma Gavey, Majeda Al Hareri and Melanie Pilkington*
 Brock University, St. Catharines.

11:20 – 11:40 **OB7** *In-situ high pressure studies on MOFs and their performance for CO₂ storage*
Yue Hu, Yang Song* and Yining Huang*
 University of Western Ontario, London.

11:40 – 12:00 **OB8** *Electrospray Ionization Mass Spectrometry: A Useful Technique for Characterization of Methylaluminumoxane Solutions*
 Tyler K. Trefz, Matthew A. Henderson, Miles Y. Wang, Scott Collins and J. Scott McIndoe*
 University of Victoria, Victoria.

12:00 – 13:40 Lunch

Many eateries are available in the Student Centre and in York Lanes (see map on p.5).

Lassonde, Lecture Hall C

OC5 *The Same Boa-ing Story?: Lanthanide Contraction Explains Trend in a Series of –[Ln-radical]- Coordination Polymers*
Adam C. Maahs,^a Elisa M. Fatila,^a Rodolphe Clérac,^b Mathieu Rouzières,^b Dmitriy V. Soldatov,^a Kathryn E. Preuss*^a
^aUniversity of Guelph, Guelph.
^bUniversité de Bordeaux, Pessac, France.

OC6 *Photoelimination Route to 1,3-Azaborines Using N-Heterocyclic Carbene-Borane Precursors*
Sean M. McDonald and Suning Wang*
 Queen's University, Kingston.

OC7 *A strong α -donor ligand with flexible metal coordination geometries and influence of α -donation on the photophysical properties of its complexes with Ru(II/III)*
Amlan K. Pal and Garry S. Hanan*
 Université de Montréal, Montréal.

OC8 *Copper-Catalyzed Aerobic Oxidation of Phenols into Versatile Quinones*
Mohammad S. Askari^a, K.V.N. Esguerra^b, Y. Fall^b, Jean-Philip Lumb*^b, and Xavier Ottenwaelder*^a
^aConcordia University, Montréal.
^bMcGill University, Montréal.

Saturday Lassonde, Lecture Hall B

13:40 – 14:00 **OB9** *Sulfur Tetrafluoride in the Solid-State*
James T. Goettel,^{a,b} Nathan Kostiuk,^a and Michael Gerken*^a
^aUniversity of Lethbridge,
 Lethbridge.
^bMcMaster University, Hamilton.

14:00 – 14:20 **OB10** *Vibrational Studies of Group 8 Metallocenes*
Yann Desjardins-Langlais and Ian S. Butler*
 McGill University, Montréal.

14:20 – 14:40 **OB11** *Exploring conformations of As_x- and apo-metallothioneins using ESI-MS and covalent labelling*
Gordon W. Irvine and Martin J. Stillman*
 University of Western Ontario,
 London.

14:40 – 15:00 **OB12** *Noble-Gas Difluoride Coordination Complexes of Hg(II); Hg(OTeF₅)₂·1.5NgF₂ (Ng = Xe, Kr)*
John R. DeBackere, Hélène P.A. Mercier, and Gary J. Schrobilgen*
 McMaster University, Hamilton.

Lassonde, Lecture Hall C

OC9 *Functionalization of Iridium (III) Complexes by Tuning of Both Ancillary Bis(arylimino)acenaphthene (Ar-BIAN) and Cyclometalating phenylpyridine (C[^]N) Ligands*
K. Hasan^a and E. Zysman-Colman^{b*}
^aUniversité de Montréal,
 Montréal.
^bUniversity of St. Andrews, St. Andrews, United Kingdom.

OC10 *A Method for the Production of Reduction-Sensitive 1,1-Diarylhydrazines as Potential Ligands in Coordination Chemistry*
Joël Poisson, Cheryl D. Bain, Julia M. Bayne, D.Scott Bohle* and Ian S. Butler*
 McGill University, Montréal.

OC11 *Toward a Step-By-Step Mechanistic Elucidation of Chain-End Stereocontrol in d⁰ Metallocene Catalyzed Polymerization of α -Substituted Olefins*
Alexandre F. Dunlop-Brière^a, Peter H. M. Budzelaar^b, and Michael C. Baird*^a
^aQueen University, Kingston.
^bUniversity of Manitoba,
 Winnipeg.

OC12 *Chromium Catalysts for CO₂-epoxide Copolymerization*
Joanna Gurnham, and Sandro Gambarotta*
 University of Ottawa, Ottawa.

Saturday

15:00 – 15:20 **Session Break** (Lassonde, Lobby)

15:20 – 16:10 **Plenary Lecture** (Lassonde, Lecture Hall C)
Catalytic Reduction of Nitrogen to Ammonia by Mononuclear Iron Complexes
 Professor Jonas C. Peters, Bren Professor of Chemistry
 California Institute of Technology

16:30 – 18:30 **Bruker–Gaussian–New Journal of Chemistry Poster Session**
 Accolade East Building, Hallway and CIBC Lounge (#92 on map)
 Titles and abstracts available online at idw.info.yorku.ca/programme

Presenters of odd-numbered (**P1, P3, P5...**) posters are asked to remain at their respective poster and be available for discussion from **16:30 – 17:30**

Presenters of even-numbered (**P2, P4, P6...**) posters are asked to remain at their respective poster and be available for discussion from **17:30 – 18:30**

19:00 **York University Banquet**
 Schulich Executive Dining Room (#94 on map)



Sunday	Lassonde, Lecture Hall B	Lassonde, Lecture Hall C
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9:00 – 9:20 **OB13** – no presentation

OC13 *Small Molecule Activation by POCOP Nickel Amide & Siloxide Complexes.*
Jingjun Hao, Boris Vabre, Berline Mougang-Soumé, and Davit Zargarian*
 Université de Montréal, Montréal.

9:20 – 9:40 **OB14** *Efficient Base-Catalyzed Hydrosilylation of Carbonyls*
Kseniya Revunova and Georgii I. Nikonov*
 Brock University, St. Catharines.

OC14 *New Silylselenium Reagents for the Synthesis of Ferrocenoyl Chalcogenoesters*
Mahmood Azizpoor Fard and John F. Corrigan*
 University of Western Ontario, London.

INORGANIC DISCUSSION WEEKEND

Sunday

Lassonde, Lecture Hall B

Lassonde, Lecture Hall C

- 9:40 – 10:00** **OB15** *Mechanistic Investigation of H/D exchange of Unactivated C-H Bonds from a Pentanuclear Nickel Cluster.*
Manar Shoshani, and Samuel A. Johnson*
University of Windsor, Windsor.
- 10:00 – 10:20** **OB16** *Developing Ti^{III} Precatalysts for the Dehydrocoupling/Dehydrogenation of Amine-Boranes*
Titel Jurcaa, and Ian Manners*
University of Bristol, Bristol, UK.
- 10:20 – 10:40** **Session Break** (Lassonde, Lobby)
- 10:40 – 11:30** **Plenary Lecture** (Lassonde, Lecture Hall C)
Advances in Olefin Metathesis by Molybdenum and Tungsten Catalysts
Professor Richard R. Schrock, Nobel Prize Laureate in Chemistry
Massachusetts Institute of Technology
- 11:30 – 12:00** **Awards Presentation and Closing Remarks**



Programme (posters only)

Saturday, 16:30 – 18:30

Accolade East Building

Abstracts are available on pages 59–141.

P1 *Ru(II) Complexes Containing the Antitubercular Ligand Isoniazid*

Inara de Aguiar^a, Leonardo B. Marino^b, Érica O. Lopes^b, Fernando R. Pavan^b, Douglas W. Franco^{*a}

^aUniversidade de São Paulo.

^bFaculdade de Ciências Farmacêuticas, Brazil.

P2 *Towards Models of the Oxygen-Evolving Complex (OEC) of Photosystem II from the Use of Optically-Active Ligands: Mn₄Ca Clusters of Relevance to Low Oxidation States of the OEC*

Alysha Alaimo^a, Luís Cunha-Silva^b, and Theocharis C. Stamatatos^{*a}

^aBrock University, St. Catharines.

^bUniversity of Porto, Portugal.

P3 *The First Family of Lanthanide Molecule-Based Magnets Assembled from Crown Ether Ligands*

Majeda Al Hareri, Emma Gavey, Amy Pham & Melanie Pilkington*

Brock University, St. Catharines.

P4 *A New Schiff Base Ligand in Metal Cluster Chemistry: Synthesis and Characterization of Ni₄, Ni₈ and Ni₁₁ Complexes*

Angeliki A. Athanasopoulou^a, Catherine P. Raptopoulou^b, Albert Escuer^c, and Theocharis C. Stamatatos^{*a}

^aBrock University, St. Catharines.

^bInstitute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Greece.

^cUniversitat de Barcelona, Spain.

P5 *Employment of 2-Pyrrolyloximes as Bridging Ligands in Transition Metal Cluster Chemistry*

Dimosthenis P. Giannopoulos, Wolfgang Wernsdorfer, George Christou, and Theocharis C. Stamatatos*

Brock University, St. Catharines.

P6 *Heptanuclear Lanthanide(III) Complexes from the Use of a New Chiral Schiff-base Ligand*

Eleni C. Mazarakioti^a, Luís Cunha-Silva^b, and Theocharis C. Stamatatos^{*a}

^aBrock University, St. Catharines.

^bUniversity of Porto, Portugal.

INORGANIC DISCUSSION WEEKEND

P7 *Access to Optically-Effective Molecular Magnetic Materials via the Employment of Quinoline-based Oximate Ligands and Fluorescence Carboxylate Groups*

Jacob Sitko^a, Luis Cunha-Silva^b and Theocharis C. Stamatatos^{*a}

^aBrock University, St. Catharines.

^bUniversity of Porto, Portugal.

P8 *H-X Bond Activation Mediated by Aluminum(I)*

Terry Chu and Georgii I. Nikonov^{*}

Brock University, St. Catharines.

P9 *Catalytic reduction of secondary amides to imines and aldehydes*

Sun Hwa Lee and Georgii I. Nikonov^{*}

Brock University, St. Catharines.

P10 *Half sandwich NHC-supported ruthenium trihydride and its silyl dihydride derivatives.*

Van Hung Mai and Georgii I. Nikonov^{*}

Brock University, St. Catharines.

P11 *Exploring the Coordination Chemistry of a Family of 2,2',6,6'-Tetracarboxamide-4,4'-Bipyridine Ligands – from Clusters to MOFs*

Jeff Regier, Niloofar Zarabbi, Roland T. Acha and Melanie Pilkington^{*}

Brock University, St. Catharines.

P12 *Thermolysis Methods: kinetics & products of precursor decomposition*

Adam P. Wells, Agnieszka Kurek, Peter J. Pallister, Jason P. Coyle and Seán T. Barry^{*}

Carleton University, Ottawa.

P13 *In situ Monitoring of the Chemical Vapour Deposition of Gold Films onto TFBG-Inscribed Optical Fibers*

M. B. E. Griffiths, D. J. Mandia, J. P. Coyle, P. G. Gordon, L. Shao, W. Zhou, J. Albert^{*}, S. T. Barry^{*}

Carleton University, Ottawa.

P14 *Quantitative Surface Coverage Calculations via Solid-State NMR for Thin Film Depositions: A Case Study for Silica and a Gallium Amidinate*

Peter J. Pallister, Sydney C. Buttera, Seán T. Barry^{*}

Carleton University, Ottawa.

P15 *The First Barium Tin(II) Bromide Fluoride*

Georges Dénès^a, Hocine Merazig^b, Abdualhafed Muntasar^a and Robyn Porterfield^a

^aConcordia University, Montréal.

^bUniversité Constantine, Algeria.

P16 *Using Mössbauer Spectroscopy to Choose the Sites that can be Occupied by Divalent Tin*

Georges Dénès^a, Hocine Merazig^b and Abdualhafed Muntasar^a

^aConcordia University, Montréal.

^bUniversité Constantine, Algeria.

P17 *Spectral Anisotropy in Tin(II)-Containing Low Dimensionality Materials*

Georges Dénès^a, M. Cecilia Madamba^a, Hocine Merazig^b and Abdualhafed Muntasar^a

^aConcordia University, Montréal.

^bUniversité Constantine, Algeria

P18 *Biomimetic catalytic oxidation of phenols with Cu(II) complexes*

Andrew Proppe^a, Mohammad S. Askari^a, Jean-Philip Lumb^b and Xavier Ottenwaelder^{*a}

^aConcordia University, Montréal.

^bMcGill University, Montréal.

P19 *Di- μ -chlorido-bis[(2-aminobenzamide- κ^2 N²,O) chloridocopper(II)]*

Maamar Damous^a, Georges Dénès^b, Sofiane Bouacida^{a,c}, Meriem Hamlaoui^a, Hocine Merazig^a and Jean-Claude Daran^d

^aUniversité Constantine, Algeria

^bMcGill University, Montréal.

^cUniversité Oum El Bouaghi, Algeria.

^dUniversité de Toulouse, France .

P20 *Tetrakis[(μ -2-phenylacetato- κ^2 O:O')bis-[[dimethylamino]pyridine- κ N¹]- cobalt(II)]*

Meriem Benslimane^a, Yasmine Kheira Redjel^a, Georges Dénès^b and Hocine Merazig^a

^aUniversité Constantine, Algeria.

^bConcordia University, Montréal.

P21 *Formation of a Second Isomeric Dimer in Malaria Pigment*

Laura J. Brothers and D. S. Bohle^{*}

McGill University, Montréal.

P22 *Late Transition Metal Nucleophilic Thiols*

David S. Bohle^{*} and Mirna Paul

McGill University, Montréal.

P23 *Novel Ruthenium(II)-Letrozole Complexes as Breast Cancer Therapeutics and Development of a Nanosensor-based Aromatase Assay Using a Magnetic Cu-Fe Nanoparticle Catalyst*

Annie Castonguay, Mary Bateman, Cédric Doucet, Michal Juhas, Chao-Jun Li,^{*} Audrey Moores^{*} and Dusica Maysinger^{*}

McGill University, Montréal.

INORGANIC DISCUSSION WEEKEND

P24 *The Reactions of [Xe₃OF₃][AsF₆] with ClO₂F and BrO₂F; the Syntheses and Structural Characterization of FXeOCIO₃, Xe(OCIO₃)₂ and [ClO₂][AsF₆]-2XeF₂*

Jamie Haner, Mathias Ellwanger and Gary Schrobilgen*
McMaster University, Hamilton.

P25 *N-substitution of benzo-2,1,3-selenadiazole*

Lucia M. Lee, Zachary Arnott, Allan He and Ignacio Vargas-Baca*
McMaster University, Hamilton.

P26 *Study of Manganese Complexes Containing Tripodal Tetradentate Ligands for Lactide Polymerization*

Pargol Kashani, Frank Schaper*
Université de Montréal, Montréal.

P27 *C-H Activation & Functionalization of Phenol Via A New Orthonickelated Phosphinite Complex*

Boris Vabre, Félix Deschamps and Davit Zargarian*
Université de Montréal, Montréal.

P28 *Functional Neutral Radicals: Design and Development of Novel Materials for Magneto-Optoelectronic Applications*

François Magnan and Jaclyn Brusso*
University of Ottawa, Ottawa.

P29 *Modeling Study on Reverse Combustion Promoted by BiVO₄*

Camilo Viasus^{a,b}, Iliia Korobkov^a and Sandro Gambarotta^a

^aUniversity of Ottawa, Ottawa.

^bUniversidad de Ciencias Aplicadas y Ambientales, Colombia.

P30 *Synthesis of Iridium Phosphonium Indenyliide Complexes*

Kourosh Purdavaie, Michael Baird*
Queen's University, Kingston.

P31 *Pd(η^3 -1-Ph-C₃H₄)(η^5 -C₅H₅), an Unusual Catalyst Precursor for Buchwald-Hartwig Amination Reactions*

Sogol Borjjan Borojeni, Michael C. Baird*
Queen's University, Kingston.

P32 *Synthesis and Photochemistry of Highly π -Conjugated Organoboron Compounds Containing N-Heterocyclic Carbenes*

Soren K. Møllerup and Suning Wang*
Queen's University, Kingston.

P33 *Bright Blue and White Electrophosphorescent Triarylboron-Functionalized C[∧]N-Chelate Pt(II) Compounds*

Xiang Wang,^a Yi-Lu Chang,^b Jia-Sheng Lu,^a T. Zhang,^b Zheng-Hong Lu,^b Suning Wang^{a*}

^aQueen's University, Kingston.

^bUniversity of Toronto, Toronto.

P34 *Pyrazole-Based NCN-Type Ni Complexes: Synthesis by Direct Metallation, Characterisation and Reactivities*

Jean-Philippe Cloutier, Quentin Bourdon, Boris Vabre and Davit Zargarian
Université de Montréal, Montréal.

P35 *Synthesis and characterization of Ru(II) building blocks for light-harvesting applications based on a new 1,3,5-triazine ligand.*

Baptiste Laramée-Milette, Félix Lussier and Garry S. Hanan*

Université de Montréal, Montréal.

P36 *C-C, C-N, C-Si and Si-Si Coupling Reactions Catalyzed by POCOP Nickel Complex.*

Jingjun Hao, Boris Vabre, Berline Mougang-Soumé and Davit Zargarian*

Université de Montréal, Montréal.

P37 *TOF vs Electronic Spectroscopy: A Study of Hydrogen Photo-Catalysis reactions based on Rh₂-Re_n assemblies*

Daniel Chartrand and Garry S. Hanan*

Université de Montréal, Montréal.

P38 *Cyclometallation of Aza-Dipyrromethene on Neutral Ruthenium Complex: Toward New Photosensitizers in the NIR*

André Bessette^{a,b}, Janaina G. Ferreira^a, Mihaela Cibian^a, Francis Bélanger^b, Denis Désilets^b and Garry S. Hanan^{*a}

^aUniversité de Montréal, Montréal.

^bSaint-Jean Photochemicals Inc., Saint-Jean.

P39 *A Special Case of Solvatomorphism Inducing both Geometry and Spin Change at the Metal Center*

Mihaela Cibian, Sophie Langis-Barsetti and Garry S. Hanan*

Université de Montréal, Montréal.

P40 *Synthesis and Characterization of N-Bridged Bis-Hydroxyamidines/ α -aminonitrone (AMOX) as Synthons in Supramolecular Chemistry*

Mathieu Leblanc, Marine Devos, Mihaela Cibian and Garry S. Hanan*

Université de Montréal, Montréal.

INORGANIC DISCUSSION WEEKEND

P41 *Synthesis of Pincer-like Iron Compounds for Lactide Polymerization*
Arek Keuchguerian, Berline Mougang, F. Hein Schaper*, Davit Zargarian*
Université de Montréal, Montréal.

P42 *4,5-Diazafluorene Derivatives as Multipurpose Ligands*
Vincent T. Annibale, Rhys Batcup, Daniel A. Dalessandro, Tao Bai, Ustina Huh, Sarah J. Hughes and Datong Song*
University of Toronto, Toronto.

P43 *Low Oxidation State Phosphorus Macromolecules*
Stephanie C. Kosnik, Gregory Farrar, Erin L. Norton and Charles L.B Macdonald*
University of Windsor, Windsor.

P44 *Modeling Magnetic Interactions in Sulfur-Nitrogen Radical Chemistry*
Natalia M. Mróz and Jeremy M. Rawson *
University of Windsor, Windsor.

P45 *Stimuli-Responsive Supramolecular Gelation in Organometallic Peptide Conjugates*
Rouzbeh Afrasiabi^{a,b}, Heinz-Bernhard Kraatz^{*a,b}
^aUniversity of Toronto, Toronto.
^bUniversity of Toronto, Scarborough.

P46 *New Pincer-Type Ruthenium Complexes Designed for Small Molecule Activation via Metal-Ligand Cooperation*
Demyan E. Prokopchuk, Tsz Ho Tsui, Alan J. Lough and Robert H. Morris*
University of Toronto, Toronto.

P47 *A trans-Dihydride Complex as a Potential Molecular Rotor*
Ernest Prack^a, Alan J. Lough^a, Robert W. Schurko^b, Daniel Klauke^b and Ulrich Fekl^{1*a}
^aUniversity of Toronto, Toronto.
^bUniversity of Windsor, Windsor.

P48 *Toward Homogeneous Hydrodesulfurization Using a Low Valent Molybdenum Complex*
David B. Armstrong, Muhammad Qureshi and Ulrich W. Fekl*
University of Toronto, Mississauga.

P49 *Synthesis and Reactivity of Tantalum Complexes of a Bulky o-Phenylenediamide Ligand*
Trevor Janes and Datong Song*
University of Toronto, Toronto.

P50 *New Designs for 1,2,3,5-dithiadiazolyl Radical Ligands: A little Bit a this and a little Bit a that!*

Carolyn Michalowicz, Kathryn E. Preuss*
University of Guelph, Guelph.

P51 *Towards the Synthesis of the first 1,2,3,5-dithiadiazolyl Radical containing a thiocyanato moiety.*

Cuyler Trapp, Kathryn E. Preuss
University of Guelph, Guelph.

P52 *Substituent effects on the nitrogen chemical shift tensors in N-methylpyridinium salts*

Travis Fillion, Glenn Penner* and Rebecca Jamieson
University of Guelph, Guelph.

P53 *Paramagnetic thiazyl ligands for the design and synthesis of molecular materials displaying luminescent properties*

Scott Mackenzie, Kathryn Preuss*
University of Guelph, Guelph.

P54 *Metal-Radical Complex Exhibiting Magnetic Properties: 1D Heisenberg Chain*

R. Alex Mayo,^a Ian S. Morgan,^a Dmitriy Soldatov,^a Michael Jennings,^b Rodolphe Cl rac,^c Kathryn Preuss*^a

^aUniversity of Guelph, Guelph.

^bFreeLance Crystallography, London.

^cUniv. Bordeaux, France.

P55 *Rational design for mixed supramolecular pairs*

Michelle Mills and Kathryn E. Preuss*
University of Guelph, Guelph.

P56 *Di-Oxime Complexes of the First Row Transition Metals*

Katie Harriman, Nathan Yutronkie and Jaclyn Brusso*
University of Ottawa, Ottawa.

P57 *The Effects of Extended Conjugation and Heteroatoms on the Properties of 2-Dimensionally Fused Small Molecules*

Sean F. Robertson, Alicea A. Leitch, Kimberly A. Stobo, Ilia Korobkov, Jaclyn L. Brusso*

University of Ottawa, Ottawa.

P58 *Development of the bis-thiadiazinyl radicals for optoelectronic applications*

Nathan Yutronkie, Katie Harriman, Jaclyn Brusso*
University of Ottawa, Ottawa.

INORGANIC DISCUSSION WEEKEND

P59 *Reversible Inactivation of Bismuth Vanadate in the Photocatalytic Reduction of CO₂*

Jacob Sommers, Camilo Viasus and Sandro Gambarotta*
University of Ottawa, Ottawa.

P60 *Using Molecular Simulation to Aid in the Interpretation of Solid-State NMR of Metal Organic Frameworks*

Bianca R. Provost^a, Lei Guo^a, Thomas D. Daff^a, Andre Sutrisno^b, Yining Huang^{*b} and Tom K. Woo^{*b}

^aUniversity of Ottawa, Ottawa.

^bWestern University, London.

P61 *New Molybdenum and Tungsten Complexes with Pyridinediphosphinite Pincer Ligands*

Ruth Castro-Rodrigo and William D. Jones*
University of Rochester, United States.

P62 *C–S bond activation of thioethers using (dippe)Pt(NBE)₂*

Sabuj Kundu, Benjamin E. R. Snyder, Aaron P. Walsh, William W. Brennessel and William D. Jones*
University of Rochester, United States.

P63 *Complexes and reactivity of Ge(II) dications with small molecules*

Jennifer H. Nguyen^a, Rajoshree Bandyopadhyay^a, Ala'aeddeen Swidan^a, Jonathan W. Dube^b, Paul J. Ragogna^b and Charles L.B. Macdonald^{*a}

^aUniversity of Windsor, Windsor.

^bWestern University, London.

P64 *Oxidative Addition of Tetrathiocines: Synthesis, Structures and Properties of Group 10 Dithiolene Complexes and the Effect of the Phosphine Ligand*

Justin D. Wrixon, John J. Hayward, Osman Raza and Jeremy M. Rawson*
University of Windsor, Windsor.

P65 *Efforts Towards the Polymerization of Goedken's Macrocyclic*

Joseph A. Paquette and Joe B. Gilroy*
University of Western Ontario, London.

P66 *Phosphorous as a Scaffold for Transition Metals: Synthesis, Characterization and Reactivity of Organometallic Phosphonium Salts*

Amir Rabiee Kenaree, Jacquelyn T. Price, Paul J. Ragogna and Joe B. Gilroy*
University of Western Ontario, London.

P67 *Raman Study of Guest-Host Interactions of Halocarbons in Metal Organic Frameworks*

Maxwell Goldman, Yining Huang*
University of Western Ontario, London.

P68 *Homo- and diblock copolymers derived from a mixed sandwich cobaltocene: Overcoming a tight coil to give a real “Co” polymer.*

Mahboubeh Hadadpour, Yuqing Liu and Paul J. Ragogna*
Western University, London.

P69 *Running the Gauntlet: Interactions of Organometalldrugs with Metallothionein*

Daisy Wong, Duncan E. K. Sutherland, Martin J. Stillman*
University of Western of Ontario, London.

P70 *Effects of peripheral substituents on the electronic structure of Zn-anthraquinonoporphyrins*

Brittany Lewis^a, Tasha A. Jarisz^b and Martin J. Stillman*^a

^aUniversity of Western Ontario, London.

^bUniversity of Victoria, Victoria.

P71 *Guest Dynamics in Metal-Organic Framework Studied by ²H and ¹³C Solid-State NMR*

Farhana Gul-E-Noor, Jun Xu, Wei D. Wang, Haiyan Mao and Yining Huang*
University of Western Ontario, London.

P72 *Investigation of structural stability of MOF α -Mg₃(HCOO)₆ by Raman and FTIR Spectroscopy under High External Pressures*

Haiyan Mao^{a,b}, Jun Xu^a, Yue Hu^a Yining Huang*^a and Yang Song*^a

^aWestern University, London.

^bNanjing Forestry University, China.

P73 *MRI PARACEST agents that improve amide-based CEST measurements by eliminating inner sphere water T₂ exchange*

Mark Milne^a, Melissa M. Lewis^a, Nevin McVicar^b, Mojmir Suchy^{a, b}, Robert Bartha^b and Robert H. E. Hudson*^a

^aWestern University, London.

^bRobarts Research Institute, London.

P74 *Searching for the loose end: Proteolysis of Metallothionein*

Jasjit Singh^{a,b}, Maria T. Salgado^a and Martin J. Stillman*^a

^aUniversity of Western Ontario, London.

^bRyerson University, Toronto.

P75 *Antimicrobial UV cured surfaces*

Tyler J. Cuthbert^a, Ryan Guterman^a, Solmaz Karamdoust^a, Elizabeth R. Gillies*^{a,b} and Paul J. Ragogna*^a

^aDepartment of Chemistry and the Centre for Materials and Biomaterials Research, Western University, London.

^bDepartment of Chemical and Biochemical Engineering, Western University, London.

INORGANIC DISCUSSION WEEKEND

P76 *Studies on Benzodiazaphospholes: Towards Diazaphospholyl Radicals*

Thao T. P. Tran, Adam Dunmore and Jeremy M. Rawson*

University of Windsor, Windsor.

P77 *Selective Catalytic C=O Hydrogenation of Unsaturated Aldehydes, Ketones and Esters*

Denis Spasyuk and Dmitry G. Gusev*

Wilfrid Laurier University, Waterloo.

P78 *Preparation and Functionalization of Monodisperse Iron Oxide/Silica Core-Shell Magnetic Nanoparticles for Flow Purification*

Xia Chen, Michael G. Organ, William Pietro*

York University, Toronto.

P79 *Synthesis, Characterization and Reactivity Study of Bis(imino)-N-Heterocyclic Carbene Chromium(III), Iron(II) and Cobalt(II) Complexes*

Jameel Al Thagfi and Gino G. Lavoie*

York University, Toronto.

P80 *Reactivity Studies of Imino-N-Heterocyclic Carbene Complexes of Nickel and Palladium*

Anna C. Badaj and Gino G. Lavoie*

York University, Toronto.

P81 *Coordination and Reactivity Study of Functionalized Bidentate Monoanionic Imidazol-2-Imine Ligands to Group 4 and 10 Metals*

Michael B. Harkness, Timothy G. Larocque and Gino G. Lavoie*

York University, Toronto.

P82 *Electrochemical and Spectroelectrochemical Studies of the Reduction of Oxygen on Cobalt Phthalocyanines*

Maryam Hariri¹, Mahdiah Atighi², Alexandre Brolo², Sylvie Morin*¹

¹York University, Toronto.

²University of Victoria, Victoria.

P83 *Supported Transition Metal Catalysts for Use in the MACOS System*

Christopher W. Schruder, Michael G. Organ and William J. Pietro*

York University, Toronto.

Oral Presentations
OB Abstracts

OB1

Pressure Induced Phase Transitions and Metallization of a Neutral Radical Conductor

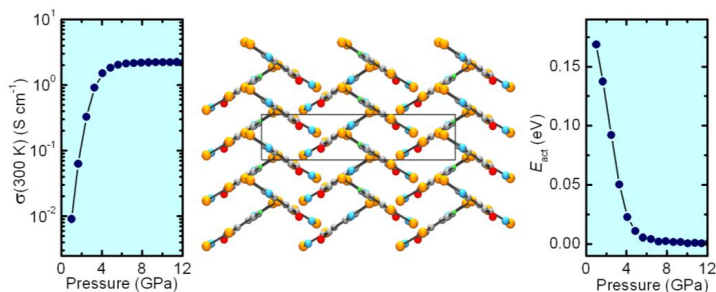
Joanne W. L. Wong, Aaron Mailman, Kristina Lekin, Stephen M. Winter and Richard T. Oakley*

Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1

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The crystal structure and charge transport properties of the prototypical oxobenzene-bridged 1,2,3 bisdithiazolyl radical are highly dependent on pressure. At ambient pressure, the radical is a Mott insulator displaying high, but activated conductivity, with $\sigma(300\text{ K}) = 6 \times 10^{-3}\text{ S cm}^{-1}$ and $E_{\text{act}} = 0.16\text{ eV}$.^[1] Compression of the α -phase, $Fdd2$, results in two additional phases, both in the $Pbn2_1$ space group, which displays an increase in conductivity by 3 orders of magnitude and the thermal activation energy is reduced to zero, heralding the formation of a metallic state. High pressure infrared absorption and reflectivity measurements are also consistent with closure of the Mott-Hubbard gap near 5 GPa. The results are discussed in the light of DFT calculations on the molecular and band electronic structure of the radical. The presence of a low-lying LUMO gives rise to high electron affinity which, in turns creates an electronically much softer radical with a low onsite Coulomb potential U . In addition, considerable crystal orbital (SOMO/LUMO) mixing occurs upon pressurization, so that a metallic state is readily achieved at relatively low applied pressure.



References:

- [1] Wong, J. W. L.; Mailman, A.; Winter, S. M.; Robertson, C. M.; Homberg, R. J.; Murugesu, M.; Dube, P. A.; Oakley, R. T. *Chem. Commun.* 2013, DOI:10.1039/C3CC46686H.

OB2

Sensitization of Rare Earth Metals with Boron Functionalized β -diketones

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Rare Earth metals have become increasingly attractive as materials for lighting applications due to their intriguing photophysical properties.^{1,2} The lanthanides have narrow $f \rightarrow f$ emission bands, long decay lifetimes and large Stokes shifts.² Unfortunately, the low extinction coefficients and forbidden nature of the $f \rightarrow f$ transitions means that the emission is usually very weak.² However, this can be enhanced by judicious choice of a ligand that produces an antenna effect, whereby electron density is transferred from the ligand to the metal's triplet state causing phosphorescence.³ Ligands commonly used for this purpose are based on the β -diketonate framework.¹ Triarylboron moieties are highly effective in this sensitization because the low-lying p_{π} -orbital has an appropriate triplet energy state to transfer the energy necessary to stimulate luminescence from either europium or terbium.⁴ The empty orbital on the boron substituent is also ideal for small anion sensing, which could be monitored by absorption or emission spectroscopy.⁴ This presentation will describe the synthesis and photophysical properties of four triarylboron functionalized β -diketone ligands and their corresponding lanthanide complexes, as well as their sensitivity to small anions.



Figure 1. Boron functionalized β -diketone ligands sensitize the emission of europium leading to a highly luminescent complex.

References:

- [1] Binnemans, K. *Chem. Rev.* 2009. **109**. 4283.
- [2] Georges, J. *Analyst.* 1993. **138**. 1481.
- [3] Bhaumik, M.L., El-Sayed, M. A., *J. Phys. Chem.* 1965. **69**. 275.
- [4] Varlan, M., Blight, B.A., Wang, S., *Chem Commun.* 2012. **48**. 12059.

OB3

Preliminary Surface Mechanisms and *In situ* Optical Monitoring for Metal Deposition from Group 11 Iminopyrrolidates by CVD

David J. Mandia¹, Matthew. B.E. Griffiths¹, Peter J. Pallister¹, Jason P. Coyle¹, Wenjun Zhou², Jacques Albert², Seán T. Barry*¹

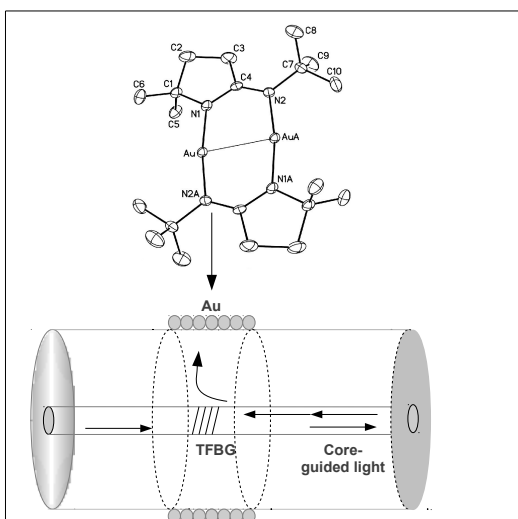
¹Carleton University, Department of Chemistry, 1125 Colonel By Drive, Ottawa, ON K1S 5B6

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The robust thermal and surface chemical properties of copper(I), silver (I) and gold(I) *tert*-butyl-imino-2,2-dimethylpyrrolidates ($[\text{M}^{\text{I}}(\text{Me}_2\text{-}^t\text{Bu-ip})]_2$; M=Cu, Ag, Au) have been explored extensively towards a broader understanding of their candidacy as precursors for vapour deposition techniques such as atomic layer deposition (ALD) and chemical vapour deposition (CVD). Thermogravimetric analysis (TGA), ¹H-NMR, and surface studies have been used to study and exploit these properties. Additionally, preliminary results from the CVD of gold and silver films have been studied by



scanning tunneling microscopy (SEM), atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS). An optical monitoring technique based on a tilted fiber Bragg grating (TFBG)^{1,2} that was used previously to study CVD growth of plasmonic metal thin films from gold(I) and silver (I) guanidates was also adapted to study the growth of gold thin films (6-65 nm) from $[\text{Au}^{\text{I}}(\text{Me}_2\text{-}^t\text{Bu-ip})]_2$. The precursor chemistry for copper, silver, and gold films both for CVD and ALD of metal films on flat substrates and optical fibers will be discussed, as well as general trends.

¹ Mandia, D. J.; Griffiths, M. B. E.; Zhou, W.; Gordon, P. G.; Albert, J.; Barry, S. T. *Phys. Procedia* **2013**, *46*, 12–20.

² Zhou, W.; Mandia, D. J.; Griffiths, M. B. E.; Bialiaieu, A.; Zhang, Y.; Gordon, P. G.; Barry, S. T.; Albert, J. *Opt. Express* **2013**, *21*, 245–55.

OB4

Property-based evolutionary design and optimisation of functionalised metal organic frameworks

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Metal organic frameworks (MOFs) have attracted significant attention in a number of fields, including gas separation, capture and storage, drug delivery and catalysis. For example, solid sorbents have the potential for cost-effective CO₂ scrubbing from flue gas since some have extremely large CO₂ capacities with more energy-efficient regeneration than current aqueous amine technologies. MOFs present an almost infinite design space with innumerable combinations of inorganic, organic and functional group building units. Our key

development is an algorithm to systematically replace symmetric positions in the MOF with functional groups, which generates billions of chemically distinct derivative structures from our library of substituents. Using this, we developed a fine-tuned evolutionary algorithm that will efficiently optimise the positions and combinations of functional groups to improve any property that we can calculate, screening only a small subset of the possible MOFs. We support these methods with a code that automates the complicated procedure for computationally measuring the performance of a MOF such that we can easily screen hundreds of thousands of our MOFs with tuneable accuracy. We can, for example, target structural properties like internal surface area, or optimise the gas adsorption capacity or selectivity. This functionalisation procedure has been applied to already known MOFs that will maintain their structures after functionalisation, thereby providing lab scientists realistic synthetic targets. We have increased the CO₂ capacity of MOFs (e.g. Figure 1) but, ultimately we are able to calculate and combine all the properties necessary for us to estimate the parasitic energy and monetary cost to a power plant for implementing our best performers.

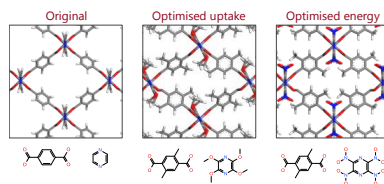


Figure 1. A MOF (CO₂ uptake 0.74 mmol/g) has functional groups optimised with an evolutionary algorithm to increase uptake to 4.17 mmol/g or combinations of properties.

OB5

New Families of 4f- and 3d/4f-Metal Complexes Exhibiting Single-Molecule Magnetism, Magnetic Refrigeration and Photoluminescence Properties

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One of the most fascinating challenges in modern coordination chemistry is undoubtedly the combination of an aesthetically pleasing structure with an interesting physical property or occasionally with more than one properties within the same molecular species. Polynuclear homometallic 4f- and heterometallic 3d/4f-metal compounds are clearly excellent candidates to satisfy such expectations. This is due to the pronounced ability of these metal ions to form and stabilize high-nuclearity and structurally complicated metal-oxido/hydroxido inorganic cores surrounded in the periphery by organic bridging/chelating ligands. From an application viewpoint, 4f- and 3d/4f-metal complexes have shown a remarkable ability to act either as single-molecule magnets (SMMs), mainly when the f-block ions are highly anisotropic and possess a significant spin (i.e., Dy^{III}, Tb^{III}), or as magnetic refrigerants when the molecules are isotropic and high-spin, conditions which are fulfilled by the co-presence of, for instance, Gd^{III} and Cu^{II} metal ions.^[1] We shall herein present our recent results from the combination of the above mentioned properties with the photoluminescence one, in an attempt to construct 'hybrid' molecular magnetic materials.

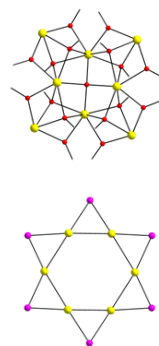


Figure. Representative $[Ln_8]$ and $[TM_6Ln_6]$ complexes to be discussed in the presentation [Ln = Lanthanide; TM = Transition Metal].

References:

- [1] D. Dermitzaki, G. Lorusso, C. P. Raptopoulou, V. Psycharis, A. Escuer, M. Evangelisti, S. P. Perlepes and Th. C. Stamatatos, *Inorg. Chem.*, **2013**, 52, 10235.

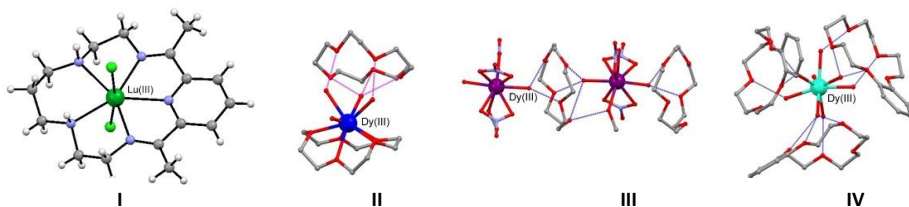
OB6

Magnetically Interesting Lanthanide Complexes of Schiff-Base
Macrocycles and Crown EthersEmma Gavey, Majeda Al Hareri and Melanie Pilkington*¹¹Brock University, 500 Glenridge Ave, St. Catharines, ON L2V 2L5E-mail of presenting author: eg08yp@brocku.caE-mail of corresponding author: mpilkington@brocku.ca

From the first lanthanide single-ion magnet (SIM) reported by Ishikawa,^[1] complexes based on phthalocyanine and its derivatives have comprised the largest category of SIMs. The small cavity size of the cyclic phthalocyanine ligand appears to encourage the formation of an anisotropy-enhancing 'sandwich-type' structure.^[2] Two classes of cyclic ligand which remain relatively unexplored for the synthesis of magnetic materials are Schiff-base macrocycles and crown ethers. Our research objectives are to exploit these ligands for the synthesis of novel magnetic compounds.

While lanthanide complexes of a few Schiff-base macrocycles have been reported (I),^[3] none have been magnetically characterized. We have prepared a family of five new Dy(III) complexes based on pentadentate oxa-aza Schiff-base macrocycles, which display interesting spin-glass-like behavior.

Crown ether complexes of lanthanides have been of interest for some time for their potential applications as luminescent materials.^[4] Focusing on Dy(III), Tb(III) and Er(III), we have prepared a number of new Ln(III)-crown ether species (such as II, III and IV). The synthesis, structural and magnetic properties of these compounds will be discussed.



References:

- [1] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694.
 [2] D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield. *Chem. Rev.* **2013**, *113*, 5110.
 [3] W. Radecka-Paryzek, V. Patroniak, V. M. Kubicki. *Polyhedron.* **2003**, *22(20)*, 2773.
 [4] M. F. Belian, G. F. de Sa, S. Alves, A. Galembeck. *J. Luminescence.* **2011**, *131(5)*, 856.

OB7

In-situ high pressure studies on MOFs and their performance for CO₂ storage

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Metal-Organic Frameworks (MOFs), are crystalline nanoporous materials comprised of small metal clusters connected three-dimensionally by organic ligands. MOFs have been widely studied due to their high porosity, surface area and thermal stability, which make them promising candidates for gas capture and storage. In contrast to the extensive studies under ambient conditions, only a small number of MOFs have been studied under high pressure (e.g., in the gigapascal range). It is known that pressure can be used to achieve structural modifications, including changes in pore size, opening and geometry, that will subsequently affect the sorption behaviors of the porous materials. In this study, we report the first *in situ* high-pressure investigation of ZIF-8 and MIL-68 (In) and their performance for CO₂ storage by FTIR spectroscopy. We observed several pressure-induced transformations of the frameworks upon compression and examined the reversibilities of these transformations upon decompression. Furthermore, the IR profiles of CO₂ as well as the frameworks show direct evidence of the interactions between CO₂ and the frameworks, indicating enhanced storage of CO₂ in the frameworks. In addition, the storage behavior was found to be strongly pressure dependent, and the interaction mechanism was explored. These findings demonstrated that MOF based materials have great potential in greenhouse gas storage.

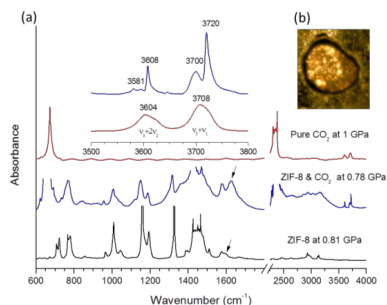


Figure. IR spectrum of ZIF-8 loaded with CO₂ (middle) compared with that of pure CO₂ (top) and that of pure ZIF-8 (bottom).

OB8

Electrospray Ionization Mass Spectrometry: A Useful Technique for Characterization of Methylaluminoxane Solutions

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Electrospray ionization mass spectrometry (ESI MS) is a powerful method for detection, and in favourable cases, identification of charged analytes in solution. It's application to the study of air-sensitive, organometallic complexes has been restricted by the need to use polar and/or donor solvents, as well as eliminate adventitious hydrolysis and oxidation, prior to or during analysis. Our research group has developed a number of refinements that allow for analysis of air-sensitive compounds, even in non-polar media.^[1] We have applied some of these techniques to the analysis of aluminoxane solutions, where these Lewis acidic materials are capable of generating charged species through reaction with neutral or charged additives.^[2]

These studies shed important light on the elusive mechanism of action of methylaluminoxane (MAO) co-catalysts and illustrate that the mechanism of e.g. metallocene catalyst activation is significantly different than originally proposed. In this presentation we will describe further details of this work, including our attempts to quantitate the amount of charged species formed under various conditions; in particular, we hope that ESI MS will provide insight as to the reasons for a large excess of MAO needed for metallocene catalyst activation in solution vs. supported on e.g. silica.

References:

- [1] (a) Lubben, A.T.; McIndoe, J. S.; Weller, A.S. *Organometallics* 2008,27, 3303-3306. (b) Henderson M. A.; McIndoe J. S. *Chem. Commun.* 2006, 2872-2874.
- [2] (a) Trefz, T. K.; Henderson, M. A.; Wang, M. Y.; Collins, * S.; McIndoe,* J. S. *Organometallics*, 2013, 32, 3149–3152. (b) Henderson, M.A.; Trefz, T. K.; Collins, S.; Wang, M. Y.; McIndoe,* J.S. *Organometallics*, 2013, 32, 2079-2083.

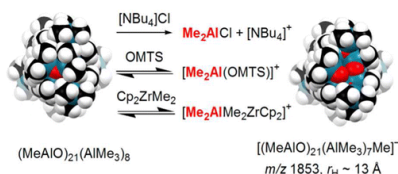


Figure. Depiction of a neutral methylaluminoxane molecule, reacting with neutral or charged additives to form ions featuring the same counter-anion, partnered with different cations. Both ions are detected by ESI MS in fluorobenzene solution.^[2a]

OB9

Sulfur Tetrafluoride in the Solid-State

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Recently, our lab has synthesized a range of protonated nitrogen-base fluoride salts containing SF₄. These structures, which were characterized by X-ray crystallography and Raman spectroscopy, exhibit a surprising range of bonding modalities between fluoride and SF₄ and provide an extensive view of SF₄ in the solid state. The [HNC₅H₃(CH₃)₂]⁺₂F⁻[SF₅]⁻•4SF₄ salt contains layers of SF₄. Subsequently, we were able to obtain an X-ray crystal structure of neat SF₄, a reactive gas at room temperature with a melting point of -121 °C.^[1] The solid-state structure of this important binary main-group fluoride has been subject of many speculations, and attempts to obtain the crystal structure had failed in the past. Its structure can best be described as a network with weak intermolecular S⋯F contacts.

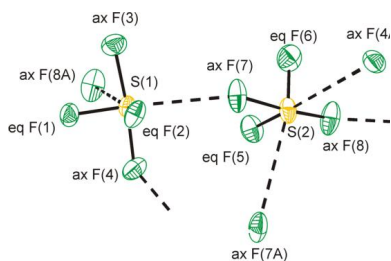


Figure. Thermal ellipsoid plot of SF₄.
Ellipsoids are set at 50% probability.

References:

[1] J. T. Goettel, N. Kostiuk, M. Gerken, *Angewandte Chemie International Edition*, **2013**, *125*, 8195-8198

OB10

Vibrational Studies of Group 8 Metallocenes

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Metallocenes have generated a lot of interest over the years in their application as catalysts, as anticancer drugs and in non-linear optics.^[1] The most famous metallocene is ferrocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Fe, which is part of the group 8 metallocene family. Much of the previous research on ferrocene and other group 8 metallocenes has been focused on using Raman or infrared spectroscopy to study the effects of temperature. Very few variable-pressure studies have been performed on group 8 metallocenes.^[2,3] Only infrared spectroscopy has been used to observe the effects of pressure on ferrocene and ruthenocene. We have used a diamond-anvil cell (DAC) to perform variable-pressure Raman spectroscopy on ferrocene, ruthenocene and osmocene. In addition, photoacoustic and variable-temperature Raman measurements are included for further comparisons to the literature.

References:

[1] Long, N. J. *Metallocenes, An introduction to sandwich complexes*; Blackwell Science Ltd., Oxford, 1998, p 227-271.

[2] Adams, D. M.; Williams, A. D., *Spectroscopy at very high pressures—XXV: The IR spectrum of ferrocene at high pressures*. *J. Phys. Chem. Solids* 1980, 41 (10), 1073-1078.

[3] Roginski, R. T.; Shapley, J. R.; Drickamer, H. G., *High-pressure spectroscopic studies of ferrocene, nickelocene, and ruthenocene*. *J. Phys. Chem.* 1988 ; 92 (15), 4316-4319.

OB11

Exploring conformations of As_x- and apo-metallothioneins using ESI-MS and covalent labellingGordon W. Irvine¹ and Martin J. Stillman*¹¹ The University of Western Ontario, 1151 Richmond St, London, ON N6A 5B7E-mail of presenting author: girvine@uwo.caE-mail of corresponding author: martin.stillman@uwo.ca

Metallothioneins are cysteine rich, metal binding proteins found ubiquitously in nature. While the fully metallated species have been studied widely, the metalation reaction of the metal-free (apo-) and partially metallated protein is poorly understood with the exception of arsenic binding^[1]. Key to the metalation pathway is the protein conformation of the intermediates and the arrangement of the coordinating cysteines prior to metalation. Computational results of Rigby-Duncan & Stillman predicted a loose globular conformation for the apo-MT at neutral pH when hydrogen bonding was extensive with the cysteinyl thiols located on or near the exterior surface^[2]. We report experimental verification of these calculations based on detailed cysteine modification experiments using ESI-MS. Previously we have demonstrated a difference in cysteine accessibility in the alpha and beta domains when partially metallated with arsenic using these methods^[3]. The mass spectral results are complicated but show that apo- α -metallothionein 1a adopts very different conformations at low pH compared with neutral pH. These conformations exhibit significantly different reaction properties when exposed to the cysteine modifier benzoquinone. We suggest that the structure of apo-metallothionein can be thought of as being primed for metal binding in its native state and that denaturation results in a marked decrease in metal-binding rates. Similar studies were performed on metallothionein partially metallated with As³⁺. Even at low pH these partially metallated species show significant structural features implying that metalation is the most important factor in MT folding although not the only one. These results reinforce the notion that modification of cysteine residues in MT is a useful tool in determining the conformation of the protein in solution.

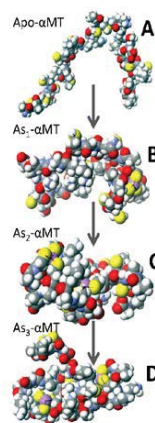


Figure 1. Conformations of metallothionein species during metalation

References:

- [1] Ngu, T. T. et al. *J. Am. Chem. Soc.* **2008** 130(50):17016-17028.
 [2] Rigby, K.E. et al. *Biochem. Biophys. Res. Comm.* **2004** 325(4):1271-1278.
 [3] Irvine, G. W. et al. *Biochem. Biophys. Res. Comm.* **2013**. 433(4): 477-483

OB12

Noble-Gas Difluoride Coordination Complexes of Hg(II); Hg(OTeF₅)₂·1.5NgF₂ (Ng = Xe, Kr)

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Among the group 12 elements, mercury appears to be the best candidate for the stabilization of the +IV oxidation state owing to relativistic and spin-orbit coupling effects. A matrix-isolation study has provided evidence for the formation of Hg(IV) as HgF₄.¹ The latter compound proved to be unstable, decomposing to HgF₂ and F₂ upon warming the matrix above 10 K. Quantum-chemical calculations indicate that derivatives of the highly electronegative –OChF₅ (Ch = Se, Te) groups could provide avenues to the bulk syntheses of Hg(IV) compounds, e.g., Hg(OChF₅)₄ and F₂Hg(OChF₅)₂.² In the present work, the synthetic precursor, Hg(OTeF₅)₂, has been synthesized in high purity and high yield and structurally characterized along with its isomorphous binary noble-gas coordination complexes, Hg(OTeF₅)₂·1.5NgF₂ (Ng = Xe, Kr). The latter compounds were characterized by low-temperature single-crystal X-ray diffraction, Raman spectroscopy, and quantum-chemical calculations. The Hg(OTeF₅)₂·1.5KrF₂ complex (Figure) is the first reported example in which KrF₂ is coordinated to a mercury center. Moreover, it provides the first example of a bridging KrF₂ molecule and is only the second KrF₂ coordination complex to be structurally characterized by X-ray diffraction.³ The photolysis or reaction of these complexes, such as with AsF₅, may lead to Hg(IV) derivatives, e.g., F₂Hg(OTeF₅)₂, FHgOTeF₅⁺AsF₆⁻, and reduction of Ng(II) to Ng gas.

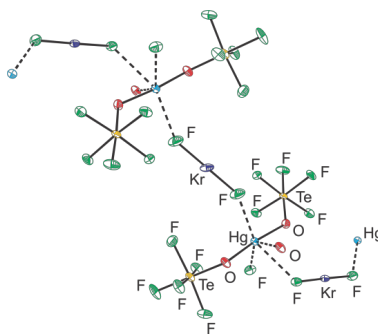


Figure. The X-ray crystal structure of Hg(OTeF₅)₂·1.5KrF₂ (P2₁/n, Z = 2, –173  C) showing the repeat unit in its fluorine-bridged network.

References:

- [1] Wang, X.; Andrews, L.S.; Riedel, S.; Kaupp, M.; *Angew. Chem. Int. Ed.* **2007**, *46*, 8371–8375.
 [2] Riedel, S.; Straka, M.; Kaupp, M.; *Chem. Eur. J.* **2005**, *11*, 2743–2755.
 [3] Brock, D.S.; Casalis de Pury, J.J.; Mercier, H.P.A.; Schrobilgen, G.J.; Silvi, B.; *J. Am. Chem. Soc.* **2010**, *132*, 3533–3542.

OB14

Efficient base-catalyzed hydrosilylation of carbonyls.

Kseniya Revunova and Georgii I. Nikonov*

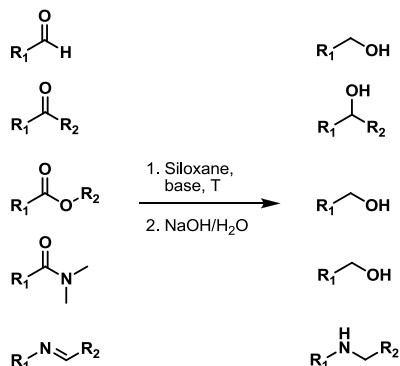
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For decades catalytic hydrosilylation of carbonyls has been the domain of transition metals, whereas reports on metal-free hydrosilylation are relatively rare and mostly limited to catalysis with boranes^[1] and fluorides.^[2]

In this communication we demonstrate a simple technique for metal-free reduction of aldehydes, ketones and esters into alcohols by using cheap siloxanes as the hydrogen source and hydroxides/alkoxides as catalysts. The method was also extended to the reduction of aldimines and tertiary amides. Practical reaction conditions were developed for each type of substrate.

The base-induced defragmentation of siloxanes into light silanes was observed and proved to be essential for this reduction process. Mechanistic studies substantiated the notion that reduction happens via intermediate formation of silicate species.



Scheme 1. Reductive hydrosilylation with siloxane/base system

References:

- [1] D. J. Parks, W. E. Piers, *J. Am.Chem.Soc.* **1996**, *118*, 9440-9441.
 [2] C. Chuit, R. J. P. Corriu, R. Perz, C. Rey , *Synthesis* **1982**, *1982*, 981-984.

OB15

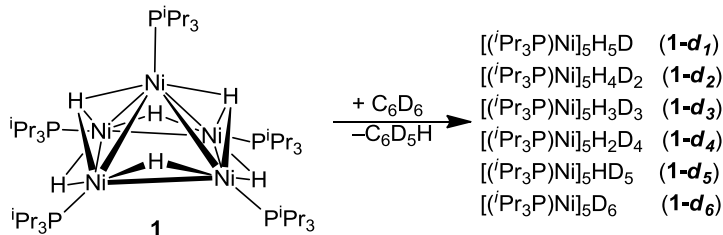
Mechanistic Investigation of H/D exchange of Unactivated C-H Bonds from a Pentanuclear Nickel Cluster.

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C–H bonds generally have large dissociation energies and are unreactive under typical organic transformations. Several mechanisms of C–H activation exist, such as oxidative addition, electrophilic substitution and σ -bond metathesis. Unactivated C–H bonds are found in common laboratory solvents such as benzene, toluene and THF. The pentanuclear nickel hydride cluster $\text{Ni}_5\text{L}_5\text{H}_6$ ($\text{L}=\text{P}^i\text{Pr}_3$) was shown to activate C–D bonds from several deuterated complexes while exchanging hydrogen from the hydride in the cluster. The process resulted in the observation of several isotopologues via $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR. The cluster was also found to catalytically exchange deuterium between several substrates. The cluster has a temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR, which suggests a singlet ground state and a low lying triplet state. Studies to better understand the mechanism of C–H activation will be discussed.

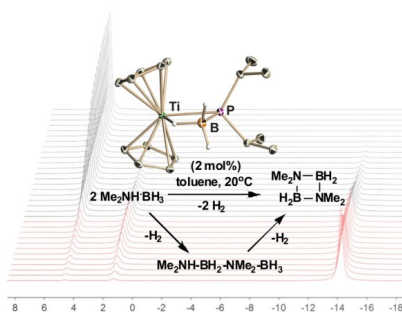


Beck, R; Shoshani, M; Johnson, S.A. *Angew. Chem. Int. Ed.* **2012**, 47, 11923-11926.

OB16

Developing Ti^{III} Precatalysts for the Dehydrocoupling/Dehydrogenation of Amine-BoranesTitel Jurca¹, and Ian Manners*¹¹School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TSE-mail of presenting author: titel.jurca@bristol.ac.ukE-mail of corresponding author: ian.manners@bristol.ac.uk

Catalytic dehydrocoupling/dehydrogenation of amine-boranes has become a field of intense interest and rapid growth; largely driven by potential applications in hydrogen storage, transfer hydrogenations, and synthesis of novel inorganic polymers. Consequently, a wide variety of catalysts systems have been developed to promote this reaction, with the majority based on late transition metals.¹ Our group has previously reported that first-row Group 4 metallocene [Cp₂Ti] is an efficient homogeneous catalyst for the dehydrogenation of secondary amine-borane adduct Me₂NH·BH₃ to give cyclodiborazane [Me₂N·BH₂]₂, proceeding via the detected linear diborazane Me₂NH·BH₂·NMe₂·BH₃. Prior mechanistic understanding of this reaction centered around the interplay of Ti intermediates in the +2 and +4 oxidation states.²



Recently our group reported the isolation of several analogous paramagnetic Ti^{III} species as potential intermediates in the catalytic dehydrogenation process. A Ti^{III} amidoborane complex [Cp₂Ti-NMe₂-BH₃], and a Ti^{III} phosphidoborane complex [Cp₂Ti-PPh₂-BH₃]. Both species proved to be highly active catalysts for the catalytic dehydrocoupling of Me₂NH·BH₃.³ We report the synthesis of several new Ti^{III} complexes, and report their catalytic activity for the dehydrocoupling of Me₂NH·BH₃ and dehydrogenation of *i*Pr₂NH·BH₃. Our results reinforce the proposal that paramagnetic Ti^{III} species play a key catalytic role in the dehydrogenation chemistry, as opposed to the conventional proposal of a Ti^{II}-Ti^{IV} cycle. Moreover, our work delivers a viable Ti^{III} phosphido-borane precatalyst that is easily accessible, has minimal side products and mirrors the activity of the highly sensitive and difficult to synthesize reaction intermediate [Cp₂Ti-NMe₂-BH₃].

References:

- [1] Leitao, E. M.; Jurca, T.; Manners, I. *Nature Chem.* **2013**, *5*, 817-829.
 [2] (a) Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582-9583. (b) Sloan, M. E.; Staubitz, A.; Clark, T. J.; Russell, C. A.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 3831-3841.
 [3] Helten, H.; Dutta, B.; Vance, J. R.; Sloan, M. E.; Haddow, M. F.; Sproules, S.; Collison, D.; Whittell, G. R.; Lloyd-Jones, G. C.; Manners, I. *Angew. Chem. Int. Ed.* **2013**, *52*, 437-440.

Oral Presentations
OC Abstracts

OC1

Effective Iron Catalysts for the Asymmetric Reduction of Ketones and Imines

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The asymmetric transfer hydrogenation of prochiral ketones and imines is a valuable transformation because it allows the production of enantiopure alcohols and amines for the use in the pharmaceutical fragrance and food industries. Currently the industrial catalysts use ruthenium or iridium for these processes, elements that are much more expensive and rare than iron. Where such alcohols or amines are synthesized using these platinum metal catalysts for use as pharmaceutical intermediates, it is important that all traces of the toxic metal are removed. Iron on the other hand is an essential element. We describe the discovery of selective and unusually active iron-based homogeneous catalysts based on our previous efforts.^[1] This enables the production of enantio-enriched alcohols and amines used in the pharmaceutical and fine chemical industry without the need of expensive conventional platinum metal complexes. A new method to make enantiopure ligands is introduced that takes advantage of the iron(II) ion as a template. These new ligands permit the efficient, multi-component synthesis of a wide range of highly active iron catalysts with varied structural features. The catalytic mechanism is elucidated by detecting hydride intermediate in an extremely efficient transfer of a hydride plus a proton to ketone substrates.

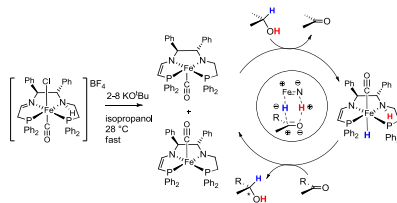


Figure. The proposed mechanism for the asymmetric hydrogenation of acetophenone by transfer from isopropanol catalyzed by an iron(II) P-N-N(H)-P catalyst

References:

- [1] *Sui-Seng, C.; Freutel, F.; Lough, A. J.; Morris, R. H. Angew. Chem., Int. Ed.* **2008**, *47*, 940; *Mikhailine, A.; Lough, A. J.; Morris, R. H. J. Am. Chem. Soc.* **2009**, *131*, 1394; *Sues, P. E.; Lough, A. J.; Morris, R. H. Organometallics* **2011**, *30*, 4418; *Lagaditis, P. O.; Lough, A. J.; Morris, R. H. J. Am. Chem. Soc.* **2011**, *133*, 9662; *Mikhailine, A. A.; Maishan, M. I.; Lough, A. J.; Morris, R. H. J. Am. Chem. Soc.* **2012**, *134*, 12266.

OC2

4,5-Diazafluorene Derivatives: Binucleating Ligands for the Synthesis of Heterobimetallic Compounds

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The potential catalytic application of heteromultimetallic complexes in organic synthesis has recently become a topic of interest. Combining two or more metals with different properties may lead to metal-metal cooperativity unseen by the monometallic or homomultimetallic derivatives. However, the synthesis of heteromultimetallic compounds is not a trivial task. 4,5-Diazafluorene (L^-) is a binucleating ligand that contains an N,N-chelate and a Cp moiety.^[1] The majority of metals coordinate to the N,N-chelate with few exceptions.^{[1], [2]} To compete with the N,N-chelate a tethered phosphine arm was placed at the 9-position to provide a P,C-chelate.^{[3], [4]} Mesityl groups placed at the *ortho*-positions of the N-donors prevent bulky metal fragments from coordinating to the N,N-chelate.^[2]

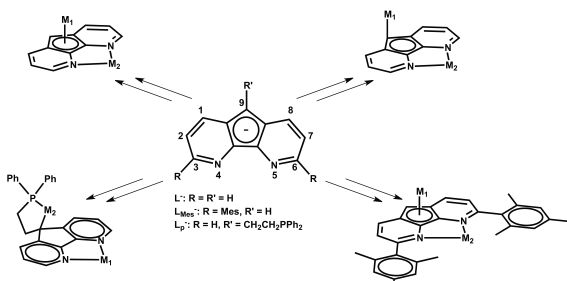


Figure 1: Binding modes for 4,5-diazafluorene derivatives.

We present the use L^- and its derivatives: 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorene (L_p^-) and 3,6-dimesityl-4,5-diazafluorene (L_{Mes}^-) as binucleating ligands in the synthesis of heterobimetallic complexes with metals ranging from groups 8 to 11. Pt(II)-Cu(I) heterobimetallic compounds were synthesized using L^- and L_p^- . For L_p^- the tethered phosphine secured the Pt(II) centre to the carbanion leaving the Cu(I) centre at the N,N-chelate. For L^- the Pt(II) centre coordinated to the N,N-chelate and the Cu(I) coordinated to the carbanion in an $\eta^1(\pi)$ -fashion.^[4] A $[RuCp^*]^+$ fragment is able to coordinate to the C₅ ring of L^- and L_{Mes}^- in an η^5 -fashion^[2] allowing for the synthesis of a series of Ru(II)-M heterobimetallic complexes (M = Fe, Co, Pd, Pt, Cu).

References:

- [1] Jiang, H.; Song, D. *Organometallics* **2008**, *27*, 3587-3592
- [2] Annibale, V. T.; Batcup, R.; Bai, T.; Hughes, S.; Song, D. *Organometallics* **2013**, DOI: 10.1021/om400846f
- [3] Tan, R.; Chiu, F. S. N.; Hadzovic, A.; Song, D. *Organometallics* **2012**, *31*, 2184-2192
- [4] Batcup, R.; Chiu, F. S. N.; Annibale, V. T.; Huh, J.-E.; Song, D. *Dalton Trans.* **2013**, DOI: 10.1039/C3DT52135D

OC3

Ligand Formation and Open Site Creation Through Nucleophilic Addition to the Ligand on a Molybdenum Tris(dithiolene) Complex

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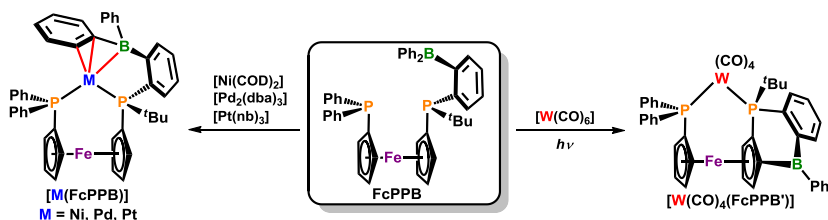
When transition metal complexes undergo reactions, the supporting ligands normally are "spectator ligands". While the sulfur centers of dithiolenes can be expected to be attacked by electrophiles (e. g., alkylating agents), it is still rare that a dithiolene ligand is attacked by a nucleophile. We now report the addition of a nucleophile to one of the ligands in molybdenum trisdithiolene $\text{Mo}(\text{S}_2\text{C}_2\text{R}_2)_3$. This creates an open site at the metal center by converting a bidentate dithiolene ligand into a monodentate zwitterionic ligand. Computational modeling suggests the complex to have a square pyramidal structure. The product complex is a structural DMSO reductase model.

OC4

Transition Metal Complexes of a Ferrocene-Based Bisphosphine-Borane Ligand

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The reactivity of a new ferrocene based borane-containing ambiphilic ligand, FcPPB (see Scheme below), with various transition metal precursors has been explored. Reactions with the Group 10 metal precursors [Ni(COD)₂] (COD = 1,5-cyclooctadiene), [Pd₂(dba)₃] (dba = dibenzylideneacetone) and [Pt(nb)₃] (nb = norbornene) lead to co-ligand-free metal complexes, [M(FcPPB)] (M = Ni, Pd, Pt), which feature κ^2 -bisphosphine coordination and η^3 -BCC bonding of the diphenylborane unit in FcPPB (η^3 -BCC coordination of a pendent BPh₂ unit has also been reported by the Emslie Group in a Pd(0) complex, a Ni(0) complex, and a Rh-Fe heterobimetallic complex featuring TXPB; a phosphine/thioether/borane ligand).[1,2] Reacting [Pt(FcPPB)] with CO and CNXyl results in terminal coordination of the external substrate, and facile interconversion of the η^3 -BCC coordinated borane-unit to η^2 -BC and η^1 -B metal-borane bonding modes, respectively. In addition, H₂ oxidatively adds to [Pt(FcPPB)] forming a complex which contains one hydride bound terminally to the metal centre, and one hydride residing in a bridging position between platinum and the pendant borane. Finally, upon reaction of the FcPPB ligand with [W(CO)₆] under photochemical conditions κ^2 -bisphosphine coordination is observed, however B-C and C-H bond cleavage are observed within the pendent BPh₂ unit and one of the cyclopentadienyl groups, respectively, yielding benzene and [W(CO)₄(FcPPB')] (where the FcPPB' ligand contains a fused tricyclic ring system, see Scheme below). X-ray crystallographic, NMR and IR spectroscopic data will be presented here-in.



References:

- [1] Emslie, D. J. H.; Harrington, L. E.; Jenkins, H. A.; Robertson, C. M.; Britten, J. F. *Organometallics* **2008**, *27*, 5317.
 [2] Oakley, S. R.; Parker, K. D.; Emslie, D. J. H.; Vargas-Baca, I.; Robertson, C. M.; Harrington, L. E.; Britten, J. F. *Organometallics* **2006**, *25*, 5835.

OC5

The Same Boa-ing Story?: Lanthanide Contraction Explains Trend in a Series of $-\text{[Ln-radical]}-$ Coordination Polymers

Adam C. Maahs,¹ Elisa M. Fatila,¹ Rodolphe Clérac,² Mathieu Rouzières,² Dmitriy V. Soldatov,¹ Kathryn E. Preuss^{*1}

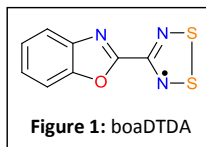
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Compounds containing the neutral thiazyl radical heterocycle 1,2,3,5-dithiadiazolyl (DTDA)[1] have demonstrated a wide range of interesting magnetic behaviour when varied to include desired substituents at the 4 position.[2,3] The use of a DTDA nitrogen atom in bidentate N,N' or N,O ligands, when appropriately substituted, has resulted in numerous transition metal[4,5] and lanthanide ion complexes.[6,7] Using the



boaDTDA ligand,[4] a series of isostructural 1D $-\text{[Ln}^{3+} - \text{radical]}-$ chain complexes (Ln = Ce, Pr, Nd, Sm, Eu) has been synthesized featuring a $\text{Nd}(\text{hfac})_3\text{boaDTDA}$ complex which is a ferrimagnet below 2.2K. As a result of the lanthanide contraction, the Ln – O,O'(hfac) and Ln – N,N'(boaDTDA) distances of the 10 coordinate Ln(III) ions in the chain decrease with increasing atomic number, while the Ln – N,O'(boaDTDA) distance increases to the point where the Gd^{3+} complex forms discrete molecular units of a different morphology.[7]

- 1) Vegas, A.; Pérez-Salazar, A.; Banister, A. J.; Hey, R. G.; *J. Chem. Soc., Dalton Trans.*, **1980**, 1812.
- 2) Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. J. R.; Palacio, F.; *Angew. Chem., Int. Ed. Engl.*, **1996**, *25*, 2533.
- 3) Alberola, A.; Less, R. J.; Pask, C. M.; Rawson, J. M.; Palacio, F.; Oliete, P.; Paulsen, C.; Yamaguchi, A.; Farley, R. D.; Murphy, D. M.; *Angew. Chem., Int. Ed.*, **2003**, *42*, 4782.
- 4) Fatila, E. M.; Goodreid, J.; Clerac, R.; Jennings, M.; Assoud, J.; Preuss, K. E.; *Chem. Commun.*, **2010**, *46*, 6569.
- 5) Hearn, N. G. R.; Preuss, K. E.; Richardson, J. F.; Bin-Salamon, S.; *J. Am. Chem. Soc.*, **2004**, *126*, 9942.
- 6) Fatila, E. M.; Clérac, R.; Rouzières, M.; Soldatov, D. V.; Jennings, M.; Preuss, K. E.; *Chem. Commun.*, **2013**, *49*, 6271.
- 7) Fatila, E. M.; Rouzières, M.; Jennings, M. C.; Lough, A. J.; Clérac, R.; Preuss, K. E.; *J. Am. Chem. Soc.*, **2013**, *135*, 9596.

OC6

Photoelimination Route to 1,3-Azaborines Using N-Heterocyclic Carbene-Borane Precursors

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Novel activation pathways present a great opportunity to discover and develop new chemistry. Often these discoveries lead to new commercial materials or allow for new catalytic processes. B,N-heterocyclic compounds have recently emerged as a class of very promising and important materials for many different applications.^{1,2}

Recently in the Wang group, a new photoactivated coupling reaction across a carbon-boron bond was discovered, producing a new synthetic route to 1,2-azaborines.³ This new chemistry has driven us to study the role of the ligand in inducing photoelimination. The ligand class we have selected to mimic this photoreactivity is the N-heterocyclic carbene (NHC). NHCs were selected because they are highly tuneable for electronics, solubility and stability. Secondly, the predicted photoproduct contains an imbedded 1,3-azaborine, which is the least thermodynamically stable azaborine isomer and very few synthetic routes exist to create them.⁴

In this study, NHCs were designed to mimic the bonding motifs that were established by the phenylpyridine ligands. New reactivity was discovered when applying limiting conditions on the parent NHC. Studies were monitored by the use of ¹H and ¹¹B NMR in conjunction with UV/visible and fluorescence spectroscopy.

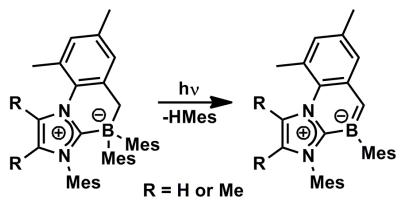


Figure 1: Representative scheme for the photoelimination of mesitylene for N-heterocyclic carbene-BMe₂ chelates.

References:

- [1] Jaska C. A.; Emslie D. J. H.; Bosdet M. J. D.; Piers W. E.; Sorensen T. S.; Parvez M.; *J. Am. Chem. Soc.* **2006**, *128*, 10885.
- [2] Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y.; *Angew. Chem. Int. Ed.* **2012**, *51*, 6074.
- [3] Lu J. S.; Ko S.-B.; Walters N. R.; Kang Y.; Sauriol F.; Wang S.; *Angew. Chem. Int. Ed.* **2013**, *52*, 4544.
- [4] Xu S.; Zakharov L. N.; Liu S.-Y.; *J. Am. Chem. Soc.* **2011**, *133*, 20152.

OC7

A strong σ -donor ligand with flexible metal coordination geometries and influence of σ -donation on the photophysical properties of its complexes with Ru(II/III)

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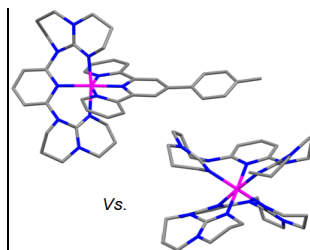
Polypyridyl ligands have produced an amazing number of fascinating Ru(II)-complexes exhibiting tunable ground and excited-state properties.^{1a-b} Among these complexes red-emitting photosensitizers that maintain relatively long excited-state lifetimes are of particular interest as they find potential applications in biological systems.²

In this context, mononuclear red-emitting Ru(II) complexes could be easily synthesised by strategic modification of their heterocyclic ligands (ring size, functionalization, nature, number and positions of the heteroatoms).³ A neutral tridentate N^AN^AN-type strong donor ligand (**L1**) was synthesized and attached with (tpy)RuCl₃ to furnish *mer*-[Ru^{II}(tpy)(**L1**)](PF₆)₂ (**1** and **2**) (tpy = substituted-2,2':6',2''-terpyridine) complexes. In cyclic voltammetric studies, the complexes exhibit a Ru^{III/II} couple, which is 800 mV less positive than the Ru^{III/II} couple in Ru(tpy)₂²⁺. The ¹(ML)LCT and ³(ML)LCT states of all the complexes are considerably bathochromically shifted (150 nm) compared to that of Ru(tpy)₂²⁺. Complexes **1** and **2** display emission, with associated lifetime of ~ 100 ns at room temperature, from a Ru^{II}-to-tpy ³(ML)LCT state, which is rarely the emitting state at $\lambda \sim 850$ nm, in [Ru(tpy)₂(**L1**)]²⁺ complexes.

Surprisingly, the homoleptic Ru-complex (**3**) of **L1** exhibits *fac*-coordination around the metal ion, where the strong σ -donating ligand favors Ru(III). Due to this higher oxidation state, the ³LMCT emission maxima of **3** is now blue-shifted by ~ 300 nm compared to **1** and **2**.

References:

- [1] (a) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991 and references cited therein, (b) Medlycott, E. A.; Hanan, G. S. *Chem. Soc. Rev.* **2005**, 34, 133.
- [2] Anderson, P. A.; Keene, F. R.; Meyer, T. J. et.al. *Dalton Trans.* 2002, 3820.
- [3] (a) Nag, S.; Hanan, G. S. et. al. *Inorg. Chem.* **2011**, 50, 7. (b) Pal, A. K.; Hanan, G. S. et. al. *Inorg. Chem.* submitted.



Crystal structures of **2** (top) and **3** (bottom), showing *mer*- and *fac*-geometries, respectively.

OC8

Copper-Catalyzed Aerobic Oxidation of Phenols into Versatile Quinones

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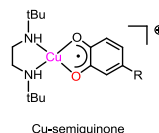
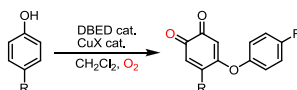
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The catalytic aerobic oxidation of phenols into *ortho*-quinones constitutes an atom-economical pathway in the functionalization of aromatic C-H bonds. This functionalization is reminiscent of



the oxidation of tyrosine by the ubiquitous Cu-containing enzyme tyrosinase in the first step of melanin biosynthesis. We developed a fully catalytic procedure for the aerobic oxidation of phenols into substituted *ortho*-quinones that uses the Cu(I) complex of N,N'-di-*tert*-butylethylenediamine. The efficiency and selectivity of this reaction offers a unique opportunity to study the mechanism of Cu-catalyzed phenolic oxidations

Based on model complexes, the currently accepted mechanism for the aerobic oxygenation of phenols is through the formation of side-on peroxodicopper(II) complex which converts into a bis(μ -oxo)dicopper(III) complex upon phenolate binding. The phenolate is subsequently oxygenated at the *ortho* position via electrophilic aromatic substitution to give a semiquinone-Cu complex. Although these intermediates have previously been spectroscopically observed in the stoichiometric reaction of side-on Cu-peroxo complexes with phenolate salts,[1] this is the first time that they are directly observed under catalytic conditions. In this study we report the spectroscopic detection of these intermediate in addition to demonstrating the power of Cu-semiquinone complexes to harness the reactivity of *ortho*-quinones. A putative catalytic cycle based on the intermediates observed is proposed and compared to the intermediates proposed in the oxygenation and oxidation of tyrosine in the initial step of melanogenesis.

[1] Mirica, L. M.; Vance, M.; Rudd, D. J.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; Stack, T. D. P. *Science*, **2005**, *308* (5730), 1890-1892

OC9

Functionalization of Iridium (III) Complexes by Tuning of Both Ancillary Bis(arylimino)acenaphthene (Ar-BIAN) and Cyclometallating phenylpyridine (C[^]N) Ligands

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Bis(arylimino)acenaphthenes (Ar-BIANs) are a class of compounds that have been frequently used as sterically bulky diimine ligands. Easy synthesis, low cost and highly tunable electronics makes these ligands highly desirable with both transition and main group metals, and lanthanides. We recently reported the first systematic spectro-electrochemical study of Ar-BIANs.^[1] In this presentation, I will detail our work with these ligands and their complexation with iridium(III). Notably, complexes of the form [(C[^]N)₂Ir(Ar-BIAN)]PF₆ (**A**) absorb light out to 800 nm.^[2,3] Further modification of the structure of these complexes [(MeOppy)₂Ir(Ar-BIAN-R')]₂PF₆ (**B**) renders them electronically compatible as dyes in DSSCs. Synthesis, spectroscopic and electrochemical characterization for a series of complexes, supported by DFT calculations are discussed in this talk.

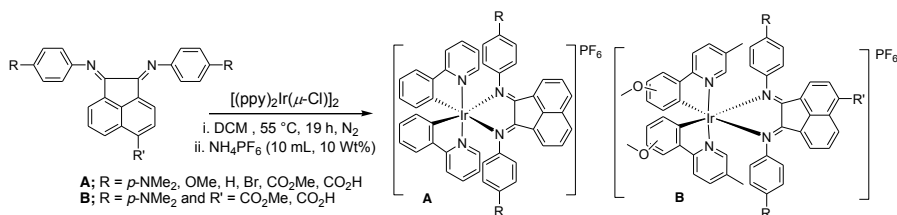


Figure 1. Synthesis of [(C[^]N)₂Ir (Ar-BIAN)]PF₆ complexes.

References:

- [1] Hasan, K. and Zysman-Colman, E. *J. Phys. Org. Chem.* 2013, 26(3), 274-279.
- [2] Hasan, K. and Zysman-Colman, E. *Inorg. Chem.* 2012, 51(22), 12560-12564.
- [3] Hasan, K. and Zysman-Colman, E. *Eur. J. Inorg. Chem.* 2013, 2013, 4421-4429.

OC10

A Method for the Production of Reduction-Sensitive 1,1-Diarylhydrazines as Potential Ligands in Coordination Chemistry

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1,1-diarylhydrazines are found in the frameworks of many anti-cancer agents. They are most often produced through reduction of a 1,1-diarylnitrosamine. The number of synthetic pathways to 1,1-diarylhydrazines being limited, however, they have not been extensively examined. In addition, certain amines such as those containing nitro- and carboxyl- functionalities are incompatible with the standard reductive conditions hence, the reactivities of their corresponding hydrazines remains unexplored. Presented here is a method for the production of 1,1-diarylhydrazines containing nitro- and ester linkages through the conversion of amines to their corresponding 1,1-diarylureas and subsequent base-catalyzed Hofmann rearrangement. The potential use of these molecules for the production of N-heterocyclic nitrenium ions and their use in coordination compounds will also be discussed.

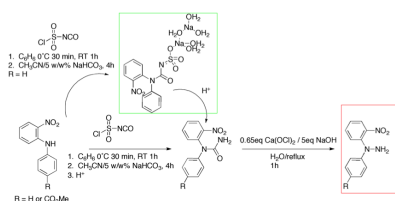


Figure 1. Method for the stepwise synthesis of disubstituted 1,1-diarylhydrazines from 1,1-diarylamines.

OC11

Toward a Step-By-Step Mechanistic Elucidation of Chain-End Stereocontrol in d^0 Metallocene Catalyzed Polymerization of α -Substituted Olefins

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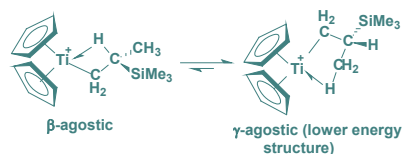
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Group IV metallocene complexes are widely used for catalytic polymerization of olefins and yield high quality polymers. Because of low activation barriers and, hence, high reaction rates, the intermediates in these systems are elusive and few examples have ever been isolated and characterized. We shall describe low temperature reactions of $[\text{Cp}_2\text{TiMe}]^+$ with mono-substituted olefins of the type $\text{CH}_2=\text{CHR}$ ($\text{R} = \text{CMe}_3$,^[1] SiMe_3 ,^[2] or SiEt_3) which give single-insertion products, $[\text{Cp}_2\text{Ti}(\text{CH}_2\text{CHMeR})]^+$. In addition to being unusual by their very existence, these products also exhibit remarkable agostic properties; while one ($\text{R} = \text{CMe}_3$) is α -agostic with one α -H preferentially agostic because of the chirality at C2, the others are in equilibrium between γ - and β - agostic conformers, resulting in a slow exchange between H atoms at α -, β - and γ - positions, in a much unusual and new fashion. In some cases, secondary insertion reactions also occur and recent advances in characterizing these new diastereoisomeric products suggest that there is stereoselectivity at the second migratory-insertion reaction. The relevance of our findings to coordination polymerization mechanisms will be discussed.



Scheme 1. Exchange between the β -agostic conformer and the γ -agostic conformer. At temperatures below ~ 180 K, the γ -agostic conformer dominates and the C-C bond rotation of the Me is slowed down enough that the 3^1H resonances start de-coalescing, with the γ -agostic H at ~ 7.4 ppm.

References:

[1] Dunlop-Brière, A. F.; Baird, M. C.; Budzelaar, P. H. M. *Organometallics*, **2012**, *31*, 1591.

[2] Dunlop-Brière, A. F.; Budzelaar, P. H. M.; Baird, M. C.; Budzelaar, P. H. M. *accepted in J. Am. Chem. Soc. with minor revisions*.

OC12

Chromium Catalysts for CO₂-epoxide Copolymerization

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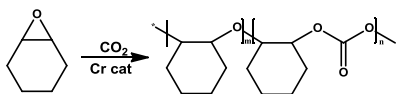
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The manufacture of polymers is a rapidly growing industry, and of particular interest is the development of polymeric materials from renewable precursors. We have investigated the use of chromium catalysts for the synthesis of polycarbonate from the copolymerization of CO₂ and epoxide.^[1] The use of CO₂ in industrial processes is highly attractive as CO₂ is an abundant, renewable, non-toxic C1 feedstock that is compatible with several current polymerization processes.^[2]

The first successful CO₂-epoxide copolymerization catalytic system consisted of an ethyl zinc complex, and, since this initial discovery, other transition metals have been used for polycarbonate synthesis, including chromium. Chromium porphyrin complexes and chromium salen complexes are some of the only reported chromium catalysts to have shown promising activity in the conversion of CO₂ and epoxide to polycarbonate.^[3,4] We herein report several new chromium complexes and their activity for the copolymerization of CO₂ and epoxide.

Imino-pyrrole, amino-pyrrole and aminophosphine ligands were complexed with various chromium sources, producing nine new chromium catalysts that were tested for their catalytic behavior towards various polymerizations, including polycarbonate. Cyclic and linear products were obtained, and both poly(ether-carbonate) and polycarbonates were produced.



Scheme 1: Catalytic conversion of CHO to polycarbonate under CO₂ pressure.

References:

- [1] Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Comm.* **2011**, *47*, 141–163.
- [2] Bolm, C.; Beckmann, O.; Dabard, O. a. G. *Angew. Chem. Int. Ed.* **1999**, *38*, 907–909.
- [3] Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–410.
- [4] Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6618–6639.

OC13

Small Molecule Activation by POCOP Nickel Amide & Siloxide Complexes.

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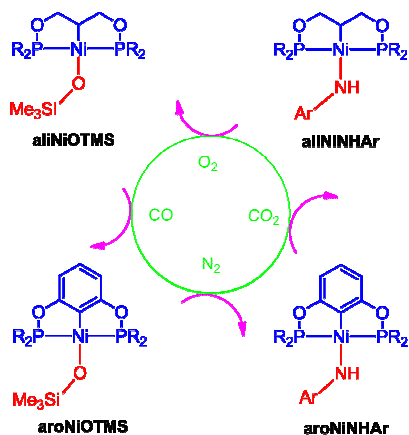
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The knowledge that small molecule chemistry plays a central role in many biological processes has inspired chemists to elucidate the various mechanisms involved in these processes. It has also driven organometallic chemists to develop non-natural mimics of these processes with the objective of functionalizing small molecules such as O_2 , N_2 , CO, and CO_2 . Structural biologists have established the involvement of mid-to-late first-row transition metals such as Mn, Fe, Ni, Cu, and Zn in the structures of enzymes that orchestrate biological functions of interest,^[1] thus providing one more compelling reason for exploring the reactivities of these metals in the context of small molecule activation.

It is generally accepted that nickel amide or alkoxide complexes are more reactive than their alkyl counterparts. This is particularly true when the Ni centre bears strongly electron-donor auxiliary ligands that make its complexes good candidates for activating small molecules. POCOP-type pincer ligands have been widely employed in complexes of many transition metals thanks to their adjustable steric and electronic properties and their ability to stabilize various oxidation states. POC_{sp3}OP ligands featuring an aliphatic framework are expected to bestow greater electron density to metals, whereas POC_{sp2}OP ligands featuring aromatic frameworks lead to more stable complexes.^[2] This presentation will describe the synthesis and characterization of four POCOP ligated nickel complexes (shown above) and their reactivities toward O_2 , N_2 , CO and CO_2 . Reactivity comparisons will serve to elucidate the impact of ligand framework and X-ligands on the reactivity modes.



References:

[1] (a) S. W. Flegsdale, *Curr. Opin. Chem. Biol.*, 1998, 2, 208–215; (b) R. P. Hausinger, *Microbiol. Rev.*, 1987, 51, 22–42; (c) U. Ermler, W. Grabarse, S. Shima, M. Goubeaud and R. K. Thauer, *Curr. Opin. Struct. Biol.*, 1998, 8, 749–758.

[2] van Koten, G.; Milstein, D. *Organometallic Pincer Chemistry*, Springer-Verlag Berlin Heidelberg, New York, NY, 2012.

OC14

New Silylselenium Reagents for the Synthesis of Ferrocenoyl Chalcogenoesters

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Methods to prepare chalcogenoesters continue to attract considerable attention due to in part the importance of these systems in organic synthesis.¹ In this context the reaction between silylated selenium reagents and acyl halides as an efficient method for the synthesis of polyselenoesters has recently been illustrated.²

As part of our continued interest in developing the chemistry of polychalcogenoesters, a new group of poly chalcogeno trimethylsilanes ($\text{Ar}(\text{CH}_2\text{ESiMe}_3)_n$, $\text{E} = \text{S}, \text{Se}$, $n = 2, 3$ and 4) has been prepared. The reaction of 1,2,4,5-tetrakis-(bromomethyl)benzene, 1,3,5-tris-(bromomethyl)-2,4,6-trimethylbenzene and 1,4-bis-(bromomethyl)-2,3,5,6-tetramethylbenzene with $\text{Na}[\text{ESiMe}_3]$ at room temperature leads to formation of new silylated chalcogen compounds in good yields. The new chalcogenoethers have been characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction.

Polychalcogenoesters can be prepared from the reaction of these prepared silylchalcogenoethers and ferrocenyl acid chloride via thermolysis reactions. The synthesis, structures, spectroscopic and electrochemical properties of 1,4-($\text{FcC}(\text{O})\text{ECH}_2$)₂(C_6Me_4), 1,3,5-($\text{FcC}(\text{O})\text{ECH}_2$)₃(C_6Me_3) and 1,2,4,5-($\text{FcC}(\text{O})\text{ECH}_2$)₄(C_6H_2) ($\text{Fc} = \text{Fe}(\text{C}_5\text{H}_4)_2$, $\text{E} = \text{S}, \text{Se}$) will be described.

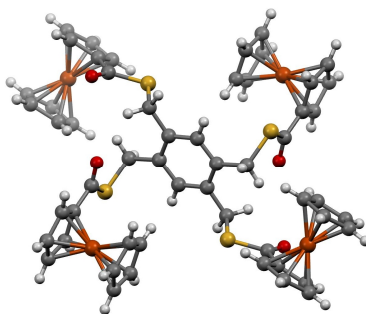


Figure. 1,2,4,5-($\text{FcC}(\text{O})\text{ECH}_2$)₄(C_6H_2)

References:

¹ Fujiwara, S.-I.; Kambe., N. *Top. Curr. Chem.* **2005**, *251*, 87

² (a) Taher, D; Corrigan, J. F. *Organometallics* **2011**, *30*, 5943, (b) Capperucci, A. Degl'Innocenti A. Tiberi C. *Synlett* **2011**, 2248

OC15

Hydrogen-Bond-Supported Dimeric Boron Complexes of Potentially Tetradentate β -Diketiminato Ligands

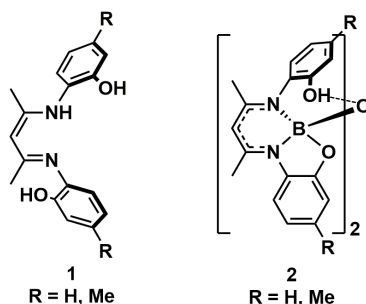
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β -diketiminates are a well known class of ancillary ligands commonly encountered in the field of coordination chemistry.^{1,2} They typically have two *N*-aryl substituents, which can be modified to increase their steric bulk, making them ideal for the stabilization of low valent metal centres. However, very few known β -diketiminates contain heteroatoms at the *N*-aryl substituents (e. g., **1**). We believe by including heteroatoms (e.g., OH) at the *N*-aryl substituents we can induce planarity between the ligand backbone and the *N*-aryl substituents when they are coordinated to transition metals and main-group elements. This planarity may allow for enhanced electronic communication and unusual spectroscopic properties in the resulting complexes.



Direct synthesis of the target ligands (**1**) proved difficult, yielding β -ketimines or benzoxazoles depending on the conditions employed. As a result, we moved on to methylation/demethylation strategies. The use of BBr_3 as a demethylation agent yielded boron complexes (**2**) containing an unusual hydrogen bond supported B-O-B bridge. These complexes were synthesized via two different routes, and their stability was evaluated via computational studies. The spectroscopic and electrochemical properties of the fluorescent boron complexes (**2**) and their monomeric boron difluoride precursors were studied in detail. These properties as well as the details of our synthetic endeavours will be discussed in detail during this presentation.³

References:

[1] Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031-3065.[2] Tsai, Y.-C. *Coord. Chem. Rev.*, **2012**, *256*, 722-758.[3] Barbon, S. M.; Staroverov, V. N.; Boyle, P. D.; Gilroy, J. B. *Dalton Trans.* DOI:10.1039/C3DT52188E.

OC16

Photo-induced Reversible Activation of White Phosphorus with Main Group Compounds

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The transition metal free controlled activation of white phosphorus (P₄) has recently been achieved by a variety of N-heterocyclic carbenes and related heavier p-block element carbenoids.¹⁻² Insertion into one, two, or three bonds of P₄ can occur, in addition to degradation to P₁ and P₂ fragments or aggregation to P₈ and P₁₂ fragments.³ The downside of this chemistry is that there are no examples of transferring of the newly activated phosphorus fragment to a new and useful substrate. In this context, we report the ability of two dicoordinate main group systems to quantitatively release an inserted P₄ molecule upon exposure to UV light (Figure 1). These two reactions mimic the common transition metal oxidative addition and reduction elimination processes necessary for a catalytic system, which is one of the end goals for white phosphorus activation. The diarylgermylene (**1**) represents the first activation of P₄ by germanium (**2**) and is shown to reinsert efficiently after several cycles. The full details regarding the synthesis, reversibility, recyclability, and complementary theoretical work will be discussed.

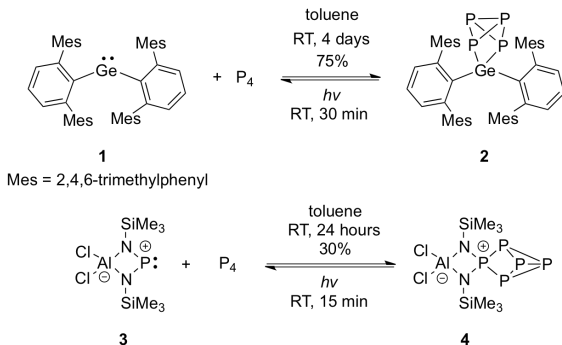


Figure 1: Photo-induced reversible activation of white phosphorus

References:

- [1] Griffin, N. A., Masuda, J. D. *Coord. Chem. Rev.* **255**, 1342-1359 (2011).
- [2] Scheer, M., Balazs, G., Seitz, A. *Chem. Rev.* **110**, 4236-4256 (2010).
- [3] Khan, S., Sen, S. S., Roesky, H. W., *Chem. Commun.* **48**, 2169-2179 (2012).

Poster Presentations
P Abstracts

P1

Ru (II) COMPLEXES CONTAINING THE ANTITUBERCULAR LIGAND ISONIAZID

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Among the infectious diseases, tuberculosis caused by *Mycobacterium tuberculosis* (MTb) is the second leading cause of death from an infectious disease worldwide, after the human immunodeficiency virus (HIV) [1]. The prodrug isoniazid (isonicotinic acid hydrazide, INH) synthesized in 1912 is recognized as the best drug to treat this disease [2]. We have found tetraammine- and pentaammineruthenium (II/III) isoniazid complexes to show excellent *in vitro* activity against MTb inside and outside of the macrophage cell and also to have low cytotoxicity against the host cells. In this work, selected ruthenium (II) complexes containing the metal center in different ligand environments were prepared and their properties studied. The influence of the coordination on the anti-tuberculosis activity of the INH molecule was investigated, *in vitro* tests and some correlations between structure and activity proposed. Among the compounds containing the INH ligand, the MIC values increase as the potential for the coordinated INH oxidation to Ru(II)ammine complexes (E_{p_a}) becomes less positive. The $t\text{-[Ru}^{\text{II}}(\text{NH}_3)_4(\text{INH})\text{SO}_2]^{2+}$ complex showed $E_{p_a} = 0.823$ V with an MIC value of 0.875 $\mu\text{g/mL}$ whereas $t\text{-[Ru}^{\text{II}}(\text{NH}_3)_5(\text{INH})]^{2+}$ showed $E_{p_a} = 0.836$ V with an MIC value of 0.598 $\mu\text{g/mL}$.

Table 1. Data of MIC, IC_{50} and $E_{p_a}(\text{INH})$ for the Ru(II) compounds and INH against the H₃₇Rv and resistant strains

	MIC ($\mu\text{g/mL}$)						IC_{50} ($\mu\text{g/mL}$)	$E_{p_a}(\text{INH})$ (V)
	H ₃₇ Rv	SD (\pm)	Resistant strain 1	SD (\pm)	Resistant strain 2	SD (\pm)		
isoniazid	0.068	0.018	>25.000	*	>25.000	*	500	1.029
$t\text{-[Ru}(\text{NH}_3)_5(\text{INH})]^{2+}$	0.598	0.170	22.552	1.063	24.261	0.539	250	0.836
$t\text{-[Ru}(\text{NH}_3)_4(\text{SO}_2)(\text{INH})]^{2+}$	0.875	0.503	>25.000	*	>25.000	*	500	0.823

The complex $t\text{-[Ru}(\text{NH}_3)_5(\text{INH})]^{2+}$ was active in both resistant and sensible strains, different from free INH, which showed no activity in the resistant strain. These results suggest that, the oxidation process is necessary for the drug activity, however the ease of oxidation of INH does not lead to an increase in the INH activity.

References:

[1] WHO. *Global Tuberculosis Control: WHO report 2011*.

[2] Meyer, H. and J. Mally, *Über Hydrazinderivate der Pyridincarbonsäuren*. Monat. für Chem., **33** (4), 1912.

P2

Towards Models of the Oxygen-Evolving Complex (OEC) of Photosystem II from the Use of Optically-Active Ligands: Mn₄Ca Clusters of Relevance to Low Oxidation States of the OECAlysha Alaimo¹, Luís Cunha-Silva², and Theocharis C. Stamatatos^{*1}¹Department of Chemistry, Brock University, St. Catharines, L2S 3A1, ON, Canada²REQUIMTE & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

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Among the various reasons for the current intense interest in manganese chemistry is the existence of this metal at the active sites of several redox enzymes, the most important of which is the oxygen-evolving complex (OEC) on the donor side of photosystem II (PS II) in green plants, algae and cyanobacteria. The OEC catalyzes the oxidation of H₂O to molecular dioxygen through a four-electron process; the latter involves various oxidation states of the OEC, the so-called S_n Kok states (n = 0 to 4), and is the source of essentially all the O₂ on this planet. The OEC has long been known to contain four Mn and one Ca²⁺ ions, but the exact metal topology was only recently revealed in detail from the crystal structure of PS II from the cyanobacterium *Thermosynechococcus vulcanus* at 1.9 Å.^[1] The Mn oxidation states at the various S_n Kok states involve a mixture of Mn^{III} and Mn^{IV}; the dark-stable S₁ state is 2Mn^{III},2Mn^{IV}, and S₂, the most studied Kok state, is Mn^{III},3Mn^{IV}. In addition, the presence of Ca²⁺ ion is vital for the WOC activity; without its existence the OEC could not advance to the S₃ state. The synthesis and detailed study of synthetic analogues of this {Mn₄Ca} cluster would greatly enhance our understanding of the spectroscopic, physical and catalytical properties of the WOC, as well as its reactivity and functional characteristics. In this work, we present our initial results from the employment of fluorescence carboxylate ligands in Mn/Ca chemistry as a means to combine the bioinorganic perspective of our research with the field of optics.

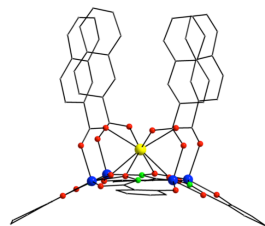


Figure. One of the Mn₄Ca clusters discussed in the present work.

References:

[1] Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya, *Nature*, **2011**, 473, 55.

P3

The First Family of Lanthanide Molecule-Based Magnets Assembled from Crown Ether Ligands

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Our research interests lie in the development of lanthanide-containing molecule-based magnets. To date there have been reports of both nitrogenated (phthalocyanine) and organometallic (cyclooctatetraene) sandwich-type complexes of lanthanide ions as mononuclear single molecule magnets.¹ Our approach to these materials is to use a combination of oxygen-rich crown ethers² and highly anisotropic lanthanide ions to form sandwich complexes which enhance the innate anisotropy of the metal ion. To this end, the synthesis, X-ray crystal structures and magnetic properties of several novel crown ether–lanthanide complexes will be presented.

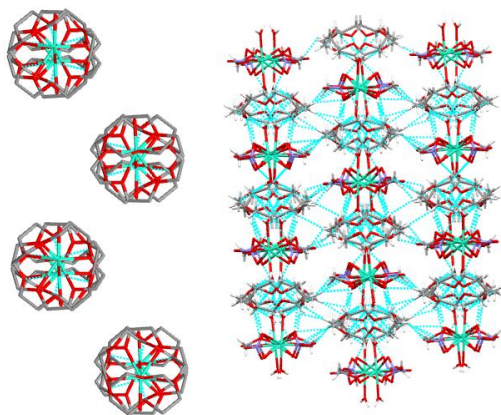


Figure 1. Molecules of $[\text{Dy}(\text{15C5})(\text{H}_2\text{O})_4](\text{ClO}_4)_3 \cdot 15\text{C5}$ packed as dimers (left) and molecules of $[\text{Dy}(\text{NO}_3)_2(\text{15C5})]^+$ packing as H-bonded chains (right).

References:

[1] D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield. *Chem. Rev.* **2013**, 113, 5110.

[2] C. J. Pederson. *J. Am. Chem. Soc.* **1967**, 89, 7017.

P4

A New Schiff Base Ligand in Metal Cluster Chemistry: Synthesis and Characterization of Ni₄, Ni₈ and Ni₁₁ Complexes

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Metal complexes with Schiff bases as ligands have been known since 1840. Since then, they have played a key role in the development of modern coordination chemistry resulting in an enormous number of reports, ranging from pure synthesis to advanced physicochemical and biochemical studies. The research areas dealing with metal complexes of Schiff-base ligands are very broad due in part to their involvement in various fields such as metal cluster chemistry, molecular magnetism, bioinorganic chemistry, catalysis and optics. An interesting group of the family of tetradentate Schiff bases comprises ligands derived from the condensation of derivatives of salicylaldehyde with derivatives of 2-aminobenzoic acid. These Schiff bases contain an ONOO donor set which upon deprotonation of both -OH and -COOH groups could bridge more than two metal centers and thus foster the formation of polynuclear metal species. The parent ligand is *N*-salicylidene-2-aminobenzoic acid (Figure), which has been rather intensively studied in coordination chemistry.^[1] In contrast, complexes of ring-substituted derivatives (with non-donor groups) have received only scant attention. With respect to the latter type groups, we herein describe the synthesis, spectroscopic and physicochemical characterization of new polynuclear Ni(II) complexes with beautiful structures and interesting properties.

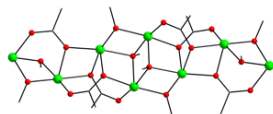
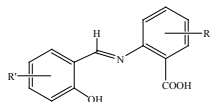


Figure. The general structural formula of the tetradentate Schiff bases discussed in the text and a representative Ni^{II}₈ cluster.

References:

[1] H. Ke, G.-F. Xu, Y.-N. Guo, P. Gamez, C. M. Beavers, S. J. Teat and J. Tang, *Chem. Commun.*, **2010**, 46, 6057.

P5

Employment of 2-Pyrrolyloximes as Bridging Ligands in Transition Metal Cluster Chemistry

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The continuing interest in the synthesis and study of high-nuclearity 3d molecular metal clusters at moderate-to-high oxidation states is driven by numerous reasons. Among these is the search for various nuclearity oxide-bridged metal clusters to model M_x sites in biomolecules and the fact that such molecules, especially the ones containing Mn^{III} , Fe^{III} , Co^{II} and Ni^{II} , often display fascinating structures, along with interesting and occasionally attractive magnetic properties, including high-spin (*S*) ground-state values and single-molecule-magnetic (SMM) behavior.^[1] A major challenge in the field of polynuclear metal complexes remains the development of new synthetic routes to such molecules through the employment of novel chelating/bridging organic ligands, especially ones containing alkoxide and/or oximate functionalities. This is due to the ability of such groups to foster the formation of polynuclear products with unprecedented structural motifs and fascinating magnetic properties. Many groups^[2] have had success in synthesizing high-nuclearity 3d metal clusters and SMMs based on 2-pyridyloxime ligands, (py)C(R)NOH (*R* = various). We have now decided to replace the 2-pyridyl group of these ligands with the 2-pyrrolyl one and explore the coordination chemistry of the resulting 2-pyrrolyloximes, which had negligible previous use in cluster chemistry. Herein, we shall attempt to discuss our first results from the use of praoh₂ and mpraoh, the simplest members of the 2-pyrrolyloxime family of ligands, in high-nuclearity Fe(III) and Mn(III) cluster chemistry.^[3]

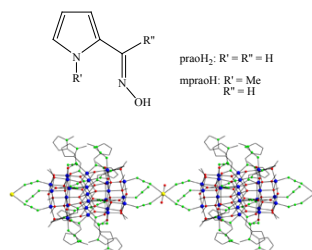


Figure. The ligands (top) and a representative $[Mn^{III}_{25}Na]$ cluster (bottom) discussed in the text.

References:

- [1] G. Aromi and E. K. Brechin, *Struct. Bonding (Berlin)* **1997**, 88, 1.
 [2] C. J. Milios, Th. C. Stamatatos and S. P. Perlepes, *Polyhedron* **2006**, 25, 134.
 [3] E. S. Koumoussi, A. Routzomani, T. N. Nguyen, D. P. Giannopoulos, C. P. Raptopoulou, V. Psycharis, G. Christou and Th. C. Stamatatos, *Inorg. Chem.*, **2013**, 52, 1176.

P6

Heptanuclear Lanthanide(III) Complexes from the Use of a New Chiral Schiff-base Ligand

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Molecular electronics is undoubtedly an exciting area of research which promises to deliver new technology and modern devices to society. It is based on the construction and fabrication of molecular species with intriguing magnetic properties, pronounced stability and robustness, and capability to be deposited on electrical conducting surfaces. Furthermore, in order to gain access into some real applications for these species, such as molecular spintronics, transistors and spin valves, we need to combine their magnetic properties with one or more additional properties, such as conductivity, chirality and luminescence.^[1] Owing to important perspectives in fundamental science and applications in nanotechnology or molecular electronics, these 'hybrid' (or multifunctional) molecular materials are the subject of considerable efforts which involve coexistence, interplay or synergy between the multiple physical properties. Chirality is an important property which can be introduced to molecular nanoscale magnetic materials. In principle, the synthesis of new chiral single-molecule magnets (SMMs) will bring to technology novel functions such as magnetochiral dichroism, non-linear optics and ferroelectricity. A successful route toward the construction of chiral SMMs would be the use of highly anisotropic and paramagnetic metal ions bound to a chiral organic bridging ligand. In the present work, we shall show our recent efforts from the initial employment of a chiral Schiff-base ligand in lanthanide(III) chemistry which afforded a family of isostructural, heptanuclear metal species with an unusual capped trigonal prismatic topology (Figure).

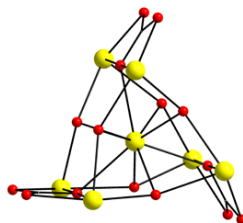


Figure. The core of one of the Ln₇ clusters discussed in the present work.

References:

- [1] (a) L. Ouahab, "Multifunctional Molecular Materials", Pan Stanford Publishing Pte. Ltd. **2013**; (b) M. Morimoto, H. Miyasaka, M. Yamashita and M. Irie, *J. Am. Chem. Soc.*, **2009**, 131, 9823.

P7

Access to Optically-Effective Molecular Magnetic Materials via the Employment of Quinoline-based Oximate Ligands and Fluorescence Carboxylate Groups

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Owing to important perspectives in fundamental science and applications in nanotechnology or molecular electronics, 'hybrid' molecular materials are the subject of considerable efforts which involve coexistence, interplay or synergy between the multiple physical properties.^[1] Toward this end, various attempts have been made to study molecular nanomagnets at the single-molecule level by depositing them on different surfaces and investigating their conducting behavior. However, problems related to the determination of the molecules' exact positions and dispersion on the surfaces usually render assignments and conclusions inaccurate and superficial. In principle, when single-molecule magnets (SMMs) are coupled with photoluminescence properties, it may be possible to precisely detect the positions of molecules on surfaces, and thus open a new perspective in the field of molecule-based electronics. The self-assembly synthesis of such emissive magnetic materials has been limited to the use of lanthanide ions in complexes with various organic bridging ligands. However, direct effect of the latter organic groups in the light emission of the SMM is totally unpredictable and of dubious origin. In the absence of any previous studies on the designed synthesis of emissive, transition metal-based magnetic materials we decided to begin a program aiming at the deliberate replacement of non-emissive organic ligands with their optically-active analogues, without affecting the metal-core structure and magnetic properties. We herein present a family of $\{Ni^II_6\}$ cyclic compounds which solely contain fluorescent oximate and carboxylate groups as bridging ligands (Figure).

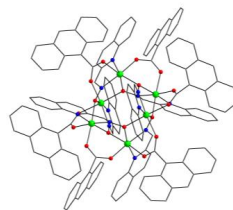


Figure. One of the discussed in the text $\{Ni^II_6\}$ clusters.

References:

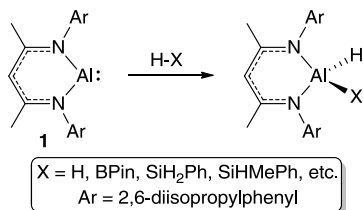
[1] M. Urdampilleta, S. Klyatskaya, J.-P. Cleuziou, M. Ruben and W. Wernsdorfer, *Nat. Mater.*, **2011**, 10, 502.

P8

H-X Bond Activation Mediated by Aluminum(I)

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Much of the success of transition metals in catalysis can be attributed to the activation and cleavage of stable single bonds, H-X (where X = H, C, Si, etc.), on a metal centre, M, to give products of oxidative addition, H-M-X. This mode of reactivity is demonstrated by a variety of transition metals and has been extensively studied.^[1] In contrast, very little is known about H-X bond activations on main-group element centres. Recent examples include the cleavage of H-H and H-N bonds on stable carbenes^[2] and splitting of dihydrogen by Frustrated Lewis Pairs.^[3] The utilization of main-group complexes as catalysts can afford significant advantages over transition-metals, particularly due to the toxicity of the metals currently utilized as well as their high costs and low abundance.



Recently, we were drawn to the β -diketiminato stabilized complex of aluminum in the +1 oxidation state, **1**, prepared by Roesky *et al.*^[4] Interesting and novel chemistry of the aluminum (I) complex with unsaturated substrates have been demonstrated.^[5] However, the reactivity of **1** with single bonds has not been studied. Due to the highly reducing nature of complex **1**, we envisaged it as a potential platform for H-X bond activation. In our hands, complex **1** undergoes facile activation of

H-H, H-B, H-Si bonds and others to give novel aluminum hydride complexes. Their synthesis and characterization is reported along with the subsequent insertion chemistry and applications toward catalysis.

References:

- [1] Hartwig, J. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, 2010.
- [2] Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.
- [3] Welch, C. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.
- [4] Cui, C.; Roesky, H.W.; Schmidt, H.; Nollentmey, M.; Hao, H.; Cimpoesu, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 4274.
- [5] Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457.

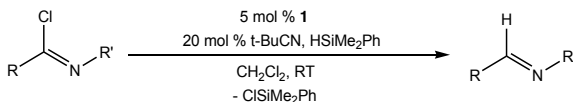
P9

Catalytic reduction of secondary amides to imines and aldehydes

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Reduction of amides to amines, aldehydes and imines has been widely studied due to their importance for pharmaceutical and agrochemical industries.^[1-3] However, traditional reduction methods fail for multifunctional substrates, and therefore the develop chemoselective reduction of amides in the presence of other functional groups is of great interest. Catalytic reduction of amides by silanes to amines has been actively investigated.^[3] However, transformation of amides to imines is more challenging because imines are usually more active in reductions. Only a handful of studies on stoichiometric and catalytic reduction of amides to the corresponding imines have been reported.^[1]

We have recently reported highly chemoselective catalytic reduction of acid chloride to aldehydes^[4] and now we report a related conversion of secondary amides into corresponding imines and/or aldehydes via intermediate formation of imidoyl chlorides and their reduction by HSiMe₂Ph catalyzed by [CpRu(PPR₃)(CH₃CN)₂]PF₆(**1**). The reactions were achieved under mild conditions (Scheme 1).

Scheme 1. Reduction of imidoyl chlorides catalyzed by **1**

References:

- [1] (a) Schedler, D. J.; Godfrey, A. G.; Ganem, B., *Tetrahedron Lett.* **1993**, *34*, 5035-5038. (b) Schedler, D. J. A.; Li, J.; Ganem, B., *J. Org. Chem.* **1996**, *61*, 4115. (c) Pelletier, G.; Bechara, W. S.; Charette, A. B., *J. Am. Chem. Soc.* **2010**, *132*, 12817. (d) Cheng, C.; Brookhart, M., *J. Am. Chem. Soc.* **2012**, *134*, 11304.
- [2] (a) Das, S.; Addis, D.; Junge, K.; Beller, M., *Chem. Eur. J.* **2011**, *17*, 12186. (b) Reeves, J. T.; Tan, Z.; Marsini, M. A.; Han, Z. S.; Xu, Y.; Reeves, D. C.; Lee, H.; Lu, B. Z.; Senanayake, C. H., **2013**, *355*, 47.
- [3] (a) Hanada, S.; Tsutsumi, E.; Motoyama, Y.; Nagashima, H., *J. Am. Chem. Soc.* **2009**, *131*, 15032. (b) Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M., *Angew. Chem. Int. Ed.* **2009**, *48*, 9507. (c) Volkov, A.; Buitrage, E.; Adolffson, H., *Eur. J. Org. Chem.* **2013**, 2066. (d) Li, Y.; Molina de La Torre, J. A.; Grabow, K.; Bentrup, U.; Junge, K.; Zhou, S.; Brückner, A.; Beller, M., *Angew. Chem. Int. Ed.* **2013**, *52*, 1.
- [4] Gutsulyak, D.V.; Nikonov G.I., *Adv. Synth. Catal.* **2012**, *354*, 607.

P10

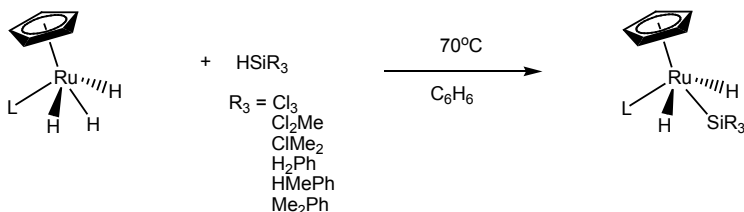
Half sandwich NHC-supported ruthenium trihydride and its silyl dihydride derivatives.

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The novel half sandwich ruthenium trihydride complex (**1**) bearing a bulky NHC (N-heterocyclic carbene) ligand has been synthesized. Reactions of **1** with different silanes at 70°C in benzene results in the formation of half sandwich ruthenium silyldihydride complexes. These silyl NHC complexes of Ru were fully characterized by using X-ray crystallography, IR, NMR spectroscopy, and elemental analysis.



P11

Exploring the Coordination Chemistry of a Family of 2,2',6,6'-Tetracarboxamide-4,4'-Bipyridine Ligands – from Clusters to MOFs

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4,4'-Bipyridine units have been used extensively in coordination chemistry as rigid spacers between metal ions,^[1] and we are interested in exploring these spacers in our program directed towards the synthesis of molecule-based magnets. The tetracarboxamide (Figure 1, a) derivatives of 4,4'-bipyridine are less well-explored as ligands,^[2] yet have multiple sites for derivatisation and thus can exhibit substantial structural versatility. X-ray crystal structures of metal complexes has shown them to bind in a polydentate fashion.

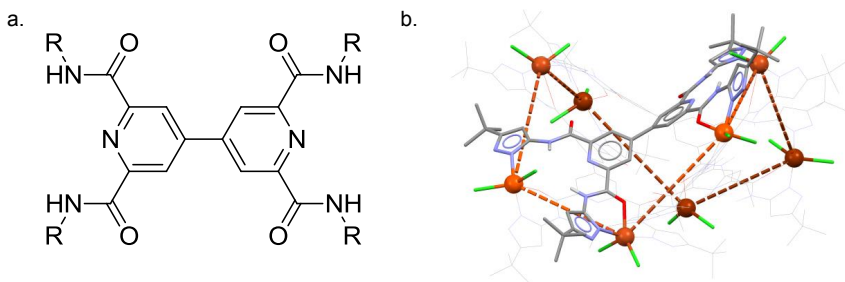


Figure 1 a) Core structure of ligands L1-L5; b) Saddle-shape Cu(II) cluster with L5.

Our research objectives are to synthesize a family of 2,2',6,6'-tetracarboxamide-4,4'-bipyridine ligands (L1-L5) and their corresponding multinuclear coordination complexes with mid-to-late first row transition metal ions (Mn, Co, Ni, Cu, Zn) (e.g. Figure 1, b). Our targeted ligands are synthesised from a variety of amines with pendant heterocyclic rings: L1 (R = 2-pyridyl), L2 (R = 2-(2-pyridyl)ethyl), L3 (R = 2-thiazolyl), L4 (R = 2(4-ethylpyridyl)), L5 (R = 3-(5-tert-butylpyrazolyl)). The syntheses of the ligands and complexes will be presented along with our current structural and magnetic findings.

References:

[1] Irwin, M.; Kramer, T.; McGrady, J. E.; Goicoechea, J. M. *Inorg. Chem.* **2011**, *50*, 5006

[2] Mikuriya, M.; Yoshioka, D.; Handa, M.; *Coord. Chem. Rev.* **2006**, *250*, 2194

P12

Thermolysis Methods: kinetics & products of precursor decomposition

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The determination of products and rates of decomposition in precursor design is important in current vapour deposition chemistry. Particularly in the fields of chemical vapour deposition (CVD) and atomic layer deposition (ALD).¹ Products of decomposition can give important information about the mechanism through which a precursor could react with a surface. This information can help deduce reaction byproduct(s) that are most likely to form at particular temperatures and is very useful when coupled with surface exposure experiments.² The acquisition of rates can help further characterize precursor stability, at particular temperatures, and help find proper handling temperatures if a precursor is deemed viable. Methods for this type of study are not widely used despite the usefulness of the data. Here we show methods to determine decomposition products and kinetics of decomposition via solution based NMR techniques. Products of the decomposition of ALD/CVD precursors can be observed via NMR. Flame-sealed NMR tubes, with a known concentration of gold precursor in benzene, are placed in an oven over a period of two weeks. The resulting NMR spectra can be seen in the above figure. Rates can be obtained by following these decomposition products for weeks or even months. Using a known amount of precursor and solvent, the intensity of the corresponding peaks can be integrated to determine concentration over time. Although solution based methods are not always truly indicative of gas phase reactions, results from these experiments prove to aid in the determination of rates and products. Our results show a simple method that can yield very useful results in the field of precursor design for vapour deposition.

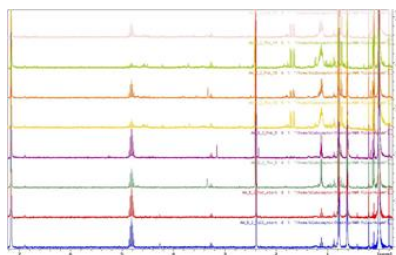


Figure: solution based NMR decomposition of gold CVD precursor over two weeks.

References:

- (1) Barry, S. T. *Coord. Chem. Rev.* **2013**, *257*, 3192–3201.
- (2) Coyle, J. P.; Pallister, P. J.; Kurek, A.; Sirianni, E. R.; Yap, G. P. a; Barry, S. T. *Inorg. Chem.* **2013**, *52*, 910–7.

P13

In situ Monitoring of the Chemical Vapour Deposition of Gold Films onto TFBG-Inscribed Optical Fibers

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Tilted fiber Bragg grating (TFBG)-inscribed fiber optic filaments are an exciting new sensor platform. The core-guided light is diffracted into the cladding of the fiber where it interacts with the fiber-air interface. If metal is present on the surface, multiple cladding modes can be enhanced and sensitive to the outside system as a surface plasmon. Furthermore, these cladding modes are sensitive to minute changes in the refractive index of the overlying film (if one is present).

Herein we present novel gold chemical vapor deposition (CVD) using self-reducing, single source precursors. These precursors are gold diisopropyl guanidinate $[\text{Au}(\text{N}^i\text{Pr})_2\text{CNMe}_2]_2$ and gold tert-butyl-imino-2,2-dimethylpyrrolidinate. A TFBG-inscribed optical filament was used as the deposition substrate, and was simultaneously used as a deposition monitoring tool.

A homemade, hot-walled CVD reactor was equipped with a bubbler and used to achieve continuous CVD, wherein both precursors were deposited onto TFBG fiber substrates. It was found that the differing film thicknesses gave anomalous results when refractive index information about the thin film was extracted.

The gold guanidinate precursor produced nanoparticulate metallic gold films which were found to discriminate between radially and azimuthally polarized light incident from the TFBG. This growth process was monitorable *in situ* by tracking peak-to-peak amplitude changes between cladding modes of the TFBG, as well as by tracking specific mode wavelength shifts. The thickness of the growing film was thus observable in real time. The gold iminopyrrolidinate, which is a far more thermally robust precursor, was used to deposit gold nanoparticulate films which were also monitored *in situ*. This deposition process, however, was far easier to control and thus specific film thicknesses were targetable for study of their unique optical and plasmonic properties. The complete attenuation of cladding modes at specific film nanoparticle diameters and thicknesses is observed in both cases, and is attributeable to either absorption or diffraction by the nanoparticulate film.

We anticipate this growth monitoring process to be applicable across the film deposition disciplines to accurately probe specific film thicknesses and the optical properties thereof.

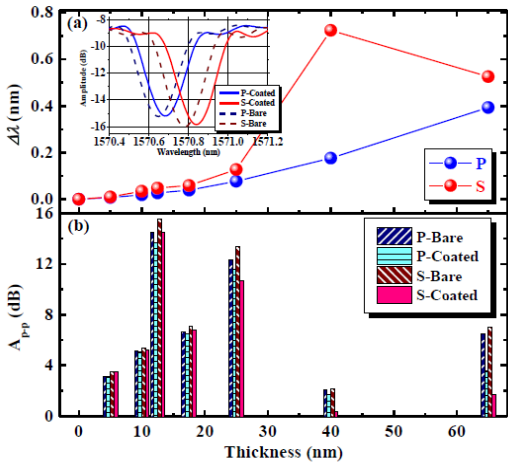


Figure 1: Peak-to-peak amplitude changes (top) and cladding mode amplitudes (bottom) as a function of gold film thickness.

P14

Quantitative Surface Coverage Calculations via Solid-State NMR for Thin Film Depositions: A Case Study for Silica and a Gallium Amidinate

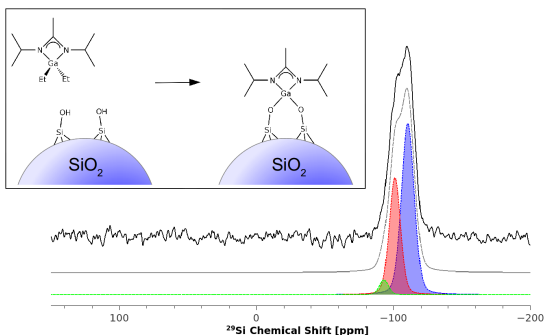
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To interrogate precursor nucleation for vapour deposition processes like atomic layer deposition (ALD) and chemical vapour deposition (CVD), a modified method for quantitative analysis of surface coverage was undertaken via NMR. The initial chemisorption of a new gallium(III) alkyl amidinate compound was investigated on high-surface area silica. N, N'-diisopropylacetamidinediethylgallium(III) (**2**) was found to have excellent volatility with no decomposition during a ramped thermogravimetric analysis experiment. Stepped-isotherm experiments showed a 1 Torr vapour pressure at 64°C. **2** was exposed to a pre-treated high-surface area silica substrate at 100°C, 200°, and 300°C and was found to exhibit stable, persistent chemisorbed surface species at all three temperatures. Substrates were analyzed by ²⁹Si and ¹³C solid-state nuclear magnetic resonance spectroscopy (SS-NMR) and ¹H high-resolution NMR. At 100°C and 200°C the reactivity of compound **2** to geminal and lone hydroxyl surface sites varied slightly eliminating either one or both ethyl groups to produce an alkylated (or non-alkylated) gallium acetamidinate on the silica surface and producing fractional coverages of 0.17-0.18. At 300°C there was a larger degree of reactivity producing a minor amount of the same surface species as at 100°C and 200°C but also producing additional chemisorbed products likely arising from the decomposition of the ligand framework but ultimately giving a fractional coverage of 0.31 on hydroxyl-terminated silica.



P15

THE FIRST BARIUM TIN(II) BROMIDE FLUORIDE

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Barium tin(II) chloride fluorides were first discovered by two of us (AM & GD) and have been extensively studied in our laboratory. By precipitation, three new compounds $\text{BaSn}_2\text{Cl}_2\text{F}_4$, $\text{BaSnClF}_3 \cdot 0.8\text{H}_2\text{O}$, and $\text{Ba}_{1-x}\text{Sn}_x\text{Cl}_{1+y}\text{F}_{1-y}$. The latter compound is a unique doubly disordered solid solution with the basic structure of BaClF . It can also be prepared at high temperature in dry conditions. Analysis of their ^{119}Sn Mössbauer spectrum shows that Sn(II)-Cl/F bonding is covalent, and the tin(II) lone pair is stereoactive in $\text{BaSn}_2\text{Cl}_2\text{F}_4$ and in $\text{BaSnClF}_3 \cdot 0.8\text{H}_2\text{O}$. In contrast, bonding in precipitated $\text{Ba}_{1-x}\text{Sn}_x\text{Cl}_{1+y}\text{F}_{1-y}$ is purely ionic with a non-stereoactive lone pair, while purely ionic bonding or a mixture of ionic and covalent bondings is obtained for materials prepared from solid state reactions, depending on the values of the compositional parameters x and y . In an effort to prepare barium tin(II) bromide fluorides for the first time, possibly similar to the chloride fluorides, precipitation reactions were carried out by mixing aqueous solutions of SnF_2 and of $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. In contrast with the chloride fluoride system, a single powdered phase was obtained throughout the $\text{SnF}_2 - \text{BaBr}_2$ system, with the yield being maximal at $X \approx 0.25$, where X is the molar fraction of barium bromide in the reaction mixture. Phase identification with the JCPDS database failed to produce a match, confirming that a new phase had been produced, and it is not similar to any of the chloride fluorides. Its exact chemical composition has not been obtained yet. Based on the X value for the maximum yield, the Sn/Ba ratio is likely to be 3/1 or 2/1. The Mössbauer spectrum at ambient conditions shows that bonding to tin(II) is covalent, therefore with the tin lone pair being stereoactive. The Mössbauer parameters ($\bar{\delta} = 3.68 \text{ mm/s}$, $\Delta = 0.99 \text{ mm/s}$) are similar to those of SnBrF and of Sn_2BrF_5 , thereby showing that tin is bonded to both fluorine and bromine, with the stereoactivity of the tin lone pair being lower than in the fluorides. The Mössbauer parameters fit well the linear correlation of the quadrupole splitting versus the isomer shift of many tin(II) compounds. The linear decrease shows that the contribution of non-spherical orbitals (p and d) to the lone pair is a much larger contributor to the quadrupole splitting than lattice distortions.

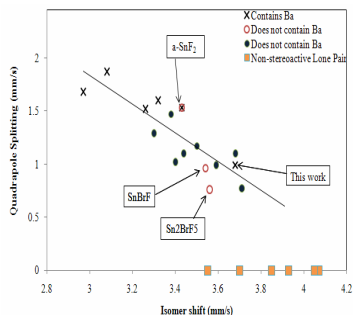


Fig. Quadrupole splitting versus isomer shift for tin(II) halides.

P16

USING MÖSSBAUER SPECTROSCOPY TO CHOOSE THE SITES THAT CAN BE OCCUPIED BY DIVALENT TIN

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Mössbauer spectroscopy can be a useful structural tool to assist crystallographic methods for site assignment when the compound under investigation contains divalent tin. The goal of this work was to show that the structure of tin(II) fluoride, also known as stannous fluoride, SnF₂, could have been solved 14 years earlier if Mössbauer spectroscopic results had been used. Several attempts to solve its crystal structure were carried out starting in 1962 and seemed to find the tin positions, however, it failed to find the positions of fluorine. Finally, the crystal structure was published in 1976. It was found that the tin sublattice determined by Bergerhoff was basically correct, except that half of the tin atoms found by Bergerhoff to be on the (4b) and (4e) special Wyckoff sites were actually on the (8f) general site. A translation of the origin of the unit-cell by the [1/8, 0, 3/16] vector allows to change the tin Wyckoff sites from (4b), (4e) and (8f) to two (8f) sites, while keeping the basic spatial distribution of tin. A method has now been designed, using ¹¹⁹Sn Mössbauer spectroscopy, to test the suitability of some Wyckoff sites for divalent tin, using the Mössbauer spectrum (fig. 1). The tin(II) doublet ($\delta = 3.40$ mm/s, $\Delta = 1.55$ mm/s) shows that the lone pair is on a hybrid orbital, hence it is stereoactive, and therefore tin cannot be on either the (4b) or (4e) tin site since both an inversion center and a 2-fold axis would generate a second lone pair (fig. 2) unless the 2-fold axis were along the tin-lone pair axis.

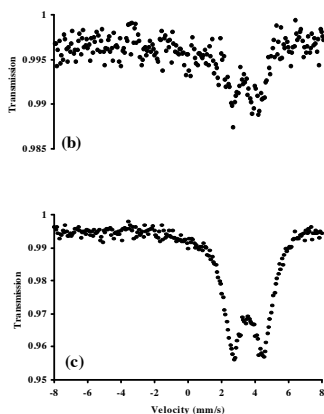
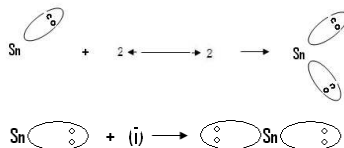
Figure 1: ¹¹⁹Sn Mössbauer of 22.8 mg of α -SnF₂ at 298K and 11K

Figure 2: Generation of a second lone pair when tin(II) is located on a two-fold axis or on an inversion center.

P17

SPECTRAL ANISOTROPY IN TIN(II)-CONTAINING
LOW DIMENSIONALITY MATERIALSGeorges Dénès¹, M. Cecilia Madamba¹, Hocine Merazig² and Abdualhafed Muntasar¹¹Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Department of Chemistry and Biochemistry, Concordia University, Montréal, Québec, H4B 1R6, Canada²Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, CHEMS, Université Constantine 1, 25000, AlgeriaE-mail of presenting author: muntsab@gmail.com and madenes@videotron.caE-mail of corresponding author: georges.denes@concordia.ca and madenes@videotron.ca

Clustering of stereoactive lone pairs in parallel planes gives rise to anisotropy in materials. Some tin(II)-containing materials are particularly prone to this phenomenon. *Isotropic* materials have the same properties in all directions of space, with the same magnitude. This requires a cubic unit-cell. All other crystal systems give rise to property *anisotropy*, i.e. direction dependence of properties and their magnitude. A reduced dimensionality, such as a layered structure (two-dimensional) is the result of unequal bond strength versus direction in space. It results that property anisotropy is usually the consequence of bonding anisotropy. Bonding anisotropy results in anisotropic crystal growth, resulting in a crystallite shape that is most of the time sheet-like (two-dimensional) or needle-like (one dimensional). Many tin(II)-containing materials are found to have very strong low dimensionality. Many compounds in the SnF_2/MCl ($\text{M} = \text{alkali metals and NH}_4$) were found to give needle shaped crystals, some looking like long thin hair. Extreme cases of two-dimensionality were observed in MSnF_4 , particularly in $\alpha\text{-PbSnF}_4$ and in the Pb/Sn/F/NO_3 system, resulting in spectral asymmetry. The spectral asymmetry may be due to: (i) crystallite preferred orientation, and (ii) vibrational anisotropy (Goldanskii-Karyagin effect). The presentation will focus on studies of variations of the Mössbauer spectrum asymmetry versus sample orientation in the γ -ray beam and versus temperature, and the relationship with the orientation of lone pair clusters in the unit-cell.

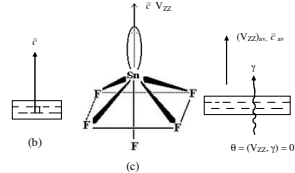


Figure A2.220: Relative orientation of the c unit-cell axis, the γ -ray beam, the tin-lone pair axis and V_{zz} in $\alpha\text{-PbSnF}_4$. (a) definition of θ , (b) highly oriented $\alpha\text{-PbSnF}_4$, (c) V_{zz} along Sn-E axis, (d) $\theta = 0$ in highly oriented $\alpha\text{-PbSnF}_4$.

Figure 1: Relationship of the lone pair direction with the crystal axes and the direction of the γ -ray beam

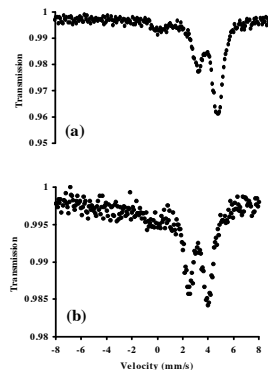


Figure 2: Tin(II) quadrupole doublet in $\alpha\text{-PbSnF}_4$ subjected to highly enhanced preferred orientation for two values of the angle between the γ -ray beam and the normal to the plane of preferred orientation: (a) 0° , (b) 45°

P18

Biomimetic catalytic oxidation of phenols with Cu(II) complexes

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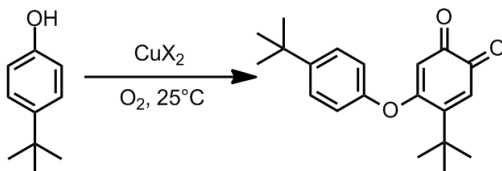
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Nature has evolved enzymes that can catalyze the oxidation of C-H bonds using dioxygen as the oxidant and releasing water as the by-product. Of particular interest is the copper-containing enzyme tyrosinase which oxygenates tyrosine to the corresponding



quinone in the process of melanin biosynthesis. The preparation of quinones in a laboratory setting often requires a stoichiometric amount of oxygen-atom donors which release significant amount of by-product. Performing such a reaction aerobically using molecular oxygen has been, however, restricted to the use of reactive metal complexes such as Cu(I).

We herein report the efficient aerobic oxidation of phenols to phenol-coupled quinones using simple, stable, and commercially available Cu catalysts and dioxygen as the active oxygenating / oxidizing agent. The easy set-up and the efficiency of this reaction offers an attractive method for the oxidation of phenol into quinones which can be further used for the synthesis of fine chemicals. Optimization studies including variation of Cu-salt, solvent, ligand, and additive screening will be presented. The scope of this reaction in the oxidation of a variety of mono-substituted phenols will be demonstrated. In addition, based on *in-situ* spectroscopic monitoring of the reaction tentative intermediates and a preliminary mechanism is proposed.

P19

Di- μ -chlorido-bis[(2-aminobenzamide- κ^2N^2,O) chloridocopper(II)]

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The title compound, [Cu₂Cl₄(C₇H₈N₂O)₂], crystallizes as discrete [CuLCl₂]₂ (L = 2-aminobenzamide) dimers with inversion symmetry. Each Cu(II) ion is five-coordinated and is bound to two bridging chloride ligands, a terminal chloride ligand and a bidentate 2-aminobenzamide ligand. The crystal structure exhibits alternating layers parallel to the (010) plane along the b-axis direction. In the crystal, the components are linked via N—H...Cl dipole-dipole interactions, to form a three-dimensional network. These interactions link the molecules within the layers and they also link the layers together and reinforce the cohesion of the structure. General background about 2-aminobenzamide derivatives and related structures can be found in references 1-4. The crystals were obtained by adding the 2-aminobenzamide ligand L to an acidic aqueous solution of copper(II) chloride.

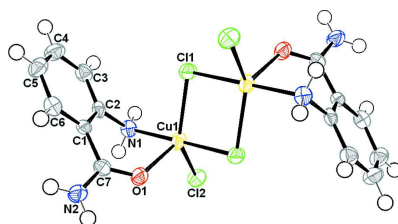


Figure. Molecular structure of the title dimer. Displacement are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radius. Only the contents of the asymmetric unit are numbered.

References:

- [1] Nagaoka, Y., Maeda, T., Kawai, Y., Nakashima, D., Oikawa, T., Shimoke, K., Ikeuchi, T., Kuwajima, H. & Uesato, S. (2006), *Eur. J. Med. Chem.* **41**, 697-708.
- [2] Butsch, K., Klein A. & Bauer, M. (2011) *Inorg. Chem.* **374**, 350-354.
- [3] Kapoor, P., Panmu, A. P. S., Sharma M., Hundal, M. S., kapoor, R., Corbella, M. & Aliaga-Alcalde, N. (2010), *J. Mol. Struct.* **981**, 40-45.
- [4] Yang, F., Chui, W., Guo, W., Jing, H., Min, X. & Yi, F., *Bioorg. Med. Chem. Lett.* **22**, 4703-4706.

P20

Tetrakis[(μ -2-phenylacetato- κ^2 O:O')bis-[(dimethylamino)pyridine- κ N¹]- cobalt(II)]Meriem Benslimane¹, Yasmine Kheira Redjel¹, Georges Dénès² and Hocine Merazig¹¹Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, CHEMS, Université Constantine 1, 25000, Algeria²Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Department of Chemistry and Biochemistry, Concordia University, Montréal, Québec, H4B 1R6, CanadaE-mail of presenting author: hmerazig@gmail.comE-mail of corresponding author: georges.denes@concordia.ca

The title compound, [Co₂(C₈H₇O₂)₄(C₇H₁₀N₂)₂], crystallizes as a centrosymmetric dimer containing two Co(II) atoms bridged by four bidentate phenylacetate ligands in syn-syn bridging modes. Each Co(II) atom is five-coordinated by four O atoms from four different carboxylate ligands and the ring N atom of a 4-(dimethylamino)pyridine unit, generating a distorted square-pyramidal geometry in which the four O atoms form the basal plane and the N atom occupies the axial position. In the crystal, C—H...O interactions link the dinuclear complex molecules into a three-dimensional network. The crystals were obtained by adding phenylacetic acid (C₆H₅CH₂COOH) to a solution of CoCl₂·2H₂O in methanol, stirring and then addition of 4-(Dimethylamino)-pyridine. The unit-cell is triclinic, P-1 space group, with Z = 1. Final residuals were R = 0.025 and wR = 0.060. Related work can be found in references 1-4.

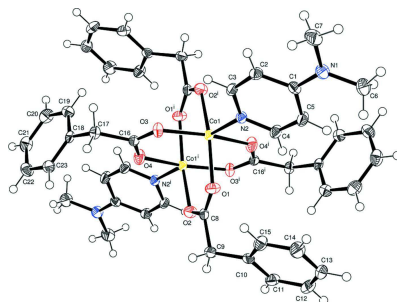


Figure. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry code, (i):1 - x, -y, -z.

References:

- [1] Satgé, C., Granet, R., Verneuil, B., Branland, P. and Krausz, P. (2004), *C. R. Chim.* **7**, 135-142.
- [2] Araki, H., Tsuge, K., Sasaki, Y., Ishizaka, S. and Kitamura, N. (2005), *Inorg. Chem.* **44**, 9667-9675.
- [3] Cui, Y., Long, D. L., Huang, X. Y., Zheng, F. K., Chen, W. D., and Huang, J. S. (1999), *Chin. J. Struct. Chem.* **19**, 9-13.
- [4] Catterick, J. and Thornton P. (1977), *Adv. Inorg. Chem. Radiochem.* **20**, 291-362.

P21

Formation of a Second Isomeric Dimer in Malaria Pigment

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One of the most prevalent infectious diseases, effecting 99 countries around the world, Malaria puts over 3 billion people at risk of contracting the disease annually [1]. The *Plasmodium* parasite responsible for malaria produces malaria pigment as a heme degradation by-product. Malaria Pigment, also known as Hemozoin (HZ), is of great interest to researchers as a potential drug target since its biosynthesis is required to detoxify heme which is essential for the parasite's survival. Although the malaria life cycle is well understood, the heme detoxification pathway is still poorly comprehended. Hematin Anhydride, also referred to as β -hematin, is the isostructural synthetic analogue of HZ. HZ consists of cyclic centrosymmetric dimers of ferric protoporphyrin IX molecules coordinated via Fe-O bonds. Adjacent dimers are reciprocally linked through the porphyrin's propionic acid groups via hydrogen bonding. HZ is chemically, spectroscopically and crystallographically identical to natural malaria pigment. In this presentation we describe and characterize a novel second isomeric dimer of hematin anhydride. The synthesis of the novel heme condensation phase is a modification of the anhydrous base annealing method by Bohle *et al.* (Figure 2). This novel heme condensation phase exhibits similar solubility and physical aspects to hematin anhydride, however some differences are present in the X-ray powder diffraction pattern, crystallinity, IR and Raman spectroscopy. It is suggested that this new phase could represent the kinetic product, a C₂ isomer of HA.

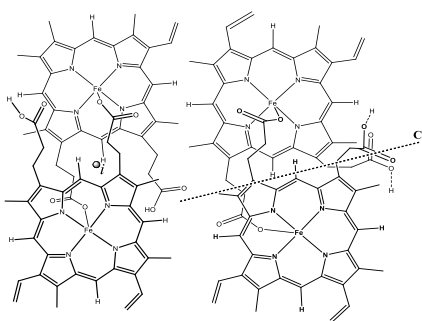


Figure 1 Left. Hematin Anhydride Right. Proposed structure for novel heme condensation phase C₂

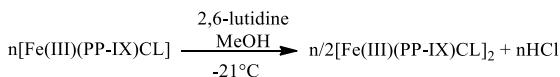


Figure 2 Synthetic route to the new C₂ phase of malaria pigment

References:

- [1] WHO, W. G. M. P. *World Malaria Report 2012*, WHO Press, 2012.
 [2] Bohle, D. S.; Kosar, A. D.; Stephens, P. W. *Acta. Cryst.* 2002, D58, 1752-1756.

P22

Late Transition Metal Nucleophilic Thiols

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In recent years considerable interest in studying transition metal thiolates has risen due to their use in biological, synthetic and environmental applications.¹ In our work we are interested in generating potent metal bound nucleophiles. This series of studies focuses on iridium(III) complexes in particular due to the relative stability that the compounds display while still retaining their high reactivity. Many iridium complexes can interchangeably undergo a number of oxidative additions but the ones of significance in this study react specifically by a *cis* mechanism when introduced to thiolate groups such as thiophenol, producing complexes that contain versatile, substitutable hydrido and thiolato ligands.² The latter ligand is of particular consequence since copious enzymatic sites that contain transition metal-sulfur often use the thiol group for catalysis mechanisms such as nitrous oxide reduction. The stereochemistry of these transition metal substituted thiols, L_nMSR, has been determined via crystallography as well as by spectroscopic methods to establish exactly how the orientation of their ligands affect the complexes' reactivity, and the chemical properties of these ligands were also examined in order to explore their catalytic potential. It's the goal of this study to investigate the receptiveness of the mercaptan group toward electrophilic substitution in hopes of eventually facilitating its subsequent use in biomimetic complex systems.

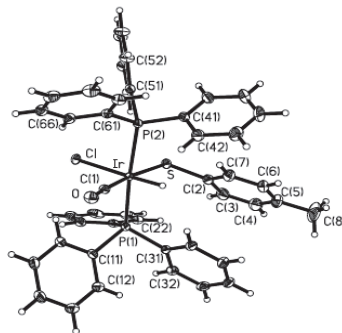


Figure. ORTEP drawing of
 $\text{HIr(III)Cl(SC}_6\text{H}_4\text{CH}_3\text{)(CO)(PPh}_3\text{)}_2$

References:

- [1] Mueting, A. M. and Boyle, P. Reaction of H_2S with phosphine complexes of Rh(I) and Ir(I) . *J. Am. Chem. Soc.*, (University of Minnesota, 1984)
- [2] Singer, H. and Wilkinson, G. Oxidative addition of acids to triphenylphosphine complexes of Ir(I) and Rh(I) . *J. Am. Chem. Soc. (Imperial College, 1968)*

P23

Novel Ruthenium(II)-Letrozole Complexes as Breast Cancer Therapeutics and Development of a Nanosensor-based Aromatase Assay Using a Magnetic Cu-Fe Nanoparticle Catalyst

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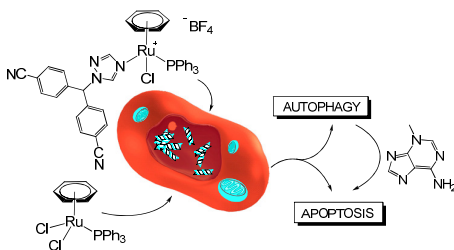
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Some ruthenium compounds are known for their cytotoxicity to cancer cells, whereas letrozole is an aromatase enzyme inhibitor, administered after surgery to menopausal women with hormonally responsive breast cancer. This presentation will discuss the preparation of the first ruthenium-letrozole complexes and the assessment of their anticancer potential by cell viability

determination of two human cancer cell types (breast and glioblastoma). The results showed that a significant *in vitro* activity was established for complex Ru(Let)PPh₃ against breast cancer MCF-7 cells, and significantly lower activity against glioblastoma U251N cells. The activity of Ru(Let)PPh₃ was even higher than RuPPh₃, a compound analogous to the well-known drug RAPTAC. Results from the combination of Ru(Let)PPh₃ (or RuPPh₃) with 3-methyladenine (3-MA) or with curcumin, respectively, indicated that the resultant cancer cell death likely involves Ru(Let)PPh₃-induced autophagy. The last part of the presentation will discuss the development of a novel nanosensor-based aromatase enzyme assay, for which a precursor was prepared using a magnetic Cu-Fe nanoparticle catalyst. This assay could allow the assessment of the aromatase enzyme inhibitory potential of the ruthenium-letrozole complexes as well as various other anticancer therapeutics, and could contribute to the identification of new endocrine disruptors from our environment.



P24

The Reactions of $[\text{Xe}_3\text{OF}_3][\text{AsF}_6]$ with ClO_2F and BrO_2F ; the Syntheses and Structural Characterization of FXeOClO_3 , $\text{Xe}(\text{OClO}_3)_2$, and $[\text{ClO}_2][\text{AsF}_6] \cdot 2\text{XeF}_2$

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The FXeOXeFXeF^+ (Xe_3OF_3^+ , Z-shaped) cation [1] has now been shown to function as both an FXeO^- synthetic equivalent and a powerful oxygen atom transfer reagent. The reaction of Xe_3OF_3^+ with liquid ClO_2F yielded FXeOClO_3 , and the XeF_2 coordination complex, $[\text{ClO}_2][\text{AsF}_6] \cdot 2\text{XeF}_2$ (eqs 1-3). The proposed reaction pathway involves the oxidation of the transient chlorate, FXeOClO_2 , to FXeOClO_3 by Xe_3OF_3^+ . The corresponding reaction of BrO_2F with Xe_3OF_3^+ is under investigation and the stability of FXeOBrO_3 will also be discussed. The perchlorates, FXeOClO_3 and $\text{Xe}(\text{OClO}_3)_2$, were fully characterized for the first time by low-temperature ^{19}F and ^{129}Xe NMR spectroscopy ($-50\text{ }^\circ\text{C}$) in SO_2ClF and in the solid state by low-temperature Raman spectroscopy ($-150\text{ }^\circ\text{C}$) and single-crystal X-ray diffraction ($-173\text{ }^\circ\text{C}$; Figures 1a and 1b). The other major reaction product, $[\text{ClO}_2][\text{AsF}_6] \cdot 2\text{XeF}_2$, was crystallized from ClO_2F and anhydrous HF and characterized by low-temperature Raman spectroscopy and single-crystal X-ray diffraction (Figure 1c). Each ClO_2^+ center coordinates two XeF_2 molecules through bridging $\text{Cl}\cdots\text{F}$ contacts that are significantly shorter than the sum of the Cl and F van der Waals radii.

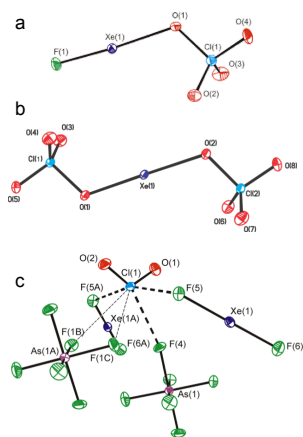
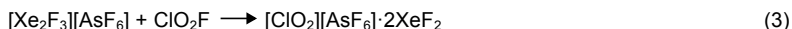
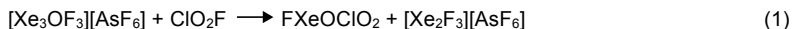


Figure 1. The low temperature ($-173\text{ }^\circ\text{C}$) X-ray crystal structures of (a) FXeOClO_3 (b) $\text{Xe}(\text{OClO}_3)_2$ and (c) $[\text{ClO}_2][\text{AsF}_6] \cdot 2\text{XeF}_2$.

Reference:

[1] M. Gerken, M. D. Moran, H. P. L. Mercier, B. E. Pointner, G. J. Schrobilgen, B. Hoge, K. O. Christie, J. A. Boatz, *J. Am. Chem. Soc.* **131**, (2009) 13474–13489.

P25

N-substitution of benzo-2,1,3-selenadiazole

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Secondary bonding interactions (SBIs) are common between chalcogens and atoms that contain one or more lone pairs of electrons. In particular, the 1,2,5-chalcogenadiazole rings associate with each other by formation of the [E-N]₂ (E=S, Se, Te) *supramolecular synthon*, a virtual four-membered ring defined by two antiparallel E—N intermolecular SBIs.¹ Telluradiazoles form the strongest links within the family but they are easily hydrolyzed. The selenium analogues are more convenient because they are more robust. Their SBIs are weaker but are enhanced after the formal attachment of a Lewis acid to one nitrogen atom.² We have extended this concept by developing syntheses for a wide range of functionalized benzoselenadiazoles, including borane derivatives and dicationic molecules capable to infinite catenation. DFT calculations have provided a rationale for the strengthening of the secondary links and explained the ability of halide binding to compete with the [Se-N]₂ supramolecular synthon.

References:

- [1] a) Cozzolino, A. F.; Vargas Baca, I.; Mansour, S.; Mahmoudkhani, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 3184. b) Cozzolino, A. F.; Elder, P. J. W.; Vargas Baca, I. *Coord. Chem. Rev.* **2011**, *255*, 1426. c) A. F. Cozzolino, S. Hanhan, A. D. Bain, I. Vargas-Baca, *Chem. Commun.* **2009**, 4043.
[2] a) Berionni, G.; Pegot, B.; Marrot, J.; Goumont, R. *Cryst. Eng. Comm.* **2009**, *11*, 986. b) Dutton, J. L.; Tindale, J. J.; Jennings, M. C.; Ragogna, P. J. T. *Chem. Commun.* **2006**, 2474. c) Risto, M.; Reed, R. W.; Robertson, C. M.; Oilunkaniemi, R.; Laitinen, R. S.; Oakley, R. T. *Chem. Commun.* **2008**, 3278.

P26

Study of Manganese Complexes Containing Tripodal Tetradentate Ligands for Lactide Polymerization

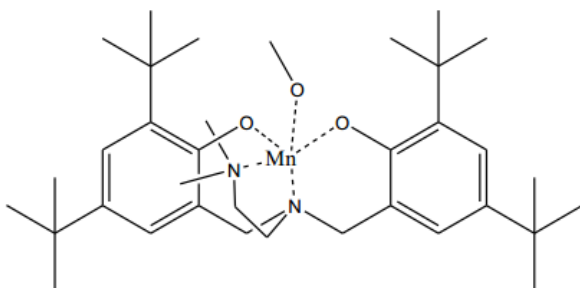
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Synthesis of manganese complexes with the general formula (L_4 MOR), where “ L_4 ” represents a dianionic tetradentate ligand, and R= Me, $\text{CH}_2\text{CH}_2\text{NMe}_2$ or $\text{CH}_2(\text{C}_5\text{H}_4\text{N})$ were attempted, with different variations on the amine-bis((2-hydroxyaryl)methyl) ligands. The 2-[Bis(2-hydroxy-3,5-di-tert-butylbenzyl)aminomethyl]methoxide five-coordinated complex was obtained from the reaction of MnCl_2 with $L_4\text{H}_2$, in methanol. Its structure has been confirmed by single crystal x-ray diffraction. Its catalytic activity in the ring-opening polymerization of rac-lactide was investigated.



2-[Bis(2-hydroxy-3,5-di-tert-butylbenzyl)aminomethyl]methoxide

P27

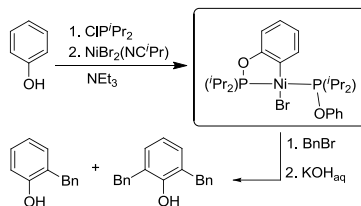
C-H Activation & Functionalization of Phenol Via A New Orthonickelated Phosphenite Complex

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Cyclometallated complexes have attracted much interest because of their remarkable activities in a wide range of catalytic processes,^[1] including C-H functionalization chemistry.^[2] Curiously, few examples exist of cyclometallated nickel compounds even though such species should have great potential in catalysis owing to the established reactivities and abundance of nickel.



This presentation will report the synthesis and characterization of new Ni(II)-phosphenite compounds featuring a cyclometallated moiety. We will discuss the mechanism of C-H nickelation step and the subsequent reaction of the cyclonickellated complex with electrophiles. The latter reaction results in the formation of a C_{sp2}-C_{sp3} bond, thus providing an efficient methodology for functionalization of phenols.

References:

[1] (a) Bedford, R. B.; Betham, M.; Charmant, J. P. H.; Haddow, M. F.; Orpen, A. G.; Pilarski, L. T.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2007**, *26*, 6346. (b) Bedford, R. B.; Hazelwood, S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 4164.

[2] (a) X.; You, J.; Gao, G.; Lan, J. *Chem. Commun.* **2013**, *49*, 662. (b) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236. (c) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788.

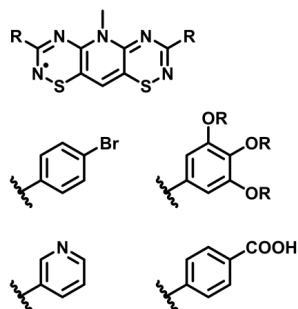
P28

Functional Neutral Radicals: Design and Development of Novel Materials for Magneto-Optoelectronic Applications

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One of our group's axes of research is the design and development of novel open-shell materials exhibiting unique liquid-crystalline, magnetic, electronic and/or optical properties, which may find use in applications such as optoelectronic and spintronic devices. Functionalized thiadiazinyls (1), stable radical species composed of nitrogen and sulfur, are of particular interest due to the enhanced stability brought by the delocalization of the unpaired spin, the opportunity for intermolecular interactions afforded by sulfur's diffuse orbitals^[1], and the ability to manipulate the structure/properties via variation of the substituents (R1, R2, R3)^[2].

In that regard, progress towards the synthesis and characterization of a variety of bithiadiazinyls derivatives, each designed with different applications in mind will be presented. Notably, tailored aggregation of the radical core through functionalization with trisalkoxybenzene mesogens can lead to conducting materials thanks to delocalization of the unpaired spin across the liquid-crystalline (LC) lattice. Compared to more traditional polymeric active substrates, which lack structural organization, this LC lattice would promote electron mobility and, by extension, device efficiency. On the other hand, functionalization of the radical core with coordinating pendant arms could allow magnetic communications between two metal centers.



Molecular structure of the neutral radical bithiadiazinyl core, along with different substituents currently being explored.

References:

[1] Beer, L. et al., *Chem. Comm.* **2005**, 41, 1218-1220.[2] Winter, S.M. et al., *Chem. Comm.* **2013**, 49, 1603-1605.

P29

Modeling Study on Reverse Combustion Promoted by BiVO₄Camilo Viasus^{1,2}, Ilia Korobkov and¹ Sandro Gambarotta*¹¹University of Ottawa, 75 Laurier Avenue East, Ottawa, ON, K1N 6N5, Canada²Universidad de Ciencias Aplicadas y Ambientales, Bogota, Cll. 72 No. 14-20, GI3C, ColombiaE-mail of presenting author: cvias005@uottawa.caE-mail of corresponding author: sandro.gambarotta@uottawa.ca

The excessive production of carbon dioxide thrown into the atmosphere require a very effective process to reuse it like methanol or ethanol production using m-BiVO₄ as catalyst, water and sunlight¹. Base on this process we proposed to use vanadium(III) species to reduce carbon dioxide. The dinitrogen fixation recently observed with a Vanadium(III) alkoxide² indicates the presence of an axial vacant active site generated upon removal of the coordinated solvent molecule. We can apply this characteristic to reduce carbon dioxide into carbon monoxide generating a vanadium(V) specie. In this work we analyzed the steric and electronic effect that might affect vanadium(III) phenoxy and pyrrol containing ligands towards carbon dioxide activation. By delaying the reaction with an electronegative atom bound to vanadium(III), we found an ester formation including in it a carbon dioxide molecule. With both steric and electronic effect we were able to obtained an oxovanadium(IV) species as intermediate.

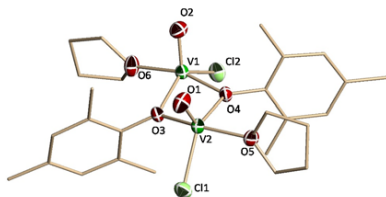


Figure. ORTEP diagram of one intermediate oxovanadium(IV) specie obtained with carbon dioxide reaction. 50% of probability.

References:

- [1] J. Mao et al., *Catalysis Communications.*, **2012**, 28, 38–41
 [2] Stanislav Groysman, et. al., *Chem. Commun.*, **2011**, 47, 10242–10244

P30

Synthesis of Iridium Phosphonium Indenylide Complexes

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Some years ago we reported^{1,2,3} on synthesis of chromium and ruthenium complexes using different phosphonium indenylide ligands **(1)**, **(2)**, **(3)** and now our current studies involve synthesis of iridium complex using Phosphonium Indenylide ligand.

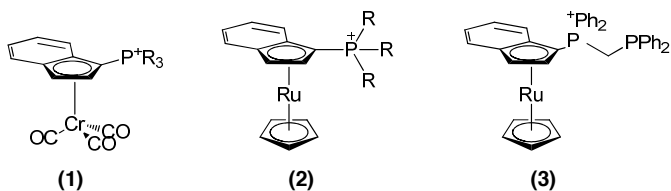


Figure 1: Chromium and ruthenium complexes with different phosphonium indenylide ligands.

In this work we also wish to report our studies on the synthesis, structure, and properties of new phosphonium indenylide ligand, 4,7-dimethyl-1-indenylide **(4)** and of the corresponding iridium complexes.

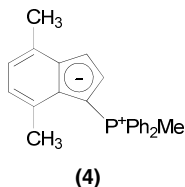


Figure 2: 4,7-dimethyl-1-indenylide **(4)**

References:

- [1]. John H. Brownie, Michael C. Baird. *Journal of Organometallic Chemistry*. 693, **2008**, 2812-2817.
- [2]. Kevin G. Fowler, Shaylyn L. Littlefield, and Michael C. Baird. *Organometallics*. 30, **2011**, 6098-6107
- [3]. Riaz Hussain, Kevin G. Fowler, Francois Sauriol, and Michael C. Baird. *Organometallics*. 31, **2012**, 6926-6932.

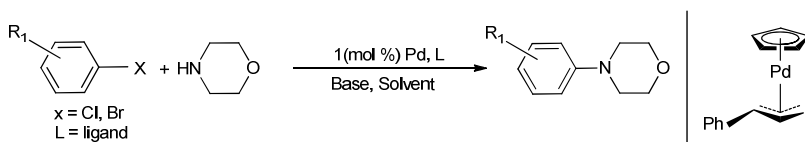
P31

Pd(η^3 -1-Ph-C₃H₄)(η^5 -C₅H₅), an Unusual Catalyst Precursor for Buchwald-Hartwig Amination ReactionsSogol Borjian Borojeni¹, Michael C. Baird*¹¹Queen's University, Kingston, Ontario K7L 3N6E-mail of presenting author: sogol.borjian@chem.queensu.caE-mail of corresponding author: bairdmc@chem.queensu.ca

Recently, it has been shown that Pd(η^3 -1-Ph-C₃H₄)(η^5 -C₅H₅) (**I**) is a much more effective catalyst precursor for Suzuki-Miyaura, Heck-Mizoroki and Sonogashira cross-coupling reactions than the catalyst systems based on Pd(PPh₃)₄, Pd₂(dba)₃, PdCl₂, and Pd(OAc)₂ using various phosphines PPh₃, PCy₃, P^tBu₃.^[1,2] Considering these advantages and the importance of Buchwald-Hartwig amination reactions in synthesis of various compounds such as pharmaceuticals and agrochemicals, the efficiency of **I** has been investigated for the amination of aryl halides specially chloroarenes because, they are inexpensive and widely available.

In this work the use of the easily synthesized and handled **I**^[3] as precursor, have been studied for Pd-catalyzed cross-coupling Buchwald-Hartwig amination reactions of 4-bromo- and 4-chloroanisole with morpholine. Comparisons were made with other Pd precursors (Pd₂(dba)₃, Pd(OAc)₂ and [Pd(η^3 -1-Ph-C₃H₄)Cl]₂) utilizing various phosphines (P^tBu₃ and Xphos) and different phosphine (L) to Pd ratios (L: Pd = 2:1 and 1:1). In all of these reactions, 1,4-dioxane and sodium tert butoxide (Na^tBu) were used as solvent and base, respectively.

Under certain conditions, the catalyst systems based on **I** are found to be significantly more active. For examples catalyst systems based on **I** and P^tBu₃, always generate higher conversions which are monitored by Gas Chromatography (GC). The formation of the active species in the catalysis of these reactions is being investigated by ¹H NMR and ³¹P NMR.



References:

- [1] (a) Fraser, A. W.; Besaw, J. E.; Hull, L. E.; Baird, M. C. *Organometallics* 2012, 31, 2470.
 [2] Jaksic, B. E.; Jiang, J.; Fraser, A. W.; Baird, M. C. *Organometallics* 2013, 32, 4192.
 [3] Norton, D. M.; Mitchell, E. A.; Botros, N. R.; Jessop, P. G.; Baird, M. C. *J. Org. Chem.* 2009, 74, 6674.

P32

Synthesis and Photochemistry of Highly π -Conjugated Organoboron Compounds Containing N-Heterocyclic CarbenesSoren K. Møllerup¹ and Suning Wang*¹¹Queen's University, 90 Bader Lane, Kingston, ON K7L 3N6E-mail of presenting author: Soren.Møllerup@chem.queensu.caE-mail of corresponding author: Suning.Wang@chem.queensu.ca

Recently, our research group reported the synthesis of new azaborines (B=N) via a photoelimination reaction of B,N-heterocycles.^[1] This unusual chemical transformation in which C-H and B-C bond breaking is observed was found to be generic for B,N-heterocycles, as both the N-heterocycle and boron substituents could be varied. The products of these photoelimination reactions display bright-green or yellow-green fluorescence in both solution and solid state (doped polymer matrix). Although the precursor compounds are stable under atmospheric conditions, the photoelimination products were found to degrade upon exposure to air. N-heterocyclic carbenes (NHCs) have long been used to stabilize rare main group species, such as borylenes,^[2] due to their stability and strong σ -donor capabilities. As a result, we set out to synthesize the highly conjugated polycyclic BN-anthracene derivatives depicted in Figure 1 (**1a**). It is postulated that these BN-anthracene systems will be more stable than their azaborine counterparts, hopefully rendering them stable towards both air and moisture. Following their syntheses, the reaction progress of each photoelimination will be monitored by NMR, UV/Vis, and fluorescence spectroscopy. This presentation will describe the syntheses of these intriguing compounds and their reactivity upon exposure to UV light.

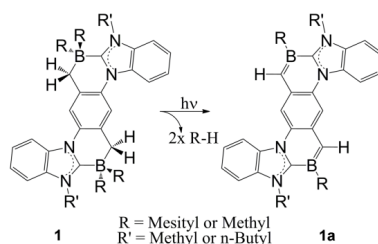


Figure 1. Anticipated photoelimination reactions within the polycyclic NHC-boron chelate complexes yielding highly π -conjugated BN-anthracene derivatives.

References:

- [1] J. S. Lu, S.-B. Ko, N. R. Walters, Y. Kang, F. Sauriol, S. Wang, "Formation of Azaborines by Photoelimination of B,N-Heterocyclic Compounds", *Angew. Chem. Int. Ed.* 2013, 17, 4544.
- [2] P. Bissinger, H. Braunschweig, A. Damme, R.D. Dewhurst, T. Kupfer, K. Radacki, K. Wagner, "Generation of a Carbene-Stabilized Bora-borylene and its Insertion into a C-H Bond", *J. Am. Chem. Soc.* 2011, 133, 19044.

P33

Bright Blue and White Electrophosphorescent Triarylboryl-Functionalized C[^]N-Chelate Pt(II) Compounds

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A new class of blue and blue-green phosphorescent C[^]N chelate Pt(II) compounds that contain a dimesitylboryl-functionalized phenyl-1,2,3-triazole ligand (Bptrz) are synthesized. The influence of three different ancillary ligands, namely, acetylacetonato (acac), picolinate (pic) and pyridyl-1,2,4-triazolyl (pytrz), on phosphorescent quantum efficiency and excimer emission is examined.^[1]



Figure. Photographs showing the emission colors of Pt(II) compounds in 10 wt% PMMA films (top), as neat solids (middle) and in Me-THF solution ($\sim 1.0 \times 10^{-5}$ M, bottom).

References:

- [1] X. Wang, Y.-L. Chang, J. -S. Lu, T. Zhang, Z. H. Lu, S. Wang*, "Bright Blue and White Electrophosphorescent Triarylboryl-Functionalized C[^]N-Chelate Pt(II) Compounds: Impact of Intramolecular H Bonds and Ancillary Ligands", *Adv. Funct. Mater.*, **2013**, in press (accepted on October 5th, 2013).

P34

Pyrazole-Based NCN-Type Ni Complexes :

Synthesis by Direct Metallation, Characterisation and Reactivities

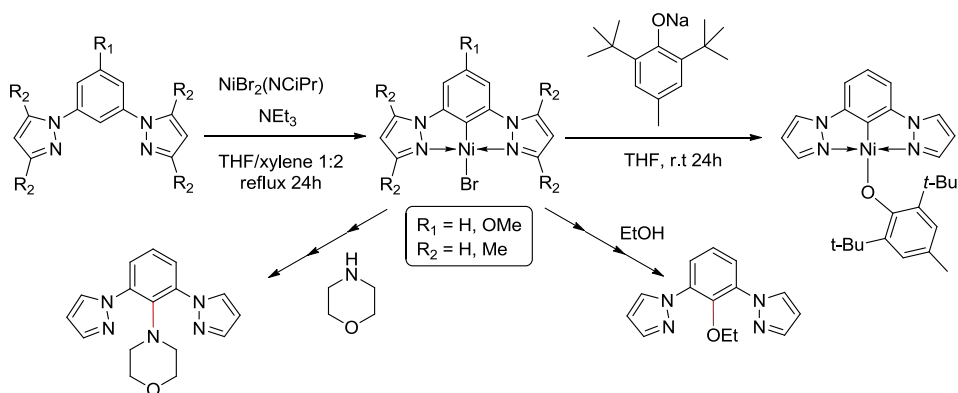
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NCN-type complexes of Ni were introduced by van Koten's group nearly three decades ago, but the chemistry of this family of complexes has remained somewhat underdeveloped due to the absence of simple synthetic routes based on direct C-H nickellation. In this context, a recent report demonstrated that NCN-Ni complexes featuring imidazole-based donor moieties are accessible via a direct C-H nickellation route (Gong, Song, et al. *Dalton* **2011**, *40*, 9012). We have also developed a similar strategy for the preparation of analogous complexes featuring pyrazole-based donor moieties

This presentation will report the synthesis and characterisation of the new NCN-type complexes (NCNpyrazole)Ni(II)X. We will also describe the preparation and reactivities of aryloxy derivatives, as well as a novel reaction that allows functionalisation of the NCN ligand through C-N and C-O bond formation.



P35

Synthesis and characterization of Ru(II) building blocks for light-harvesting applications based on a new 1,3,5-triazine ligand.

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The 1,3,5-triazine motif has become an important molecular component for organic, supramolecular and coordination chemists due to its diverse reactivity, electronic and structural influences.^[1,2] In our ongoing project, the synthesis of a new triazine ligand was optimized and its complexation by ruthenium metal ions was achieved. A series of mono-, bis- and trinuclear ruthenium(II) complexes as well as a heteronuclear Ru(II)/Pt(II) species was obtained and their optical and electronic properties as well as photo-induced hydrogen production capability were investigated.

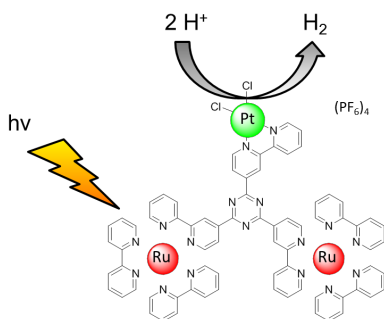


Figure 1. Photo-induced Hydrogen production via the heteronuclear Ru(II)/Pt(II) complex.

References:

[1] P. Gamez and J. Reedijk, *Eur. J. Chem.* 2006, **1**, 29.

[2] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature* 1995, **378**, 469

P36

C-C, C-N, C-Si, and Si-Si Coupling Reactions Catalyzed by POCOP Nickel Complex.

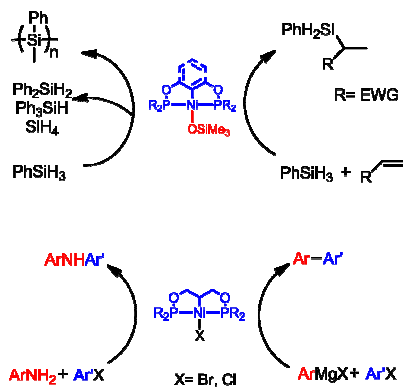
Jingjun Hao, Boris Vabre, Berline Mougang-Soumé, and Davit Zargarian*

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Transition metal catalyzed coupling reactions constitute a powerful tool in preparing new molecules having potential applications in medicinal and material chemistry. The realization of some transformations such as silane polymerization and $C_{(sp^2)}-N$ coupling normally requires low-valent nickel species undergoing oxidative addition/reductive elimination in a catalytic cycle. Such 2-electron redox reactions often mean that Ni(II) species are ineffective candidates for such coupling reactions due to inaccessibility of high valent nickel species ($Ni(II) \leftrightarrow Ni(IV)$).^[1] In this context, robust pincer complexes have proven to be effective during catalysis in keeping constant valence of central metal,^[2] particularly for late transition metals. The questions arises whether pincer complexes of Ni(II) might be able to enforce a constant-oxidation-state throughout a catalytic cycle, thus rendering them effective in catalytic coupling reactions.



This poster will present Si-Si and C-X ($X = C, N, Si$) coupling reactions (see above) catalyzed by POCOP-Ni complexes. Much effort has been made to elucidate the reaction mechanisms. Investigation of two nickel siloxide complexes toward phenyl-substituted hydrosilanes has led to identification of silane redistribution, dehydrogenative polymerization, and hydrosilylation of polar olefins. Studies of (POCOP)NiX has led to C-N and C-C coupling reactions via highly reactive nickel intermediates and single electron transfer mechanisms.

References:

- [1] (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359-1410; (b) Nagao, S.; Matsumoto, T.; Koga, Y.; Matsubara, K. *Chem. Lett.* **2011**, *40*, 1036-1038
- [2] van Koten, G.; Milstein, D. *Organometallic Pincer Chemistry*, Springer-Verlag Berlin Heidelberg, New York, NY, 2012.

P37

TOF vs Electronic Spectroscopy: A Study of Hydrogen Photo-Catalysis reactions based on Rh₂-Re_n assembliesDaniel Chartrand¹ and Garry S. Hanan*¹¹ Université de Montréal, Montréal, Québec, H3C 3J7E-mail of presenting author: daniel.chartrand.1@umontreal.caE-mail of corresponding author: garry.hanan@umontreal.ca

Multiple light sensitizing chromophores are incorporated into a hub structure serving as a supramolecular light-harvesting antenna which fuels a hydrogen evolving catalyst. Our main building blocks for forming these assemblies are rhodium amidinate dimers functionalized with pyridine moieties, where we graft Rhenium chromophores.^[1,2] These assemblies were tested for hydrogen production (measuring turn-over frequency or TOF) with cobalt catalysts under various conditions and under continuous Electronic Spectroscopy UV-vis monitoring.

As shown on the right bottom figure, hydrogen evolution (red dots, TOF) can be correlated to UV-vis data (full spectra series on top). This is very useful as it can be used to look at speciation change during photo-catalysis. In this case, the Co(III) catalyst is reduced to Co(II) and hydrogen evolution only starts when the Co(III) species is consumed. Later it can be observed that the rate of hydrogen production decays at a similar rate as the chromophore assembly, confirming it being the active species.

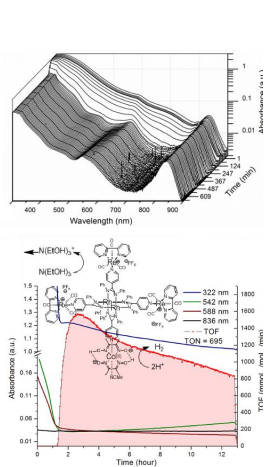


Figure. Example of Hydrogen photocatalysis study with UV-vis monitoring.

References:

[1] Chartrand, D.; Hanan, G. S. *Chem. Commun.* **2008**, 727.

[2] Chartrand, D.; Hanan, G. *Inorg. Chem.* **2013**.

P38

Cyclometallation of Aza-Dipyrromethene on Neutral Ruthenium Complex: Toward New Photosensitizers in the NIR

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As analogues of porphyrinoids and dipyrromethene families of dye, aza-dipyrromethene (ADPM) derivatives exhibit exciting photophysical properties.^{1, 2} Their high absorbance (ϵ up to $100\,000\text{ M}^{-1}\text{cm}^{-1}$) and strong near-IR luminescence are especially interesting in the context of designing new light-harvesting materials.³ In the present study, we introduce the first examples of ADPM cyclometallation on ruthenium complexes bearing either bipyridine (bpy) (see Figure) or terpyridine and demonstrate the latter support further chemical modifications toward the achievement of a new family of photosensitizers for dye-sensitized solar cells (DSSC). Photophysical characterization and modelization studies will be presented to assess the origin of the bathochromic shift in the NIR region observed. Electrochemistry of the complexes will also be discussed in the perspective of optimization toward the specific energetic levels required for DSSC.

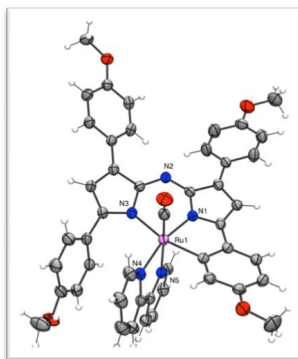


Figure. X-ray structure of $\text{Ru}^{\text{II}}(\text{ADPM})(\text{BPy})(\text{CO})$.

References:

1. A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891-4932.
2. R. Ziessel and A. Harriman, *Chem. Commun.*, 2011, **47**, 611-631.
3. A. Bessette and G. Hanan, Perspective review submitted to *Energy Environ. Sci.* (Manuscript ID: EE-PER-09-2013-043180)

P39

A Special Case of Solvatomorphism Inducing both Geometry and Spin Change at the Metal Center

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As part of our research, we investigate the characteristics of the metal-ligand interaction in metallic complexes of *N,N*-disubstituted hydroxyamidines/ α -aminonitrone (AMOXs). Herein, the synthesis and the structural characterization of Co(II), Ni(II), and Cu(II) complexes with the *N*-hydroxy-*N,N*-bis(2-biphenyl)formamidinate ligand (2-Ph-AMOX) are presented, together with their spectroscopic, electrochemical, and magnetic properties. The Co(II) analog is a special case of solvatomorphism inducing structural change (isomerization from tetrahedral to square-planar geometry around the metal). The spin change associated with this transformation for a Co(II) d^7 ion is an added feature to the system, allowing the confirmation of structural change by methods such as ESR spectroscopy (Figure 1).

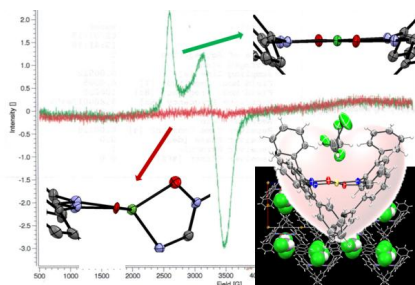


Figure 1. ESR spectra of Co(2-Ph-AMOX)₂ • 2DCM (green) and Co(2-Ph-AMOX)₂ (red) together with their solid structures.

P40

Synthesis and Characterization of *N*-Bridged Bis-Hydroxyamidines/ α -aminonitrones (AMOX) as Synthons in Supramolecular Chemistry

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N,N'-disubstituted hydroxyamidines/ α -aminonitrones (AMOXs) present high steric and electronic modularity, as substituents can be varied on the α -carbon and/or on the nitrogen atoms. This fact affords their precise electronic tunability, facilitated by the delocalization on the amidine backbone. They are good chelating ligands, forming stable 5-member chelate rings with metal ions, and they also have hydrogen bonding capacity. In our research, we exploit these properties by investigating their incorporation into supramolecular assemblies based on coordination chemistry and/ or hydrogen bonding. The properties of the metals used will dictate the function of the final assembly (e.g.: light-harvesting properties with Ru, Re, Ir or magnetic properties with Co, Fe or Mn). The type of assembly is induced by the geometry of the metal ion, in combination with the coordination vectors of the ligand (e.g.: tetrahedral metal + parallel coordination vectors = grid type assembly). Herein, we present the synthesis and characterization of *N*-bridged bis-AMOX ligands (Figure 1), and their precursors (bis-amidines).

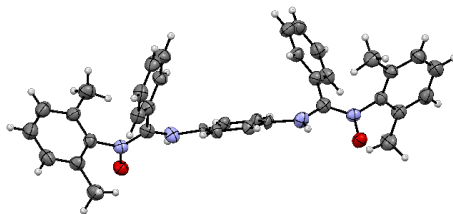


Figure 1. Solid structure of a *N*-bridged bis-AMOX ligand.

P41

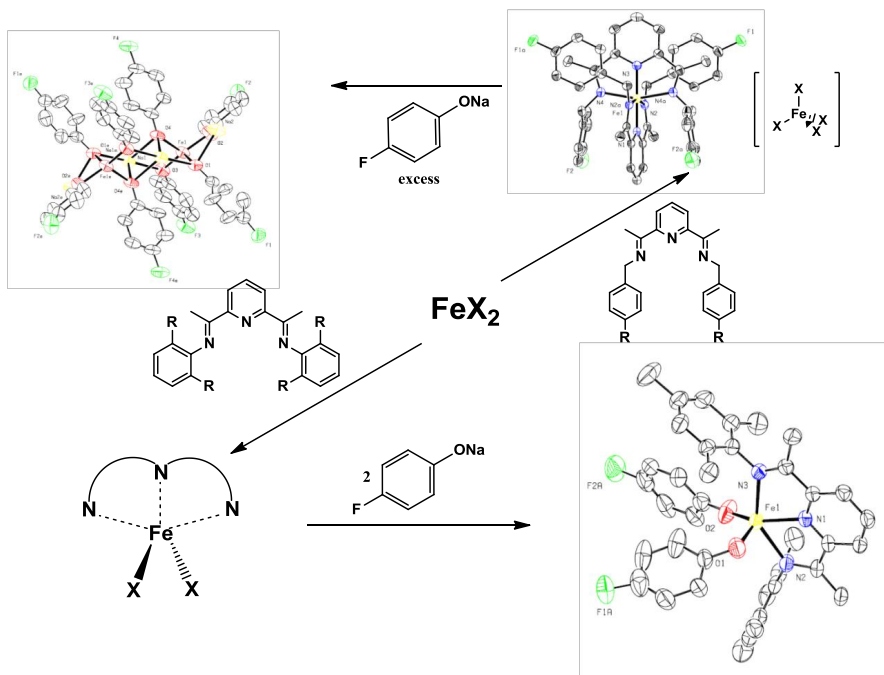
Synthesis of Pincer-like Iron Compounds for Lactide Polymerization

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Within the context of a project aimed at developing pincer-like iron based catalysts for the polymerization of lactide, we were interested in the synthesis of precursor complexes based on tridentate bis-imino pyridine ligands (NNN). Initial attempts to prepare the target complexes from FeX_2 ($\text{X} = \text{Cl}, \text{Br}$) and various NNN pincer-like ligands have led to homoleptic and heteroleptic complexes, depending on the *N*-substituents. For instance, reaction of 2,6-bis[1-(benzylimino)-ethyl]pyridine (DAPB) led only to an octahedral homoleptic complex, whereas the analogous 2,6-bis(arylimino)pyridine ligand provided the desired heteroleptic $(\text{NNN})\text{FeCl}_2$. The latter penta-coordinate complexes underwent efficient ligand substitution reactions to give the desired Fe-OR derivatives. This presentation will discuss the synthesis and characterization of these new Fe complexes and their coordination chemistry.



P42

4,5-Diazafluorene Derivatives as Multipurpose Ligands

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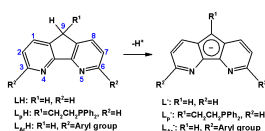
Our group has been actively exploring the chemistry and reactivity of the 4,5-diazafluorene (LH) and 4,5-diazafluorene ligands (L⁻). LH is a bipyridyl ligand with a methylene linker which can be deprotonated to form the L⁻ ligand (Scheme 1). An interesting feature of the L⁻ ligand is that it potentially has two metal-binding sites: the N-donors and the C-donors of central cyclopentadienyl-like ring (see Scheme 1). Here we demonstrate the multifunctional nature of these ligands. Diazafluorene derivatives can behave as actor ligands in small molecule activation, ambidentate ligands in coordination chemistry, and also as bulky auxiliary ligands to stabilize low-coordinate metal centres.

We were able to demonstrate that the reactivity of the L⁻ actor ligand toward CO₂ can be tuned with different spectator metal centres; resulting in either reversible tandem CO₂ and C-H activation, or the irreversible formation of metal-carboxylate complexes (Fig. 1).^[1] The ambidentate nature of LH derivatives allowed for heterobimetallic complexes to be prepared.^[2] In the coordination chemistry of LH derivatives with the {RuCp*}⁺ fragment subtle differences in either reaction sequence, or choice of counterion resulted in the formation of linkage isomers, or self-assembled macrocycles (Fig. 2).^[3]

We have also explored the analogy of L⁻ with other anionic nitrogen chelate ligands with a noninnocent carbon backbone such as nacnac ligands. A ligand family where bulky groups have been installed *ortho* to the N-donor atoms of diazafluorene, and the subsequent coordination chemistry aimed at the synthesis of complexes with low-coordinate metal centres will also be presented.

References:

- [1] a) Annibale, V. T.; Song, D. *Chem. Commun.* **2012**, 48, 5416. b) Annibale, V. T.; Song, D. *J. Am. Chem. Soc.* **2013**, DOI: 10.1021/ja4073832.
 [2] Batcup, R.; Chiu, F. S. N.; Annibale, V. T.; Huh, J.-E. U.; Tan, R.; Song, D. *Dalton Trans.* **2013**, DOI: 10.1039/C3DT52135D.
 [3] Annibale, V. T.; Batcup, R.; Bai, T.; Hughes, S. J.; Song, D. *Organometallics* **2013**, DOI: 10.1021/om400846f.



Scheme 1.

Reverse Tuning: Actor Ligand & Spectator Metal



Figure 1.

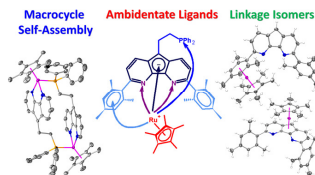


Figure 2.

P43

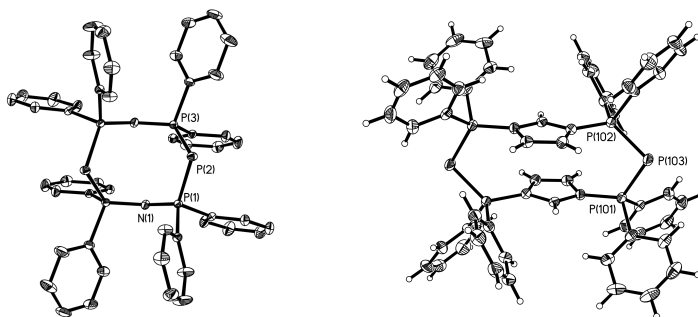
Low Oxidation State Phosphorus Macromolecules

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The utility of inorganic polymers and macromolecules has been recently well demonstrated as they feature alternative reactivities and physical properties than their organic analogues. Specifically, polyphosphazenes have been investigated extensively and used industrially for a variety of applications.^[1] The isovalent phosphorus analogue of polyphosphazenes is of interest to our group as it features a low oxidation state phosphorus centre linked by anionic phosphine fragments. Schmidpeter *et al.* has reported this type of compound by reacting phosphinous amide with elemental phosphorus.^[2] By employing our facile preparation for our triphosphenium P(I) precursor^[3], we present an improved synthesis to prepare this oligomer. Other recent syntheses and characterizations of macrocycles containing low oxidation state phosphorus centres including phosphorus rich analogues of phosphazenes will be presented in this poster.



References:

- [1] a)B. L. Lucht, N. O. St Onge, *Chemical Communications* **2000**, 2097; b)K. J. T. Noonan, D. P. Gates, *Angewandte Chemie-International Edition* **2006**, 45, 7271; c)T. J. Peckham, J. A. Massey, C. H. Honeyman, I. Manners, *Macromolecules* **1999**, 32, 2830; d)N. Burford, C. A. Dyker, M. Lumsden, A. Decken, *Angewandte Chemie-International Edition* **2005**, 44, 6196; e)R. C. Smith, J. D. Protasiewicz, *European Journal of Inorganic Chemistry* **2004**, 998.
- [2] A. Schmidpeter, F. Steinmuller, W. S. Sheldrick, *Zeitschrift Fur Anorganische Und Allgemeine Chemie* **1989**, 579, 158.
- [3] E. L. Norton, K. L. S. Szekeley, J. W. Dube, P. G. Bomben, C. L. B. Macdonald, *Inorganic Chemistry* **2008**, 47, 1196.

P44

Modeling Magnetic Interactions in Sulfur-Nitrogen Radical Chemistry

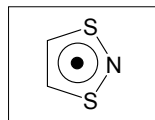
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Organic radicals have captured the attention of researchers due to their ability to exhibit magnetic order, despite the absence of metal ions. The goal of this study is to gain a better understanding of the electron-electron interactions in one such class of stable radical, known as dithiazolyls (**1**). Such data allows a much improved understanding between structure and magnetic response in these systems, which will assist in the future design process, leading to organic magnets with higher ordering temperatures.

Figure 1. DTA Radical (**1**)

We have employed the 'bottom-up' methodology^[1], pioneered by Novoa *et al.*, to determine appropriate magnetic models based on pairwise interactions between nearest neighbour molecules in the solid state, in which the strength of the magnetic communication is estimated from the energies (E) and expectation values ($\langle S^2 \rangle$) of the triplet and broken symmetry singlet configurations. Recent calculations and magnetic models for selected dithiazolyl radicals (**1**) will be presented.

References:

- [1] H. Nagao, M. N., Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka, K. Yamaguchi, *Coord. Chem. Rev.* **2000**, *198*, 265.

P45

Stimuli-Responsive Supramolecular Gelation in Organometallic Peptide Conjugates

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Peptides can be attractive building blocks for the fabrication of complex nano-architectures with predictable and tunable properties capable of promoting protein-like environmental responsiveness. These biomolecular motifs can self-assemble to form highly organised nano-structures. This is best exemplified by the in vitro formation of amyloid-like fibrils and their application in the development of new nanomaterials. One plausible application of these fibrillar assemblies is the creation of well organised supramolecular assemblies that exhibit smart response to external signals.^[1] Herein, we report novel short peptide based organometallic gelators that demonstrate reversible organogel formation in response to various external signals including thermal, sound, redox and mechanical stress. Considering the fact that serendipity in organogel research is one of the main paths to discovery, organometallic based gelators are not abundant and the compounds reported here are interesting examples of how peptide chemistry can be exploited to form organometallic gelators.

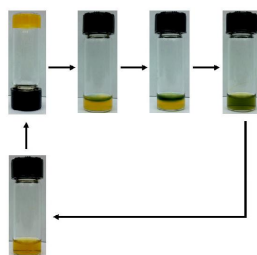


Figure. Redox-responsive phase transitions in a short peptide based Organometallic gelator.

References:

- [1] a) R. J. Mart, R. D. Osborne, M. M. Stevens, R. V. Ulijn, *Soft. Matter*. 2006, 2, 822-835; b) K. Isozaki, H. Takaya, T. Naota, *Angew. Chem. Int. Ed.* 2007, 46, 2855-2857.

P46

New Pincer-Type Ruthenium Complexes Designed for Small Molecule Activation via Metal-Ligand Cooperation

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A ligand framework that actively participates in bond making/breaking processes along with the metal center is commonly known as “metal-ligand cooperation.”^[1] We have been exploring avenues towards such systems that contain only nitrogen and carbon donors around the metal with the intent of activating small molecules such as H₂O to better understand the requirements for water splitting at a single metal center.^[2] Ruthenium complexes containing pincer-type NCN ligands with a central N-heterocyclic carbene donor and methylpyridyl (picolyl) side arms have recently been synthesized (Figure 1). The reactivity of these complexes under a variety of conditions will be discussed.

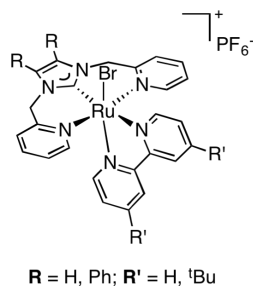


Figure 1

References:

- [1] Askevold, B.; Roesky, H. W.; Schneider, S. *ChemCatChem* **2012**, *4*, 307.
 [2] Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74.

P47

A *trans*-Dihydride Complex as a Potential Molecular RotorErnest Prack¹, Alan J. Lough¹, Robert W. Schurko², Daniel Klauke² and Ulrich Fekl¹¹University of Toronto, Department of Chemistry, ON M5S 1A1²University of Windsor, 389 Essex Hall, City of Windsor, ON N9B 3P4E-mail of presenting author: ernest.prack@mail.utoronto.caE-mail of corresponding author: ulrich.fekl@utoronto.ca

Molecular rotors have great potential for molecular machines and for information storage technology at the molecular level.

The single crystal X-ray structure (including a crystallographically located hydride position) and solid state NMR (SSNMR) data for *trans*-H₂Pt(^tBu₃P)₂ as a potential molecular rotor are presented. The *trans*-hydrides appear to be mostly localized at 147 K based on X-ray. However, preliminary ¹⁹⁵Pt SSNMR at room temperature and at 173 K shows that *d*₁₁ is unique and *d*₂₂/*d*₃₃ are the same or similar. This apparent axial symmetry could indicate that the hydrides are orbiting in a plane that is perpendicular to the P-Pt-P axis. Progress in assessing the locked-versus-rotating nature of the hydrides, potentially including other physical techniques, will be presented.

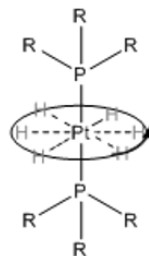


Figure. *trans*-H₂Pt(PR₃)₂ (R = ^tBu): A potential molecular rotor with the two *trans*-hydrides orbiting the platinum on a circular trajectory in a plane perpendicular to the P-Pt-P axis.

P48

Toward Homogeneous Hydrodesulfurization Using a Low Valent Molybdenum Complex

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The hydrodesulfurization (HDS) process allows for the catalytic removal of organosulfur compounds from crude oil by using H_2 as a feedstock. This process is critical to the oil and gas industry, as sulfur containing compounds are poisons to the noble metal catalysts used in the cracking process. When burned, they produce SO_2 , a toxic gas which is a primary contributor to acid rain. As deposits of high grade petroleum dwindle, it will become necessary to utilize sources of lower grade, heavy crude oils which contain higher concentrations of refractory aromatic sulfur heterocycles. Such compounds are significantly more difficult to remove via hydrodesulfurization, making new techniques for "deep" hydrodesulfurization necessary.^[1,2] The current industrial HDS method involves the use of heterogeneous MoS_2 based catalysts under high pressure and temperature conditions, but the activities of these catalysts are limited to the more easily desulfurized substrates.^[3] Homogeneous small molecule catalysts based on inexpensive metals such as molybdenum could provide low cost alternatives with greater deep HDS activity.

DFT and preliminary experimental evidence suggest that molybdenum(0) complexes bearing tripodal NHC ligands may act as robust and efficient homogeneous catalysts for the HDS process.

References:

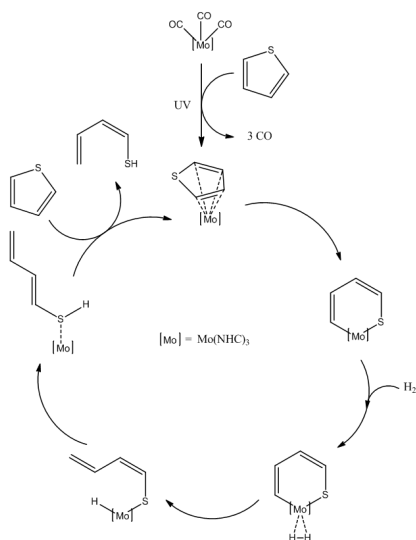
[1] T. V. Choudhary, S. Parrott, B. Johnson, *Environ. Sci. Technol.* **2008**, *42*, 1944–1947.[2] I.V. Babich, J.A. Moulijn, *Fuel* **2003**, *82*, 607-631.[3] P. G. Moses, B. Hinemann, H. Topsøe, J. K. Nørskov, *Journal of Catalysis*. **2007**, *248*, 188-203.

Figure 1. A potential catalytic cycle for the hydrodesulfurization of thiophenes using a low valent molybdenum complex bearing a tripodal NHC ligand.

P49

Synthesis and Reactivity of Tantalum Complexes of a Bulky *o*-Phenylenediamide Ligand

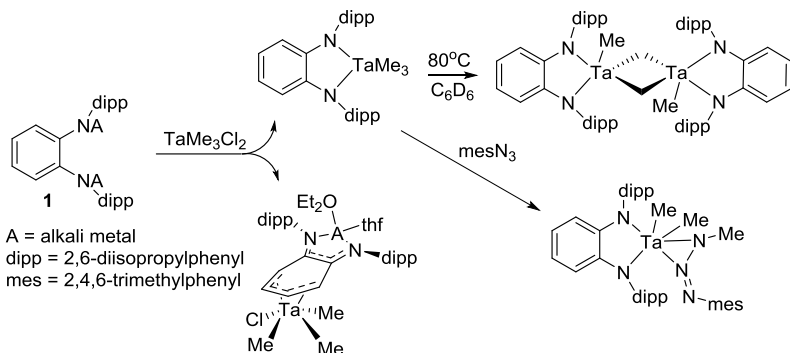
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Redox-active ligands have attracted the interest of the chemistry community.¹ While metal-centred redox events have been harnessed and exploited in catalysis with great success, ligand-centred redox events have not yet enjoyed the same prosperity. More needs to be known about the fundamental reactivity of redox-active ligands in order to realize their potential as electron reservoirs for challenging catalytic reactions.² To this end, our research group has previously investigated the reactivity of the dilithium derivative of diamide **1** towards halides of Fe, Mo, and Eu.³ This poster will present as a continuation of this work the synthesis, structural characterization, and reactivity of tantalum derivatives of **1**. Bond lengths obtained from X-ray diffraction studies will be discussed in the context of their relevance to ligand oxidation states.



References:

[1] Luca, O. R., Crabtree, R. H., *Chem. Soc. Rev.* 2013, 42, 1440-1459.

[2] Blackmore, K. J., Lal, N., Ziller, J. W., Heyduk, A. F. J. *Am. Chem. Soc.*, 2008, 130, 2728-2729.

[3] Janes, T., Rawson, J. M., Song, D. *Dalton Trans.*, 2013, 42, 10640-10648.

P50

New Designs for 1,2,3,5-dithiadiazolyl Radical Ligands:

A little Bita this and a little Bita that!

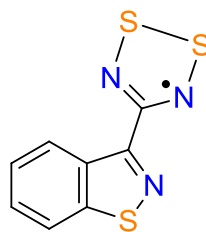
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Our group specializes in creating molecular materials based on thiazyl radicals as ligands. These spin bearing ligands are used to mediate magnetic coupling between paramagnetic metal centers.^{[1],[2]} The resulting complexes have exhibited various novel and interesting magnetic properties.^[refs] Our work makes a unique contribution to the field of molecular magnetic materials.^[2]

Thiazyl heterocycles contain primarily sulfur and nitrogen atoms.^[2] The radical presented here is a new 1,2,3,5-dithiadiazolyl (DTDA) referred to as bitaDTDA. It is the first DTDA radical that contains a sulfur atom outside of the heterocyclic ring. This sulfur atom affords an extensive network of intermolecular contacts in the crystal structure. The new bitaDTDA ligand has also been complexed to paramagnetic metals. Here we will show structural data (X-ray crystallography) demonstrating that bitaDTDA has been successfully coordinated to the Dy(hfac)₃ fragment (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato).



References:

- [1] Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, 22, 392- 398
 [2] Preuss, K. E. *Dalton Trans* **2007**, 2357- 2369

Towards the Synthesis of the first 1,2,3,5-dithiadiazolyl Radical containing a thiocyanato moiety.

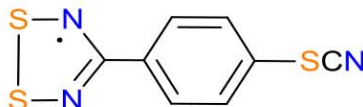
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The synthesis and characterization of molecule-based materials with controllable magnetic properties is a major area of interest in our research group. Paramagnetic molecules contain unpaired electrons and are known to exhibit magnetic properties. Our approach follows the synthesis of paramagnetic molecules based on thiazyl building blocks. Coordination to transition metal or lanthanide centers to fulfill certain functions will be the application of the new radical ligands. The 1,2,3,5-dithiadiazolyl (DTDA) fragment is a five membered heterocycle, with the molecular formula $CN_2S_2^{\cdot}$. This heterocycle is planar, with the unpaired electron residing in a singly occupied π^* antibonding orbital (SOMO)¹. When molecules containing the DTDA fragment exist in the solid state, "dimerization" forming a diamagnetic $[DTDA]_2$ unit is possible².



4-(4'-thiocyanatophenyl)-1,2,3,5-dithiadiazolyl

The synthesis of 4-(4'-thiocyanatophenyl)-1,2,3,5-dithiadiazolyl is the first attempted synthesis of a DTDA containing a thiocyanato moiety. The structure of the molecule is ideal for coordination to EMAC (extended metal atom chain) molecules through the lone pair located on the N atom of the thiocyanato group. EMAC molecules are based on multiple metal-metal bonds with four identical multidentate ligands³. When the ligand is coordinated at the axial position of an EMAC molecule, the DTDA ring can act as a supramolecular synthon⁴. The DTDA heterocycles can form trans- or twisted-cofacial dimers, and orient the EMAC molecules in 1D arrays or macrocycles⁵. Preliminary attempts at coordinating benzonitrile via the $-CN:$ to EMAC molecules were unsuccessful and we hypothesize that this is due to steric crowding. The use of the thiocyanato group will increase the length from the metal atom of the EMAC to the phenyl ring of the ligand.

References:

¹ Alange, G. G.; Banister, A. J.; Bell, B.; Millen, P. W. *J. Chem. Soc., Perkin Trans*, **1979**, 1192-1194.

² Preuss, K E. *Dalton Trans.* **2007**, 2357–2369.

³ Cotton, F. A. *Rev. Pure and Appl. Chem.* **1967**, *17*, 25-40.

⁴ Cotton, F.A.; Lin, C.; Murillo, C.A *Proc. Nat. Acad. Sci.* **2002**, *99*, 4810-4813.

⁵ Berry, J. F.; Cotton, F. A.; Murillo, C. A.; Roberts, B. K *Inorg. Chem.* **2004**, *43*, 2227-2783.

P52

Substituent effects on the nitrogen chemical shift tensors in N-methylpyridinium salts

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In this study we investigated the electron donating and withdrawing effects of the para substituent on the components of the nitrogen chemical shift tensor in a series of N-methylpyridinium iodide salts. We find that there is a linear relationship between the experimentally determined values, δ , and those calculated, σ , by quantum chemical methods, and that these tensors can be related to the electronic MO transitions. A linear relationship was also found between the isotropic chemical shift and the corresponding substituent Hammett constants. All salts were made from the pyridine derivatives upon methylation with methyl iodide.

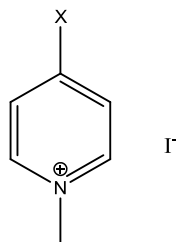


Figure 1: N-Methylpyridinium Iodide series studied by MAS ¹⁵N NMR

References:

- [1] Brown, H. C. and Okamoto, Y., *J. Am. Chem. Soc.* 1958, 80, 4979.
 [2] Solum, M. S., Altmann, K. L., Strohmeier, M., Berges, D. A., Zhang, Y., Facelli, J. C., Ougmire, R. J. and Grant, D. M. *J. Am. Chem. Soc.* 1997, 119, 9804.
 [3] Penner, G. H. and McCullough, A. *J. Org. Chem.* 2006, 71, 8794.

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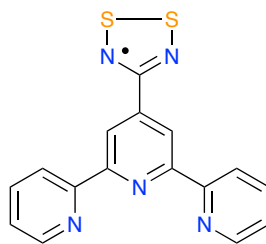
Paramagnetic thiazyl ligands for the design and synthesis of molecular materials displaying luminescent properties

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The design and synthesis of thiazyl radical ligands can be tailored in order to create molecular materials with a variety of desirable properties. The incorporation of a large aromatic system, such as terpyridine, to the thiazyl radical heterocycle will afford a compound possessing interesting luminescent behavior. By combining the luminescence of terpyridine, with the reversible monomer-dimer equilibrium characteristic of thiazyls¹, one could in theory generate a luminescent switch. Previous work in the literature has demonstrated that paramagnetic nitroxide radical derivatives show significantly diminished quantum yields and shorter fluorescent lifetimes than their diamagnetic counterparts². By altering specific conditions, dimerization of the thiazyl terpyridine can be reversed, quenching the luminescence generated from the diamagnetic system. Furthermore, bis(terpyridine) Fe(II) complexes have demonstrated an ability for fast interfacial electron transfer through an oligomer wire chain³. Using the DTDA as a supramolecular synthon, a similar thiazyl-based structure may be created on a Au(III) surface.

**References:**

- [1] Preuss, K. E. *Dalton Trans.* **2007**, 2357.
- [2] Herbelin, S.E; Blough, N.V. *J. Phys. Chem. B.* **1998**. 102, 8170.
- [3] Sakamoto, R; Ohirabaru, Y; Matsuoka, R; Maeda, H; Katagiri, S; Nishihara, H. *Chem. Commun.* **2013**, 49, 7108.

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Metal-Radical Complex Exhibiting Magnetic Properties: 1D Heisenberg Chain

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We are pioneering the chemistry of paramagnetic thiazyl heterocycles as building blocks for radical ligands. Metal-radical coordination complexes are promising for the development of molecular materials with novel electronic and magnetic properties. We have combined a methylated naphthoquinone backbone and the 1,2,3-dithiazolyl (DTA) fragment leading to a stable radical ligand with interesting coordination chemistry. Herein, we present the design and synthesis of the paramagnetic ligand, 5,8-dimethyl-naphtho[2,3-d][1,2,3]dithiazolyl-4,9-dione, and its coordination to Mn(II). X-ray crystallography is used to determine the trinuclear structure of the complex $\text{Mn}_3(\text{hfac})_6(5,8\text{-Me}_2\text{-DTANQ})_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato), and the magnetic properties are determined by SQUID magnetometry. Intermolecular contacts in the solid state are responsible for a dramatic rise in the χT product at low temperature, which is fit by the 1D Heisenberg chain model, indicating long range ferromagnetic correlations in the [110] direction with a magnetic correlation length of $\xi = 24.6 \text{ \AA}$ at 4 K.

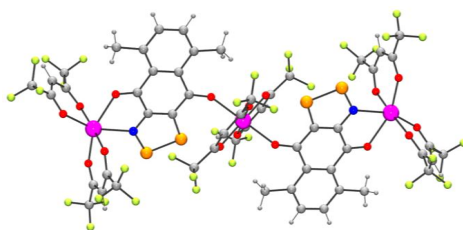


Figure: Ortep rendition of the crystal structure of a trinuclear unit of $\text{Mn}_3(\text{hfac})_6(5,8\text{-Me}_2\text{-DTANQ})_2$.

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Rational design for mixed supramolecular pairs

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The design of molecular materials with controllable magnetic properties is a major objective of our research group. Our approach is to create paramagnetic ligands using thiazyl radicals as building blocks. We have developed an entirely new family of radical ligand that offers extensive possibilities for coordination studies and investigation of diverse properties.^[1] Among our recent endeavours is a metal-radical complex, Dy(hfac)₃(boaDTDA), which forms a supramolecular [Dy(hfac)₃(boaDTDA)]₂ pair in the solid state (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; boaDTDA = 4-(benzoxazol-2'-yl)-1,2,3,5-dithiadiazolyl). The pair contains two unique molecules such that the Dy(III) ions are in different coordination environments. At zero dc field the two Dy(III) ions are weakly antiferromagnetically coupled and the pair acts as a two-dysprosium single molecule magnet (SMM). Importantly, when a very weak dc field (700 Oe) is applied, the Dy(III) ions can be decoupled and two unique one-dysprosium SMMs are observed.^[2] Such a system is a potential model for a CNOT quantum computing logic gate.

The solid state pairwise arrangement of [Dy(hfac)₃(boaDTDA)]₂ was entirely serendipitous. Here, an exploration of methodologies leading to a rational design of paired metal-radical systems is described. Our approach exploits the possibility of making mixed dimers of DTDA radicals.^[3] The goal of this project is to induce mixed dimer formation of metal-radical complexes to develop two-dysprosium systems, similar to that described above, and to examine mixed metal dimers (e.g., Dy(III)-Mn(II)). The synthesis of radical ligands and their coordination to Dy(III) and Mn(II) centres is described. The preliminary results of combining these complexes, both in solution and via cosublimation, are presented.

References:

- [1] (a) Hearn, N.G.H.; Preuss, K.E.; Richardson, J.F.; Bin-Salamon, S. J. Am. Chem. Soc. **2004**, 126, 9942-9943 (b) Hearn, N.G.H.; Clérac, R.; Jennings, M.; Preuss, K.E. **2009**. Dalton Trans. 3193-3203 (c) Fatila, E.M.; Goodreid, J.; Clérac, R.; Jennings, M.; Assoud, J.; Preuss, K.E. Chem. Commun. **2010**, 46, 6569-6571.
- [2] Fatila, E.M.; Rouzières, M.; Jennings, M.C.; Lough, A.J.; Clérac, R.; Preuss, K.E. J. Am. Chem. Soc. **2013**, 135, 9596-9599.
- [3] Allen, C.; Haynes, D.A.; Pask, C.M.; Rawson, J.M. CrystEngComm, **2009**, 11, 2048-2050.

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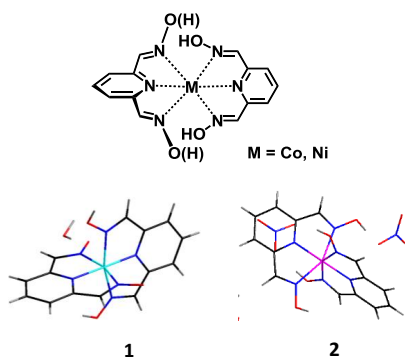
Di-Oxime Complexes of the First Row Transition Metals

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Transition metal complexes containing oxime donating ligands have a wide variety of applications such as catalysis, magnetism, and electronic materials. The importance of oxime substituted ligands in coordination chemistry was first demonstrated by Chugaev in 1905 with the use of nickel (II) salts and dimethylglyoxime [1]. We recently prepared a collection of di-oxime functionalized ligands with the purpose of coordinating first row transition metals to observe the properties of the resulting complexes. The synthesis and characterization of coordination complexes of pyridine-2,6-dicarbaldehyde oxime to two first row transition metals, cobalt, **1**, and nickel, **2**, will be presented. The magnetic, electrochemical, and photophysical properties are being explored.



Top: Molecular structure of pyridine-2,6-dicarbaldehyde oxime complexes. Hydrogen atoms in parenthesis indicate the lability of the atom.

Bottom: Crystal structure of **1** and **2**. Colour code: Co (teal), Ni (pink), N (blue), O (red), C (black), H (grey).

References:

[1] L. Tschugaeff, *Chemt. Ber.*, 1905, 38, 2520.

P57

The Effects of Extended Conjugation and Heteroatoms on the Properties of 2-Dimensionally Fused Small Molecules

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Conjugated small molecules are becoming increasingly important for semiconductor applications as progress is made towards high-temperature, air-stable systems. With stability in hand, the focus shifts to improving the mobility of charge carriers by tuning energy levels and searching for favorable solid state packing. Herein we describe the effects of extending the conjugation of the two-dimensionally fused system, Tetrathienoanthracene (TTA), in an attempt to improve intermolecular π -orbital overlap. Additionally, nitrogen may be introduced in place of a core carbon in order to tune energy levels and electronic behaviour. The solid state, electrochemical and optoelectronic properties, as well as device performance of the molecules outlined in Figure 1 will be presented.

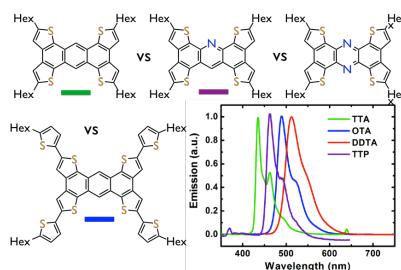


Figure 1. 2-D fused molecules and corresponding UV-Visible emission spectrum, indicating the effects of nitrogen and the extension of conjugation through additional thiophene moieties.

References:

- [1] Brusso, J. *et al. Chem. Mater.* **2008**, *20*, 2484–2494
- [2] Leitch, A.A. *et al. Eur. J. Org. Chem.* **2013**, 5854–5863
- [3] Leitch, A.A. *et al. Cryst. Growth Des.* **2012**, *12*, 1416–1421
- [4] Xie, Y. *et al. J. Mater. Chem. C*, **2013**, *1*, 3467

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Development of the *bis*-thiadiazinyl radicals for optoelectronic applicationsNathan Yutronkie¹, Katie Harriman¹, Jaclyn Brusso*¹¹ Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, CanadaE-mail of Nathan Yutronkie: nyutr055@uottawa.caE-mail of Jaclyn Brusso: jbrusso@uottawa.ca

Technological advancements have created the demand for the fabrication of smaller, lightweight, and flexible materials. In that regard, organo-main group materials are attractive candidates on account of their tunable optoelectronic properties coupled with the desirable characteristics of plastics. Incorporation of neutral radicals into the molecular framework offers additional properties associated with unpaired spins (conductivity and magnetism), thus providing an approach to the design of functional materials with specific magnetic, optical and electronic properties. In pursuit of that goal, target compounds should possess a resonance stabilized neutral radical core surrounded by several substituents that may be used to increase solubility or extend conjugation in two-dimensions. More specifically, the thiophene substituted *bis*-thiadiazinyl radical systems have been investigated along with variations at the R groups as shown in Figure 1. This presentation will focus on the synthesis and challenges associated with these neutral radical systems and their applications towards optoelectronic materials.

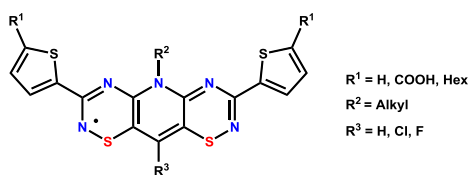


Figure 1. Synthetic approach to the BTD core

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Reversible Inactivation of Bismuth Vanadate in the Photocatalytic Reduction of CO₂

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The removal of greenhouse gasses, such as CO₂, from the atmosphere is among the greatest scientific challenges of the century. This is coupled with the search for alternative sources of energy. The process of reverse combustion provides an exciting possibility of tackling both of these problems with one technique. The use of heterogeneous photocatalytic semiconductors to reduce CO₂ into hydrocarbons and small alcohols is a growing field that, while promising, is far away from being efficient and viable on a large scale.¹ We have probed the mechanism and reversible decomposition of the crystalline semiconductor BiVO₄.

BiVO₄ was first described as a photocatalytic reducer of CO₂ to ethanol.² Unlike most semiconductors for the reduction of CO₂, BiVO₄ is active as a crystal without the use of a co-catalyst. Monoclinic BiVO₄ has also been recently reported to selectively convert CO₂ into methanol under slightly different catalytic conditions.³ The catalytic activity of BiVO₄ was shown to slow considerably over the duration of the reaction, although the catalyst is almost entirely recoverable after work up. We herein report the composition and morphology of active, inactive and reactivated BiVO₄.

References:

- [1] Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372.
- [2] Liu, Y.; Huang, B.; Dai, Y.; Zhang, X.; Qin, X.; Jiang, M.; Whangbo, M.-H. *Cat. Comm.* **2009**, *11*, 210.
- [3] Mao, J.; Peng, T.; Zhang, X.; Li, K.; Zan, L. *Cat. Comm.* **2012**, *28*, 38.

P60

Using Molecular Simulation to Aid in the Interpretation of Solid-State NMR of Metal Organic Frameworks

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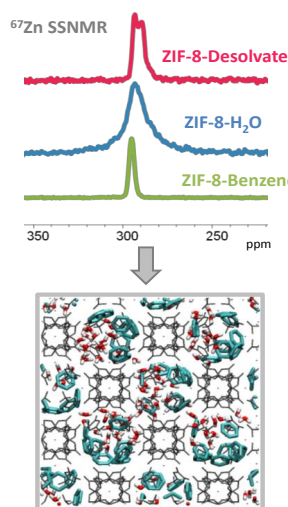
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Metal Organic Frameworks (MOFs) are a novel class of materials being developed for a wide variety of applications including catalysis, drug delivery and gas separations. The Huang group (Western) were amongst the first to make use of solid-state NMR (SSNMR) for dynamic structural characterization and interrogation of guest-host interactions in MOFs, which cannot usually be analyzed using X-ray crystallography alone.¹ We have found that coupling molecular simulation with SSNMR results in deep insight into behaviour of MOFs. Our simulations enable discoveries complementary to corresponding SSNMR results such as charge transfer interactions, the number and distribution of guest binding sites within a MOF, guest binding energies and dynamic behaviour of guest molecules within MOF pores. The techniques we have successfully used include force field-based molecular dynamics (MD) coupled with a spatial distribution function², grand canonical Monte Carlo simulation, energy decomposition, DFT studies, ab initio MD and Bader charge analysis. In addition to an overview of how the simulations are used to elucidate sometimes complex or unusual spectral data, we present the results we derive in support of ¹³C, ¹⁷O, ⁶⁷Zn, ¹¹⁵In and ¹³⁷Ba SSNMR spectra measured for a variety of MOFs. The combination of SSNMR and molecular simulation forms a powerful analytical procedure for characterizing MOFs, and this novel set of microscopic characterization techniques represents one of many efforts aimed at applying MOFs as adsorbents, catalysts and electrical conductors commercially.



References:

- [1] Sutrisno, A. & Huang, Y. *Solid-state NMR: A powerful tool for characterization of metal-organic frameworks*. *Solid State Nucl. Magn. Reson.* **49-50**, 1–11 (2013)
- [2] Sutrisno, A. et al. *Characterization of Zn-containing metal-organic frameworks by solid-state ⁶⁷Zn NMR spectroscopy and computational modeling*. *Chemistry* **18**, 12251–9 (2012).

P61

New Molybdenum and Tungsten Complexes with Pyridinediphosphinite Pincer Ligands

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Since the first report of a PCP pincer ligand in the 1970s,^[1] a great number of pincer-type ligands, with modifications on the backbone or different donor groups, has been developed.^[2] Recently, a new class of pyridinediphosphinite pincer ligands, PONOP, was reported^[3] and its reactivity towards late transition metals has been studied.^[4] This work presents a straightforward synthesis of the first PONOP complexes with early transition metals.

The species $M(\text{CO})_3(\text{NCCH}_3)_3$ ($M = \text{Mo}, \text{W}$) react with the PONOP ligand to generate the pincer derivatives (Figure 1), providing an entry for Mo- and W(PONOP) chemistry.

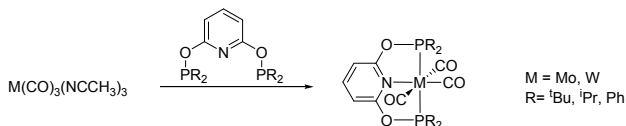


Figure 1.

The reactivity of the starting molybdenum and tungsten carbonyl compounds towards related ligands (Figure 2) is also studied.

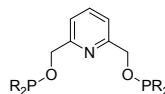


Figure 2.

References:

- [1] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
- [2] Roddick, D. M. *Top. Organomet. Chem.* **2013**, 40, 49.
- [3] Salem, H.; Shimon, L. J. W.; Diskin-Posner, Y.; Leitius, G.; Ben-David, Y.; Milstein, D. *Organometallics* **2009**, 28, 4791.
- [4] See for example: a) Kundu, S.; Brennessel, W. W.; Jones, W. D. *Inorg. Chem.* **2011**, 50, 9443. b) Findlater, M.; Schultz, K. M.; Bernskoetter, W. H.; Cartwright-Sykes, A.; Heinekey, D. M.; Brookhart, M. *Inorg. Chem.* **2012**, 51, 4672.

P62

C–S bond activation of thioethers using (dippe)Pt(NBE)₂Sabuj Kundu, Benjamin E. R. Snyder, Aaron P. Walsh,

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Cleavage of carbon-sulfur bonds plays an important role in the desulfurization of petroleum,^[1] and homogenous transition metal complexes have been extensively studied as models for the structures of intermediates involved in desulfurization.^[2] Aromatic sulfur containing compounds are the most difficult to desulfurize and many studies describe systems where thiophene type compounds are effectively desulfurized.^[3] Herein we describe the reactivity of a Pt(0) complex, (dippe)Pt(NBE)₂ (dippe = 1,2-bis(diisopropylphosphino)ethane) with a number of thioethers. Resulting complexes of C-S activation were fully characterized by NMR spectroscopy, X-ray crystallography and elemental analysis. Both S-Csp³ and S-Csp² are cleaved then further disproportionate forming complexes of the general formula (dippe)Pt(SR)₂ and reductive coupling to generate various hydrocarbons. This is consistent with an octahedral Pt(IV) intermediate.^[4]

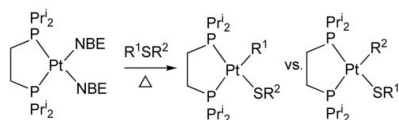


Figure. The complex (dippe)Pt(NBE)₂ (NBE = norbornene) reacts with thioethers RSR' upon heating to give C–S oxidative addition products (RSR' = Ph₂S, PhSMe, PhSallyl, MeSallyl, PhSvinyl, PhCH₂SMe, PhSCF₃, and dithiane). Continued heating leads to disproportionation and formation of R'₂ and (dippe)Pt(SR)₂ in several cases.

References:

- [1] H. Topsøe, B. S. Clausen, F. E. Massoth, *Hydrotreating Catalysis*, Springer-Verlag, Berlin, 1996.
- [2] R. A. Sanchez-Delgado, *Organometallic Modeling of the Hydrodesulfurization and Hydronitrogenation Reactions*, Kluwer Academic Publishers, Dordrecht, 2002.
- [3] a. W. D. Jones, D. A. Vivic, R. M. Chin, J. H. Roache, A. W. Myers, *Polyhedron* 16 (1997) 3115. b. R. J. Angelici, *Coord. Chem. Rev.* 105 (1990) 61.
- [4] W. D. Jones, S. Kundu, B. E. R. Snyder, A. P. Walsh, W. W. Brennessel, *Polyhedron* 58 (2013) 99.

P63

Complexes and reactivity of Ge(II) dications with small molecules

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The study of crown ether ligands stabilizing low oxidation state main group elements is a continuing interest in our research group. Previously, we have determined crown ethers to be excellent ligands in the stabilization of "naked" Ge(II) dications.^[1,2] As an extension of this work, we are investigating the reactivity of these complexes with small molecules. Notably, we have recently reported that the addition of one equivalent of water or ammonia to the [15]crown-5 Ge(II) dication produces the stable complexes [Ge[15]crown-5·H₂O][OTf]₂ and [Ge[15]crown-5·NH₃][OTf]₂, respectively.^[3] It was found that coordination to the Ge(II) centre rendered the OH and NH fragments more acidic. Currently, the deprotonated variants of these complexes are being pursued. In addition, the reactivity of the crowned Ge(II) centre with other simple molecules such as H₂S and PH₃ is also being studied. Our most recent results will be presented.

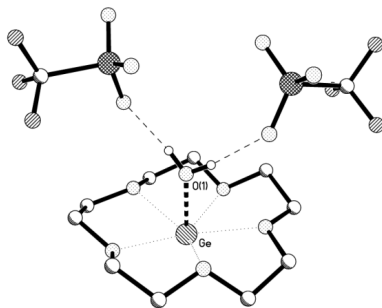


Figure 1: Ball and stick representation of [Ge[15]crown-5·H₂O][OTf]₂.

References:

- [1] Rugar, P.A., Bandyopadhyay, R., Cooper, B.F.T., Stinchcombe, M.R., Ragonna, P.J., Macdonald, C.L.B., Baines, K.M. *Angew. Chem. Int. Ed.* **2009**, *48*, 5155-5158.
- [2] F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster, W. J. Zhang. *Angew. Chem.* **2009**, *121*, 5254–5256.
- [3] Bandyopadhyay, R., Nguyen, J.H., Swidan, A., Macdonald, C.L.B. *Angew. Chem. Int. Ed.* **2013**, *52*, 3469-3472.

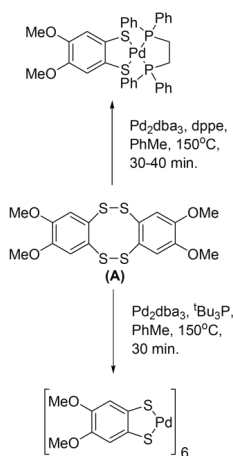
P64

Oxidative Addition of Tetrathiocenes: Synthesis, Structures and Properties of Group 10 Dithiolene Complexes and the Effect of the Phosphine Ligand

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Complexes of the redox-active dithiolene/dithiolate ligand system have continued to attract interest since initial investigations into their chemistry in the early 1960s.^[1] Recent studies in the Rawson group on the chemistry of tetrathiocenes^[2] has prompted the examination of the oxidative addition chemistry of such tetrathiocenes to low oxidation state transition metals. The oxidative addition of 4',5'-dimethoxybenzo-tetrathiocene (**A**) to zero-valent group 10 metals affords dithiolate complexes as crystalline solids with high isolated yields (>75%) in just two steps from commercially available starting materials. The synthesis, structure and properties of these complexes, and the effect of altering the phosphine ligand on the structure will be discussed.



Scheme 1. Two step synthesis of metal dithiolenes.

References:

- [1] Stiefel, E. I., Ed. *Dithiolene chemistry: Synthesis, properties, and applications*; Interscience: Hoboken, New Jersey, 2003.
- [2] Alberola, A.; Eisler, D.; Less, R. J.; Navarro-Moratalla, E.; Rawson, J. M. *Chem. Commun.* **2010**, 46, 6114-6116.

P65

Efforts Towards the Polymerization of Goedken's Macrocycle

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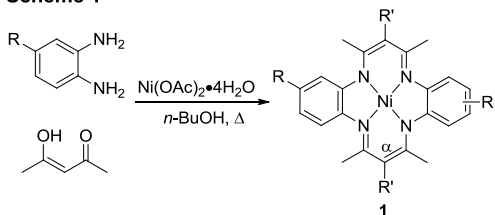
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The incorporation of transition metals into polymers has emerged as a promising strategy for the realization of materials that combine the processability of polymers and properties of transition metals (e.g., magnetism, redox activity, conductivity, catalytic properties). Although advances in the metal-containing polymer field have been truly impressive over the past two decades,¹ the development of polymerizable transition-metal complexes remains a challenge.

Goedken's macrocycle (**1**: R = H, R' = H)² initially synthesized by Jäger,³ is formed by the templating reaction shown in Scheme 1. Our initial efforts to introduce functional groups (**1**: R = Br, R' = H) at the *o*-diaminophenylene starting material did not afford a single isomer, but rather a mixture of isomers that proved difficult to separate by traditional

Scheme 1



means. Subsequent carbon-carbon cross coupling reactions of the brominated complexes also proved challenging. However, functionalization of the α -position (R') of Goedken's macrocycle through reactions with acid chlorides yielded a range of isolable complexes in high yield. This presentation will focus on recent progress towards styrene- and 4-bromophenyl-substituted analogues of Goedken's complex and their subsequent polymerization chemistry.

References:

- (1) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176.
- (2) Goedken, V. L.; Weiss, M. C.; Place, D.; Dabrowiak, J. *Inorg. Synth.* **1980**, *20*, 115.
- (3) Jäger, E. G. Z. *Anorg. Allg. Chem.* **1969**, *364*, 177.

P66

Phosphorous as a Scaffold for Transition Metals: Synthesis, Characterization, and Reactivity of Organometallic Phosphonium Salts

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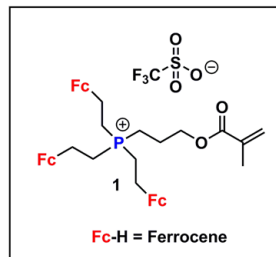
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Metal-containing polymers are a class of macromolecules that possess interesting properties such as semiconductivity, magnetism, redox activity, and preceramic characteristics due to the incorporation of transition metals into processable polymer scaffolds.¹ Although several classes of metal-containing polymers exist, there remains a need for new synthetic strategies towards the realization of metallopolymers with well-defined properties. Stable quaternary phosphonium salts have proven to be powerful tools in the generation of tunable polymers due to their versatility and stability.² However, to the best of our knowledge, these salts have not previously been employed in the synthesis of metal-containing monomers. Our efforts in this area are focused on the utilization of stable quaternary phosphonium salts as scaffolds for transition metals. The synthesis, characterization, and reactivity of polymerizable phosphonium salt **1** will be presented.



References:

- [1] Whittell, G. R.; Hager, M. D.; Schubert U. S.; Manners, I. *Nature Materials* **2011**, *10*, 176-188.
 [2] Guterman, R.; Hesari, M; Ragogna, P. J.; Workentin, M. S. *Langmuir* **2013**, *29*, 6460–6466.

P67

Raman Study of Guest-Host Interactions of Halocarbons in Metal Organic Frameworks

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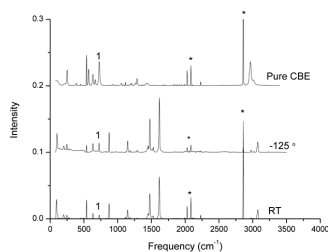
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Metal Organic Frameworks (MOFs) are an emerging class of microporous materials. While they contain multiple uses such as adsorption, storage, sensors, drug delivery, and the most prominent is that of adsorption¹. Halocarbons are used in a wide variety of applications such as pesticides, solvents, adhesives² and do not degrade naturally and incineration can cause the release of strong acids and toxins. Understanding the guest-host interactions between a framework and a halocarbon can further knowledge on MOFs adsorption properties.

Using Raman spectroscopy to study two different halocarbons (Dichloroethane and 1-bromo,2-chloroethane) in different MOFs such as MIL-53, MIL-68, MIL-53NH₂, the percentage of the population of each conformer in the different systems is determined to study in interactions between the guest molecule and the framework. Variable temperature was employed to determine the enthalpy of conformation change in each system. As well as studying the change in frequency of the vibrational modes and the FWHM can provide further insight into sorbent-sorbate interactions.

References:

- 1 Hiroyasu Furukawa, Kyle E. Cordova, Michael O'Keeffe, and Omar M. Yaghi. " The Chemistry and Applications of Metal-Organic Frameworks" *Science* 2013 (6149), 341
- 2 Gordon W. Gribble "The diversity of naturally occurring organobromine compounds", *Chemical Society Reviews* 1999 (5) 335



Raman spectra of 1-bromo,2-chloroethane as a pure liquid on top and loaded into MIL-53 at room temperature and -125 degrees.

* peaks due to glass, 1 Halocarbon stretches

P68

Homo- and diblock copolymers derived from a mixed sandwich cobaltocene: Overcoming a tight coil to give a real “Co” polymer.

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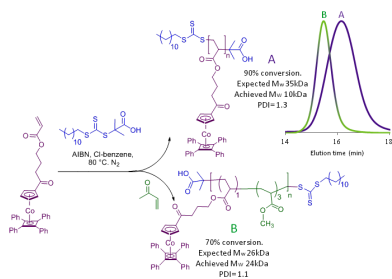
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Metal containing polymers are of interest because of the physical and chemical properties that arise from the presence of metal centers. Synthesis of well-defined metal containing block copolymers presents additional features as a result of their ability to undergo self-assembly.¹

We have previously reported the synthesis of side chain functionalized cobalt containing metallopolymers via free radical polymerization. The cobalt center is incorporated into the monomer as η^5 -cyclopentadienyl-cobalt- η^4 -cyclobutadiene (CpCoCb) units.²

In our group we are interested in the synthesis of controlled homo and block co-polymers containing CpCoCb units via a controlled polymerization method; reversible addition fragmentation transfer (RAFT). The effects of various factors in RAFT polymerization of CpCoCb monomer will be presented. Under different conditions applied for the polymerization, we learned as the polymer chain grows to an oligomeric stage, it takes on tight coil morphology, which hinders the approach of further sterically demanding monomer to increase the polymer chain length, resulting in premature termination/chain transfer reactions. To address this problem a small monomer (methyl acrylate) was copolymerized along with the bulky monomer to act as a spacer, providing the necessary space for the approach of another Co-containing monomer. This condition results in a drastic improvement in the polydispersity and the molecular weight of the end material.



Scheme. RAFT Polymerization of CpCoCb containing monomer under optimized condition (top) and the same reaction in the presence of MA as a spacer (bottom).

References:

- (a) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I., *Nat. Mater.* **2011**, *10*, 176-188; (b) Whittell, G. R.; Manners, I., *Adv. Mater.* **2007**, *19*, 3439-3468.
- Chadha, P.; Ragogna, P. J., *Chem. Commun. (Cambridge, U. K.)* **2011**, *47*, 5301-5303.

P69

Running the Gauntlet: Interactions of Organometalldrugs with Metallothionein

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Organometallic drugs are widely used methods of treatment against cancer and other diseases. However, drug resistance is of an equally important concern as the human body is quite adept at storing and detoxifying metals. Metallothioneins (MT) are a ubiquitous class of cysteine-rich proteins, which in humans primarily stores Zn^{2+} and detoxifies Cd^{2+} , but are also known to bind a wide variety of other metals.^[1] Because of metallothioneins' ability to casually scavenge metals, it may affect the required dosage of such metalldrugs, or even inactivate the complex entirely. This paper aims to summarize the known interactions of metals with metallothioneins from a pharmaceutical standpoint, specifically looking at Ru(II), Rh(II), Pt(II), As(III), Bi(III), Au(I) and Ag(I).

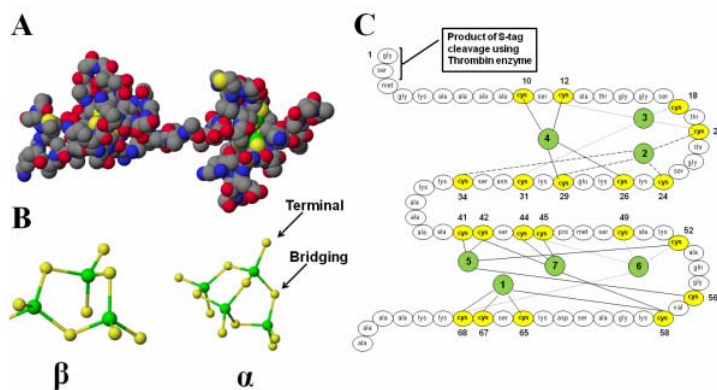


Figure 1-1. Molecular model structure of Cd7-βα-rhMT. (A) Space filling structure of cadmium metalated recombinant human MT-1a (Cd7-βα-rhMT 1a). Figure 1-1. Molecular model structure of Cd7-βα-rhMT. (B) Cadmium-cysteiny-thiolate connexions presented as a ball-and-stick model.(C) Connectivity diagram of human metallothionein 1a.

References:

[1] *Metallothioneins*, M.J. Stillman. *Coordin Chem Rev*, 1995.

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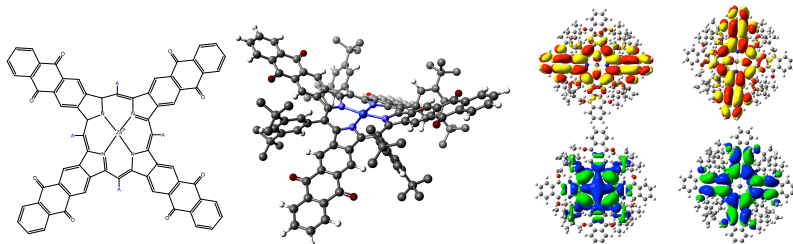
Effects of peripheral substituents on the electronic structure of Zn-anthraquinonoporphyrins

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Porphyrins are a diverse group bioinorganic molecules with a complex cyclic structure composed of four pyrrole rings. They have many unique applications in medicine and energy conversion such as photodynamic



therapies and in solar cells[1]. Inclusion of specific functional groups in porphyrins can add new properties. The effect of peripheral substituents on the electronic structure of Zn-anthraquinonoporphyrins was investigated using UV-visible absorption spectroscopy, magnetic circular dichroism (MCD) spectroscopy, and computational modeling methods. Results showed that introduction of the sequential anthraquinone functional groups together with the meso-phenyl groups distorted the symmetry resulting in significant ruffling of the porphyrin core. This resulted in red-shifting of the porphyrin absorption bands and intensifying of the Q-band. These properties, particularly shifting the Q band into the near IR, are essential in developing and extending photodynamic therapies since the closer to the IR region a porphyrin absorbs, the farther into the skin it can penetrate. As a result it becomes a more efficient photosensitizer for highly reactive singlet O_2^* production. The MO calculations confirm that even with the extensive delocalization afforded by the anthraquinones - the HOMO and LUMO MOs clearly show the dominance of the ± 4 and ± 5 units of angular momentum associated with the 18 π electron system.

We thank professor B. Kräutler for provision of the porphyrins for this study.

References

[1] S. Banala, T. Rühl, K. Wurst, B. Kräutler, *Angew. Chem. Int. Ed.* 2009, 48, 599.

P71

Guest Dynamics in Metal-Organic Framework Studied by ^2H and ^{13}C Solid-State NMR

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Metal-Organic Frameworks (MOFs), a class of porous organic-inorganic hybrid materials, have attracted great attention because of their structural diversity and potential applications in gas storage, separation, sensor, catalysis, drug delivery etc.^[1,2] Investigation of this potential material by solid-state NMR provides detailed information about the guest dynamics as well as host-guest interaction.

Here we present the solid-state NMR study of guest dynamics in two different MOFs, $\alpha\text{-Mg}_3(\text{HCOO})_6$ and Ni-MOF-74.^[3,4] Variable temperature ^2H NMR spectroscopy is employed to study the dynamics of small organic molecules (e.g., deuterated acetone, dimethylformamide, pyridine, benzene, acetonitrile etc.) in $\alpha\text{-Mg}_3(\text{HCOO})_6$ MOF and detailed motional information is obtained from its characteristics line shape analysis. ^{13}C NMR is also performed to study the host-guest interaction of CO_2 in Ni-MOF-74, even though the presence of paramagnetic metal sites in this MOF makes the NMR characterization complicated due to large paramagnetic shift and line broadening effect. Variable temperature ^{13}C wide-line NMR spectra were recorded to follow the adsorption process, dynamics of the adsorbed molecules and their interaction with the host framework.

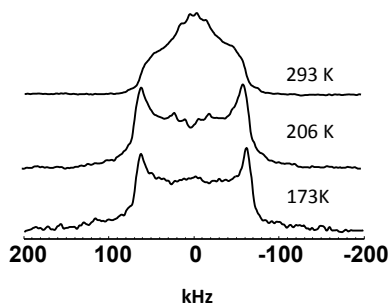


Figure. Experimental ^2H NMR lineshape of pyridine- (d_5) confined into $\alpha\text{-Mg}_3(\text{HCOO})_6$ MOF, recorded at different temperature.

References:

- [1] Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem. Int. Ed.*, **2004**, 43, 2334–2375.
- [2] Kuppler, R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J.-R.; Makal, et al. *Coord. Chem. Rev.* **2009**, 253, 3042–3066.
- [3] Rood, J. A.; Noll, B. C.; Henderson, K. W. *Inorg. Chem.*, **2006**, 45, 5521–5528.
- [4] Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvag, H. *Chem. Commun.* **2006**, 959–961.

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Investigation of structural stability of MOF α -Mg₃(HCOO)₆ by Raman and FTIR Spectroscopy under High External PressuresHaiyan Mao^{1,2}, Jun Xu¹, Yue Hu¹ Yining Huang^{*1} and Yang Song^{*1}¹Western University, 1151 Richmond Street, London, Ontario, N6A 5B7, Canada²Nanjing Forestry University, 159 Longpan Road, 210037, Nanjing, ChinaE-mail of presenting author: hmao4@uwo.caE-mail of corresponding author: yhuang@uwo.ca yang.song@uwo.ca

MOFs (Metal-organic frameworks) are a kind of new hybrid porous materials, consisting of inorganic connector and organic linkers that have great potential in applications such as separation, storage, catalysis and controlled drug delivery. In order to investigate the stability of the MOF framework for applications in gas storage, it is important to employ high pressure on the framework to follow the structural transformation.

In the present work, *in situ* high-pressure infrared (IR) and Raman spectroscopy were used for the first time to study the stability of the α -Mg₃(HCOO)₆ framework. The effect of pressure on the framework by IR and Raman was followed upon compression to 12.55 and 3.83 GPa respectively. It is observed that most of the IR absorption and Raman bands became significantly broadened, split and merged with increasing pressure. Interestingly, the IR spectra showed that the framework transformation is completely reversible upon decompression to ambient pressure while the Raman spectra indicated different behavior. To further confirm the stability of the framework, DMF loaded α -Mg₃(HCOO)₆ was also studied. The Raman and IR spectra showed that all the bands are fully recovered, elucidating the activated framework is modified or distorted due to high pressure, instead of decomposition.

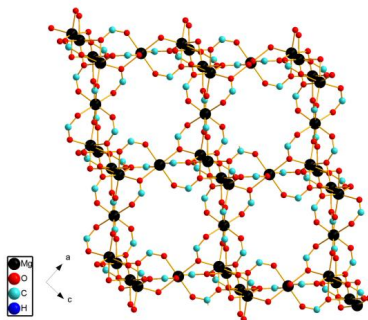


Figure. The framework of α -Mg₃(HCOO)₆ (H is omitted for clarity).

References:

M. Gimeno-Fabra, Munn A.S., Stevens L.A., Drage T.C., Grant D. M., Kashtiban R.J., Sloan J., Lester E. and Walton R.I., *Chemical Communications*, 2012,112, 673– 1268.

P73

MRI PARACEST agents that improve amide-based CEST measurements by eliminating inner sphere water T_2 exchange

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Magnetic Resonance Imaging (MRI) is a tool used in diagnostic medicine for viewing anatomical images, based on the detection of protons in water and fat which are predominant within the body.^[1] Contrast agents such as those containing Gd^{3+} , aid in the acquisition of these images by shortening the T_1 relaxation times of water protons near to the metal center.^[1] While clinically available T_1 agents have been shown to generate an increase in contrast during imaging, they are typically insensitive to environmental conditions such as pH and temperature, which are known to be altered in cancerous tissues.^[2]

A new technique termed Paramagnetic Chemical Exchange Saturation Transfer (PARACEST) has been developed to address these issues. PARACEST agents operate by reducing the bulk water proton signal through a chemical exchange site on an agent. Common sites of exchange are $-NH$, $-OH$ or a bound water molecule.^[1, 2] In addition to being more sensitive to physiological conditions, PARACEST agents allow for the contrast effect to be turned on and off at will.^[2] A series of Dy^{3+} and Tm^{3+} DOTAM tetra-*p*-substituted aniline complexes (*p*-OMe, *p*-Me, *p*-H, *p*-Cl and *p*-NO₂) has been synthesized (Figure 1) and their PARACEST and relaxation properties evaluated. A crystal structure of Tm^{3+} -*p*-OMe agent indicates a TSAP geometry with no bound water to the metal (TSAP). Due to the lack of an inner sphere water, the agents are able to provide a considerable CEST effect with little competition due to T_1 and T_2 relaxation processes. This in turn decreases signal loss due to relaxation during imaging.

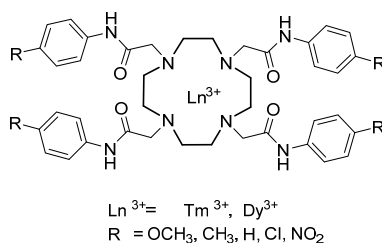


Figure 1. Dy^{3+} and Tm^{3+} DOTAM tetra-*p*-substituted aniline PARACEST agents synthesized for this study.

References:

[1] Woods, M., Woessner, D. E. and Sherry, A. D. *Chem. Soc. Rev.* **2006**, 35, 500-511

[2] Viswanathan, S., Kovacs, Z., Green, K. N., Ratnakar, S. J. and Sherry, A. D. *Chem. Rev.* **2010**, 110, 2960-3018

P74

Searching for the loose end: Proteolysis of Metallothionein

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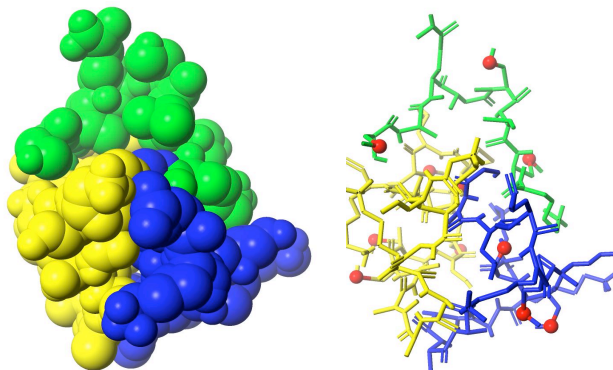
Metallothionein (MT) is a metal binding protein consisting of 60 amino acid residues, 20 of which are cysteine residues responsible for metal binding. MT folds in the presence of divalent metal ions to form two distinct metal-binding domains connected by a short linker sequence: the 9-cysteine β and the 11-cysteine α domains. The metallated structure of metallothionein is well defined and based on the effects of metal coordination. However, what yet remains unanswered is the fundamental question of metal-binding: What is the order of the metals during metallation?

Of the 20 cysteines, which one is the most exposed and thus binds to a metal first? In this study, proteolysis and electrospray ionization mass spectrometry (ESI-MS) methods were used to isolate small peptide regions of MT in the presence of a cysteine modifier, p-benzoquinone, to determine the most exposed cysteine and thus which cysteine binds p-benzoquinone first.

Figure: 3-D Structure of Apo Alpha Metallothionein.

Left: Space-filling model showing the three main Tryptic Peptides (shown in blue, yellow and green).

Right: Wireframe model with cysteines highlighted in red.



Acknowledgements

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References

- [1] Irvine, G.I. et al. *Biochem. Biophys. Res. Commun.* **2013** 433:477-483.
 [2] Sutherland, D.E.K. et al. *Biochemistry.* **2012** 51:6690-6700.

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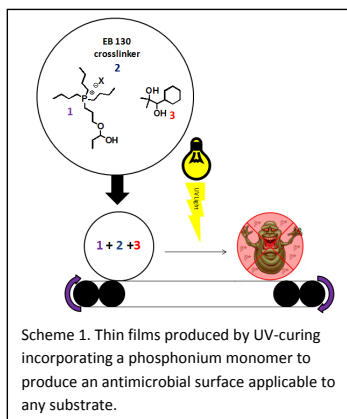
Antimicrobial UV cured surfaces

Tyler J. Cuthbert¹, Ryan Guterman¹, Solmaz Karamdoust¹, Elizabeth R. Gillies*^{1,2}, and Paul J. Ragogna*¹

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Herein we describe the incorporation of phosphonium salts into UV-cured thin crosslinked polymer network films. This method is rapid and simple, leading to films with phosphonium cations dispersed throughout the surface. Antimicrobial activity towards *Escherichia coli* and *Staphylococcus aureus* was measured for films with varying phosphonium content and it was possible to produce UV-cured thin films >99% lethality.¹ In comparison with the conventional antimicrobial nitrogen-based salts, phosphonium-based salts have been rarely used despite the increase in chemical and thermal stability, translating to enhanced material properties,²⁻⁵ as well as increased antimicrobial activity over ammonium analogues.⁶ Possible applications include prevention of persistent bacterial colonization that is problematic to infections in hospitals with regards to biomedical devices/implants, prevention of biofilm formation in water distribution systems⁷, or applications to common bacteria contaminated surfaces such as doors/knobs, restrooms, kitchens/appliances, or surfaces in public areas.



References:

1. J. J. Tindale and P. J. Ragogna, "Phosphonium Ionic Liquids and Coatings" W.O. 2009/094768 A1.
2. E.R. Kenawy and Y. Mahmoud, *Macromol. Biosci.*, **2003**, 3, 107–116.
3. E.R. Kenawy, F. Abdel-Hay, A. El-Shanshoury, M.H. El-Newehy, *Journal of Polymer Science Part a-Polymer Chemistry*, **2002**, 40(14), 2384–2393.
4. E.R. Kenawy, F. I. Abdel-Hay, A.A. El-Magd, Y. Mahmoud, *Reactive and Functional Polymers* **2006**, 66(4), 419–429
5. P. Wassercheid, *Ionic Liquids in Synthesis*, 2nd ed.; WILEY: **2008**.
6. Kanazawa, A., Ikeda, T., Endo, T., *Antimicrobial Agents and Chemotherapy*. **1994**, 38(5), 945-952.
7. O. Aviam, G. Bar-Nes, Y. Zeiri, A. Sivan, *App. Envir. Micro.Bio.* **2004**, 70(10), 6031-6063.

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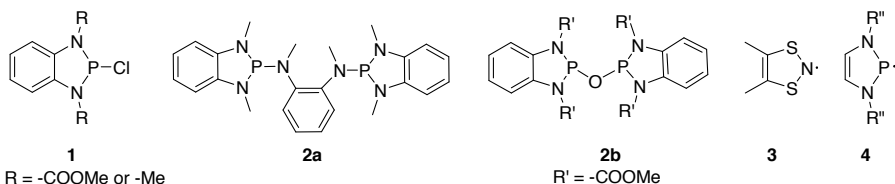
Studies on Benzodiazaphospholes: Towards Diazaphospholyl Radicals

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The exploration of stable radicals has attracted significant attention in the last few decades as building blocks for magnetic switches, conductors, magnets, OFETs (organic field effect transistors) and PV (photovoltaic) materials.^{1,2} Dithiazolyl (DTA) radicals (**3**) have been discovered to show long range magnetic order,³ and spin-transition behaviour.⁴ We have been intrigued to generate new analogues of diazaphospholyl radicals (**4**)⁵ which are isolobal with the well known DTA family. The grafting of an aromatic ring onto the C₂N₂P framework is expected to stabilize the radicals through extensive π -delocalization whilst the steric effects of the auxiliary groups (R) at N can be modulated to inhibit dimerization at P. Here we report recent investigations into benzodiazaphospholium chloride derivatives (**1**) and their reductive products (**2a, 2b**) obtained from their reactions with elemental sodium or magnesium en route to diazaphospholyl radicals.



References:

- [1] Rawson, J. M.; Alberola, A.; Whalley, A. *J. Mater. Chem.*, 2006, **16**, 2560.
 [2] "Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds", Hicks Ed, R. G. Wiley, 2010.
 [3] (a) Fujita, W.; Awaga, K.; Nakazawa, Y.; Saito, K.; Sorai, M. *Chem. Phys. Lett.*, 2002, **352**, 348; (b) Fujita, W.; Awaga, K. *Chem. Phys. Lett.*, 2002, **357**, 385; (c) Fujita, W.; Awaga, K. *Chem. Phys. Lett.*, 2004, **388**, 186.
 [4] see Rawson, J. M.; Hayward, J. J Chapter 8 in "Spin Crossover Materials: Properties and Applications" (M. Halcrow Ed.), J. Wiley, 2013.
 [5] Edge, R.; Less, R. J.; McInnes, E. J. L.; Muther, K.; Naseri, V.; Rawson, J. M.; Wright, D. S. *Chemical Communications* 2009, **0**, 1691.

P77

Selective Catalytic C=O Hydrogenation of Unsaturated Aldehydes, Ketones, and Esters

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New osmium complexes from our laboratory are today's most successful general selective C=O hydrogenation catalysts facilitating a green reduction process^[1-4] affording unsaturated alcohols from the corresponding unsaturated aldehydes, ketones, and esters under H₂ at 25 – 100 °C, while using ≤ 0.05 mol% [Os].

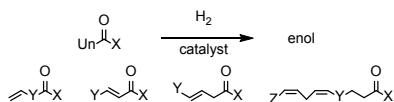


Figure. Catalytic hydrogenation and challenging substrates (Un = olefin-containing group; X = H, R, OR; Y, Z, R = organic fragment or group).

References:

- [1] D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem. Int. Ed.*, 2013, 52, 2538.
- [2] D. Spasyuk, D. G. Gusev, *Organometallics*, 2012, 31, 5239.
- [3] D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem. Int. Ed.*, 2012, 51, 2772.
- [4] D. G. Goussev, D. Spasyuk, *PCT Patent Application WO 2013/023307 A1*.

P78

Preparation and Functionalization of Monodisperse Iron Oxide/Silica Core-Shell Magnetic Nanoparticles for Flow Purification

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We fabricated novel core-shell nanoparticles having a magnetic iron oxide core encapsulated in a silica shell that has been chemically modified to bind a specific functional group for subsequent use in a magnetically steered flow purification apparatus (Figure 1). Monodisperse hydrophobic iron oxide magnetic nanoparticles (MNPs) were obtained using a modified thermal decomposition method^[1]. The resulting MNPs were stabilized and encapsulated with a layer of silica in reverse microemulsion micelles to obtain single-cored nanostructures^[2]. Cationic surfaces were created by functionalization with 3-aminopropyltriethoxysilane (APTES), followed by protonation or methylation. These protonated magnetic nanoparticles allow for the reversible complexation of anionic targets by electrostatic adsorption. The target/MNP complexes can then be magnetically steered through a capillary purification flow system, and the target subsequently desorbed at low pH, realizing a cyclic isolation and purification apparatus for flow synthesis.

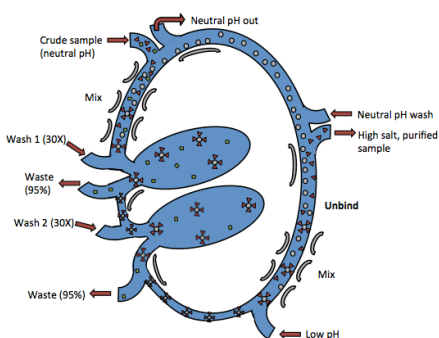


Figure 1. Schematic of closed-cycled and magnetically steered flow purification system

References:

- [1] J. Park, K. J. An, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang, and T. Hyeon. *Nat. mater.*, **2004**, 3: 891-895.
[2] H.L. Ding, Y.X. Zhang, S. Wang, J. M. Xu, S. C. Xu, and G. H. Li. *Chem. Mater.*, **2012**, 24, 4572-4580.

P79

Synthesis, Characterization and Reactivity Study of Bis(imino)-*N*-Heterocyclic Carbene Chromium(III), Iron(II) and Cobalt(II) Complexes

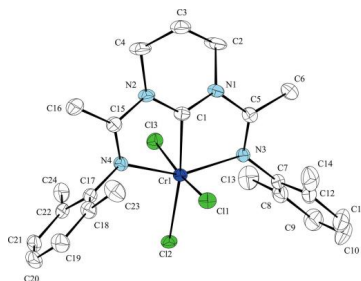
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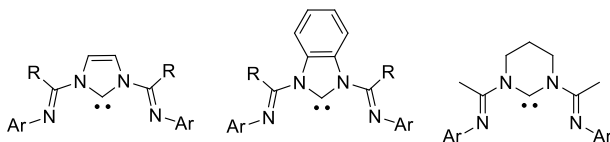
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Bis(arylimino)pyridine iron and cobalt catalysts exhibit exceptional catalytic activities for ethylene oligomerization and polymerization. However, their lifetime at elevated temperatures remains undesirable for commercial applications. Moreover, the ability of these complexes to homo- and copolymerize α -olefins with ethylene is very poor. We thus became interested in designing three new classes of the bis(imino) *N*-heterocyclic carbene (NHC) ligands that would address these shortcomings. This choice was in part driven by the enhanced thermal stability observed in catalysts containing NHCs. As determined by X-ray crystallography, the bis(imino)imidazol-2-ylidene ligand coordinated to Fe(II), Co(II) and Cr(III) in a bidentate mode through the carbene center and one iminic nitrogen atom. Similarly, a bidentate coordination fashion is predicted in the benzimidazol-2-ylidene Fe(II), Co(II) and Cr(III) complexes and the pyrimidin-2-ylidene Fe(II) and Co(II) complexes. The solid-state molecular structure of the pyrimidin-2-ylidene Cr(III) complex confirmed a tridentate coordination mode for the ligand. The catalytic activities of the bis(imino) NHC Cr, Fe and Co complexes toward ethylene polymerization were evaluated. The bis(imino) NHC Cr(III) complexes gave moderated activity up to 34 kg PE mol⁻¹ Cr h⁻¹.



ORTEP of pyrimidin-2-ylidene Cr(III) complex

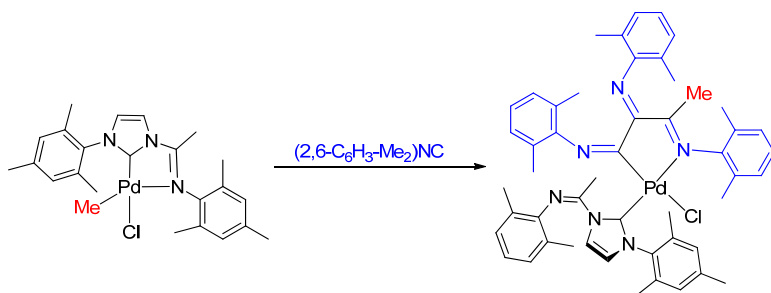


Classes of *N*-heterocyclic Carbenes Evaluated

P80

Reactivity Studies of Imino-*N*-Heterocyclic Carbene Complexes of Nickel and PalladiumAnna C. Badaj¹ and Gino G. Lavoie*¹¹Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, M3J 1P3E-mail of presenting author: anabad@yorku.caE-mail of corresponding author: glavoie@yorku.ca

The use of *N*-heterocyclic carbenes has received a great deal of attention in the field of transition metal coordination since their isolation by Arduengo.^[1] The strong σ -donating ability of carbene ligands has resulted in the formation of robust complexes exhibiting catalytic activities for a wide range of chemical reactions. Our group is interested in the coordination chemistry of bidentate ligands based on imino-*N*-heterocyclic carbenes as analogues to the α -diimines.^[2] We herein report the coordination of the imino-*N*-heterocyclic carbenes to nickel via copper(I) transmetalation as well as the various routes taken to generate both the neutral and cationic palladium complexes. Although the nickel complexes were found to be inactive for ethylene polymerization,^[3] modifications made to the substituent at the iminic carbon profoundly affects the thermal stability of the neutral palladium complexes. Reactivity studies done with the palladium methyl analogues reveal they react with CO and isocyanides to form various coordination and insertion products.^[4]



References:

- [1] Arduengo, A. J.; Harlow, R. L.; Kline, M. *Journal of the American Chemical Society* **1991**, *113*, 361.
 [2] Johnson, L. K.; Killian, C. M.; Brookhart, M. *Journal of the American Chemical Society* **1995**, *117*, 6414.
 [3] Badaj, A. C.; Lavoie, G. G. *Organometallics* **2012**, *31*, 1103.
 [4] Badaj, A. C.; Lavoie, G. G. *Organometallics* **2013**, *32*, 4577.

P81

Coordination and Reactivity Study of Functionalized Bidentate Monoanionic Imidazol-2-Imine Ligands to Group 4 and 10 Metals

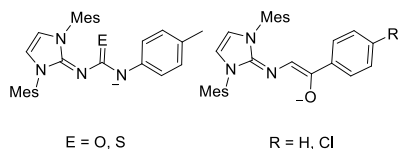
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The synthesis and isolation of *N*-imidazol-2-ylidene-*N'*-ptolylureate and thioureate proligand as well as imidazol-2-imine ethenolate ligand is described. These bidentate monoanionic ligands showed a variety of binding modes to group 4 and 10 metals as confirmed by x-ray crystallographic studies. All complexes of the corresponding ligands were tested for ethylene polymerization at ambient conditions using methylaluminoxane as a cocatalyst with activities as high as 170 kg PE mol⁻¹ h⁻¹.



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Electrochemical and Spectroelectrochemical Studies of the Reduction of Oxygen on Cobalt Phthalocyanines

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The purpose of this work is to investigate the oxygen reduction at cobalt (II) phthalocyanine (CoPc) modified gold electrodes in acidic aqueous solutions with the aim of probing the feasibility of using this metallic ligand as a as a low price, model catalyst for the reduction of oxygen. In order to study the electrochemical activity of CoPc monolayers, the formation of such layers on gold electrodes, as well as the effect of introducing oxygen on them, was probed by cyclic voltammetry, *in-situ* electrochemical scanning tunneling microscopy (*in-situ* EC-STM), as well as *in-situ* Surface Enhanced Raman Scattering (*in-situ*-SERS) approaches.

The *in-situ* EC-STM and *in-situ*-SERS techniques, as an electrochemical, and spectroelectrochemical methods were also employed to track the electrochemical reduction of oxygen at the CoPc modified surfaces. We then correlated the CoPc molecules electrocatalytic properties to their structure, since they were well-oriented on gold (111) single crystals substrates. Changes in the STM features of the adsorbed molecules were observed under oxygen, which were attributed to structural as well as electronic transformations in the interacting species, based on the proposed mechanism for the reduction of oxygen at the CoPc modified electrodes in acidic media^[1, 2].

Figure 1 indicates The Raman spectra for CoPc/roughened gold electrode at -200 mV_{SCE} DC bias in the absence and presence of oxygen. According to the results of the three applied methods, the adsorption of CoPc monolayers on the surface of gold electrodes was confirmed. In addition, our measurements confirmed the proposed mechanism for the reduction of oxygen at CoPc modified electrodes in acidic media.

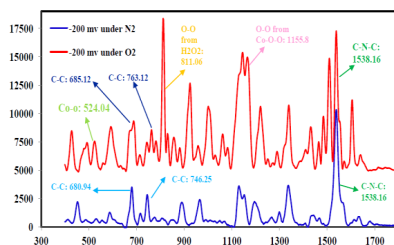


Figure 1: *in-situ* Surface Enhanced Raman Scattering spectra for CoPc modified roughened gold electrode at surface potential: -200 mV_{SCE} under argon (blue spectrum), and oxygen (red spectrum).

References:

[1] Beck, J. *Appl. Electrochem.* 1977, 7, 239.

[2] Tse, Y.-H.; Janda, P.; Lam, H.; Zhang, J.; Pietro, W. J.; Lever, A.B.P. *J. Porphyrins. Phthalocyanines.* 1997, 1, 3.

P83

Supported Transition Metal Catalysts for Use in the MACOS System

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The synthesis of Pd-doped silica microspheres with >1 μm diameter through a one-pot sol-gel process and their use as a supported catalyst in a microwave-assisted continuous flow organic synthesis (MACOS) system will be discussed. Thermal treatment of the calcinated microspheres under H_2 gas affords metallic Pd nanoparticles, confirmed by powder X-ray diffraction spectroscopy. Transmission electron microscopy shows that the Pd nanoparticles are spread throughout the entire structure of the microspheres and have a diameter of <10 nm. The Pd-doped microspheres were formed with up to a 4.33 wt.% of Pd found through elemental analysis. The Pd-doped silica spheres are found to not heat significantly under microwave irradiation, allowing for use in microwave-assisted reactions using metal catalysts without causing out of control heating, as has been observed with the use of metal films in microwave-irradiated systems.^[1]

Dithiocarbamate transition metal complexes are examined for use as metallosurfactants for the selective loading of metal nanoparticles onto the surfaces of templated substrates. A variety of transition metal dithiocarbamate complexes are synthesized from primary and secondary amines and tested in the formation of metal-doped silica microspheres. The N-(6-hexanoic acid) dithiocarbamate metal complex was observed to give almost exclusive preferential loading of metal particles towards the surface of the microspheres (Figure 2) rather than an even distribution throughout the structure. Removal of the hydrophilic end group or use of shorter alkyl chains was not observed to give appreciable preference towards loading.

References:

[1] a) Shore, G.; Morin, S.; Organ, M. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 2761-2766. b) Shore, G.; Yoo, W.-J.; Li, C.-J.; Organ, M. G. *Chem. Eur. J.* **2010**, *16*, 126-133.

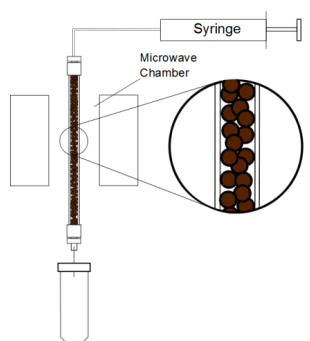


Figure 1: Schematic of the supported catalyst microspheres when used in the MACOS system

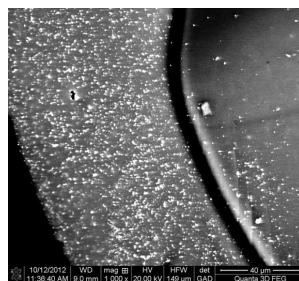


Figure 2. Scanning electron microscope image of a cross-section of a Pd-doped silica macrosphere using a dithiocarbamate metallosurfactant for controlled placement of metal particles

