



CONFERENCE PROGRAM

November 9-11, 2018 Waterloo, Ontario



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Schedule of Events

IDW2018 kicks off with a casual social event at Federation Hall on Friday evening, which is located on the University of Waterloo campus. The poster session and conference banquet will also be hosted at Federation Hall - attendees are welcome to hang their posters on Friday night.

Light breakfasts on both Saturday and Sunday morning and a light lunch on Saturday are all included in registration. These will will be served in room 1301 (the "fishbowl") in the University of Waterloo's Davis Center.

The conference poster session will be held at Federation Hall on Saturday evening, which will be followed by the Oktoberfest themed conference banquet.

	Time	Event	Event
Friday	19:00 - 24:00	Conference Mixer	FH
Saturday	8:00	registration and light breakfast	DC1301
	9:00	Keynote Lecture: James Mayer	DC1350
	10:00	coffee break	DC1301
	10:20	oral sessions	DC1350/1351
	12:00	on-site lunch	DC1301
	13:00	oral sessions	DC1350/1351
	14:40	coffee break	DC1301
	15:00	oral sessions	DC1350/1351
	16:40	transit time	
	17:00	poster session	FH
	19:00	banquet	FH
Sunday	8:30	light breakfast	DC1301
	9:00	oral sessions	DC1350/1351
	10:40	coffee break	DC1301
	11:00	Two Minutes of Silence: Remembrance Day	DC1350
	11:10	Keynote Lecture: Laurel Schafer	DC1350
	DC = Davis Center	FH = Federation Hall	

Plenary Lecture

Proton-Coupled Electron Transfer in oxygen electrocatalysis and nanocrystal reactivity

James M. Mayer

Department of Chemistry, Yale University james.mayer@yale.edu

9:00 Saturday, DC1350

Chemical oxidation and reduction (redox) reactions are typically described as the transfer of electrons, but protons often play an equally important role. Such proton-coupled electron transfer (PCET) reactions are central to many chemical processes, from catalysis in fuel cells to the biological 'electron' transport chain that powers most cells. After an introduction to the fundamentals of PCET steps, this presentation will apply these fundamentals to electro-catalysis and to materials reactivity. We are examining the use of soluble iron porphyrin complexes as electrocatalysts for the oxygen reduction reaction, $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$. By examining different catalysts under different reaction conditions, we have developed a new analysis of the relationship between the catalytic turnover frequency and the electrocatalytic challenges will likely involve reactions at the surface of an electrode. We have thus begun to examine the PCET properties of materials, starting with ZnO, TiO₂, and CeO_{2-x} nanocrystals (NCs). Because these are colloidal, they can be studied by many of the same techniques used in molecular chemistry. The last section of the presentation will describe representative PCET reactivity, such as the transfer of e⁻ and H⁺ (H⁺) from reduced ZnO NCs to nitroxyl radicals (Figure, bottom). This reactivity prompts a new view of interfacial reactivity at the nanoscale.





Plenary Lecture

Using N,O to get to Yes. Catalytic Amination for Small Molecule and Polymer Synthesis

11:10 Sunday, DC1350

Laurel L. Schafer

Department of Chemistry, University of British Columbia schafer@chem.ubc.ca

N,O-Chelated complexes of early transition metals offer unique reactivity in atom economic hydrofunctionalization transformations, such as hydroamination and hydroaminoalkylation. The efficient synthesis of selectively substituted amines and N-heterocycles from broadly available alkyne or alkene starting materials offers new opportunities for assembling small molecules and amine containing polymers. Mechanistic insights have advanced N,O-chelated catalyst development to realize improved substrate scope, enhanced regioselectivity and greater TONs and TOFs.¹ These catalyst efficiencies have been leveraged in the synthesis of amine containing polymers to access new classes of conjugated materials by hydroamination catalysis,² and pendant amine containing polymers by hydroaminoalkylation.³ These new polymers display tunable properties that can be attributed to the incorporation of unprotected amine functionality into these novel materials.



1 R. C. DiPucchio, S.-C. Rosca, L. L. Schafer, Angew. Chem., Int. Ed. 2018, 19, 3469.

2 H, Hao, K. A. Thompson, Z. M. Hudson, L. L. Schafer, Chem. Eur. J. 2018, 24, 5562.

3 D. J. Gilmour, T. Tomkovic, M. R. Perry, E. Hsiang, S. G. Hatzikiriakos, L. L. Schafer, Manuscript Submitted.

Symposium Schedule Titles and abstracts provided sequentially in next section

Saturday, November 10th

Time	Symposium 1 (DC1350)	Symposium 2 (DC1351)			
9:00	Keynote Lecture. James M. Mayer. (DC1350) Proton-Coupled Electron Transfer in oxygen electrocatalysis and nanocrystal reactivity				
10:00	Coffee Break (DC1301)				
10:20	S1. Rachel Meyer. University of Rochester	S21. Yi Liu. McGill University			
10:40	S2. Matthew V. Gradiski. University of Toronto	S22. Nadia Stephaniuk. University of Windsor			
11:00	S3. Mahmood A. Fard. Western University	S23. Haijun Li. Queen's University			
11:20	S4. Jacquelyn Egan. University of Ontario Institute of Technology	S24. Ilias Halimi. University of Ottawa			
11:40	S5. Levy Cao. University of Toronto	S25. Parisa Abbasi. Brock University			
12:00	Lunch Break (DC1301)				
13:00	S6. Brittney Petel. University of Rochester	S26. Lara Watanabe. University of Windsor			
13:20	S7. Fioralba Taullaj. University of Toronto	S27. Liu Leo Liu. University of Toronto			
13:40	S8. Nadia O. Laschuk. University of Ontario Institute of Technology	S28. Kyle Jackman. Western University			
14:00	S9. Jeffrey D. Sears. University of Rochester	S29. Zineb Ras Ali. Brock University			
14:20	S10. Natalie C. Korkola. University of Western Ontario	S30. Aathith Vasanthakumar. McMaster University			
14:40	Coffee Break (DC1301)				
15:00	S11. Sang gyu Seo. University of Toronto	S31. Riley Hooper. University of Western Ontario			
15:20	S12. Amelia Yuan. University of Western Ontario	S32. Aisha Kassymbek. Brock University			
15:40	S13. Alexander Whittingham. University of Waterloo	S33. Camilo J. Viasus. University of Ottawa			
16:00	S14. Jiliang Zhou. University of Toronto	S34. Ryan Andrews. University of Toronto			
16:20	S15. Nikita Panov. University of Ottawa	S35. Shan Jiang. Western University			
16:40	Transit time - walk to Federation Hall				
17:00	Poster Session - Federation Hall				

Sunday, November 11th

Time	Symposium 1 (DC1350)	Symposium 2 (DC1351)	
9:00	S16. Karlee L. Bamford. University of Toronto	S36. Qiuming Liang. University of Toronto	
9:20	S17. Dominique Leckie. University of Windsor	S37. Jeffrey Price. McMaster University	
9:40	S18. Anton Dmitrienko. Brock University	S38. Adyn Melenbacher. University of Western Ontario	
10:00	S19. Theresa Boddie. University of Rochester	S39. Christopher Major. University of Toronto	
10:20	S20. Matthew A. Wiebe. York University	S40. Paul A. Lummis. Queen's University.	
10:40	Coffee Break (DC1301)		
11:00	Two Minutes of Silence - Remembrance Day (DC1350)		
11:10	Keynote Lecture. Laurel Schafer. (DC1350) Using N,O to get to Yes. Catalytic Amination for Small Molecule and Polymer Synthesis		

Oral Presentations

(S1) From Lanterns to Rings: Effects of Group(XIII) Salts on Polyoxovanadate-Alkoxide Formation

Rachel L. Meyer, William W. Brennessel, Ellen M. Matson*

University of Rochester

10:20 Saturday, DC1350

Polyoxometalate (POM) clusters are molecular metal-oxide assemblies with a variety of applications in materials, medicine, energy storage, and catalysis. Polyoxovanadates (POV) are an interesting class of POMs as the flexible geometry of vanadium ions allows for a wide-range of cluster morphologies with unique physiochemical properties. In this work, the gallium-functionalized Lindqvist cluster, $[(VO)_5O(OCH_3)_{12}GaCI]$, was synthesized as a first step in incorporating main-group elements into these clusters. Infrared and electronic absorption spectroscopies confirmed that the extensive electronic delocalization characteristic in these POV clusters was retained upon installation of the $3d^{10}$ Ga³⁺ ion. Attempts at incorporating other Group(XIII) cations, e.g. In^{3+} and AI^{3+} , into the POV framework were unsuccessful, thus further studies in developing a general synthetic method are needed.

(S2) Novel PNN' & P2NN' Ligands via Reductive Amination with Phosphine Aldehydes: Synthesis and Coordination Chemistry for Catalysis

Matthew V. Gradiski, Brian T. H. Tsui, Alan J. Lough, Robert H. Morris

University of Toronto

10:40 Saturday, DC1350

Novel PNN' & P2NN' ligands based on 2-aminopyridine (**APyPNN-R**) R = Ph, Cy, iBu, 8-aminoquinoline (**AQPNN-R**) R = Ph, Cy, iBu, iPr, and 2-picolylamine (**P2NN-R**) R = Ph, Cy, iBu have been synthesized via a one-pot single step reductive amination with tertiary phosphine acetaldehydes and sodium(triacetoxy)borohydride. We demonstrate the versatility of this reaction and its use to gain access to PN based ligands in minimal synthetic steps and purification. Their coordination chemistry with Mn(I), Fe(II), and group 9 metals give rise to mononuclear and bridged dinuclear complexes of varying coordination number. Additionally, AQPNN-Cy can be treated with *n*-BuLi to give the first structurally characterized square planar Co(II) amido complex. All metal complexes presented herein have been structurally characterized.



Figure 1. Select metal complexes synthesized and presented herein.

(S3) Oxidative Addition Reactions of Cycloneophylplatinum(II) Complexes Mahmood A. Farda, Richard J. Puddephatt

Western University

11:00 Saturday, DC1350

Selective activation and functionalization of the C-H bonds of alkanes and arenes is important to understand the likely steps in proposed catalytic cycles and to be able to predict the selectivity of C-H activation reactions. There has been intensive research into related nickel(II) and palladium(II) complexes, leading to advances in understanding selectivity in C-H bond activation and in electrophilic cleavage of the metal-carbon bonds of cycloneophyl complexes, but there has not been further research into the analogous platinum(II) complexes. In this regard we described a new approach to synthesis of cycloneophylplatinum(II) complexes, and studied the selectivity of metal-carbon bond cleavage through protonolysis, as well as oxidative addition reactions of these complexes via halogenation or/and using different oxidants.



(S4) The Functionalization of Magnetic Fe₃O₄@TiO₂ by 2,6-bis(2-thienyl)pyridine Molecular Motif for the Detection of Mercury (II)

Jacquelyn G. Egan, Sarah D. King, Reza A. M. Esfahani, Iraklii I. Ebralidze, Fedor Y. Naumkin, Olena V. Zenkina University of Ontario Institute of Technology

11:20 Saturday, DC1350

Magnetic magnetite nanoparticles (Fe₃O₄NP) were synthesized using solvothermal method, they were then coated with TiO₂ using a mixed solvent method to produce titanium dioxide coated magnetite nanoparticles (Fe₃O₄@TiO₂ NP). The nanoparticles were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). 2,6-di(thiophen-2-yl)-4,4'-bipyridine (L) was anchored into the surface of the coated magnetite nanoparticles (L-Fe₃O₄@TiO₂ NP) through a siloxane template layer and was fully characterized using, X-ray photoelectron spectroscopy (XPS) and florescence spectroscopy. L-Fe₃O₄@TiO₂ NP system show strong characteristic fluorescence signal at 413 nm in the absence of Hg₂⁺ however this signal was quenched when Hg₂⁺ was introduced. XPS and Density Functional Theory (DFT) results confirm effective mercury coordination to the L core. Currently, we explore utility of L-Fe₃O₄@TiO₂ NP for mercury uptake and/or "turn off" fluorescent sensing material.

(S5) N-Heterocyclic Carbene (NHC) stabilized Aluminium Compounds

Levy L. Cao, Erika Daley, Timothy C. Johnstone, Douglas W. Stephan*

University of Toronto

11:40 Saturday, DC1350

Aluminum hydrides play essential roles in modern organic, inorganic and materials chemistry. Since Arduengo's seminal work of the isolation of the first NHC-alane adducts,¹ numerous fundamentally intriguing NHC based Al species generated from the NHC-alane adduct have been reported.²⁻⁶ In this talk we will focus on i) the generation of NHC stabilized aluminum hydride cations³ and ii) the reversible Al-H activation with cyclic (amino)(alkyl) carbene and alane.⁸

1. A. J. Arduengo, H. V. R. Dias, J. C. Calabrese and F. Davidson, J. Am. Chem. Soc., 1992, 114, 9724-9725.

2. S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones and A. Stasch, Nat. Chem., 2010, 2, 865-869.

3. L. L. Cao, E. Daley, T. C. Johnstone and D. W. Stephan, Chem. Commun., 2016, 52, 5305-5307.

4. B. Li, S. Kundu, H. Zhu, H. Keil, R. Herbst-Irmer, D. Stalke, G. Frenking, D. M. Andrada and H. W. Roesky, *Chem. Commun.*, 2017, **53**, 2543-2546.

5. P. Bag, A. Porzelt, P. J. Altmann and S. Inoue, J Am Chem Soc, 2017, 139, 14384-14387.

6. C. Fliedel, G. Schnee, T. Avilés and S. Dagorne, Coord. Chem. Rev., 2014, 275, 63-86.

7. L. L. Cao, D. W. Stephan, Chem. Commun., 2018, 54, 8407-8410.

(S6) Polyoxovanadate Clusters as Homogenous Molecular Models for Reducible Metal Oxides

B. E. Petela, E. M. Matson

University of Rochester

13:00 Saturday, DC1350

Theoretical investigations on reducible metal oxides (RMO) have revealed that the generation of surface defects, such as oxygen-atom vacancies, are crucial for the high reactivity of these materials. Limited spectroscopic techniques for in situ analysis renders the identification of the reactivity of individual oxygen-atom vacancies on the surface of RMOs challenging. This research investigates the use of Lindqvist polyoxovanadate-alkoxide (POV-alkoxide) clusters ($[V_6O_7(OCH_3)_{12}]^{-1}$) as homogenous models for RMOs in heterogeneous catalysis. Herein, we present the generation of an oxygen-atom vacancy on the POV-alkoxide cluster via addition of reductant. The generation of the reduced cluster ($[V_6O_6(OCH_3)_{12}]^{-1}$) presents the opportunity to study the effects of vacancies on the electron delocalization of the cluster as well as reactivity with oxyanions and small gaseous molecules.



Figure 1. Modelling the structural and electronic consequence of oxygen vacancy formation on bulk materials using Lindqvist polyoxovanadate clusters.

(S7) The First Adamantyl Platinum Complexes

F. Taullaj, D. Armstrong, S. Datta, A. J. Lough, U. Fekl*

University of Toronto

13:20 Saturday, DC1350

Diamondoid molecules are an extremely interesting group of molecules as they offer many of the advantages of diamonds at a molecular scale, the most desirable of which being their chemical stability and structural rigidity. Interest in adamantane, the simplest diamondoid molecule, in the organometallic community stemmed from its resistance to β -elimination. It is this characteristic that led to the synthesis of homoleptic adamantyl titanium¹, chromium² and iron³ complexes. Despite the many desirable characteristics of diamondoid molecules in organometallic chemistry, progress in metal adamantyl chemistry was limited by the inherent difficulty of synthesis of adamantyl anions, and difficulty associated with characterization of adamantyl metal species. Here we present the use of our adamantyl anion equivalents⁴ in the synthesis and characterization of the first adamantyl platinum complexes. Further reactivity of which could lead to exciting new adamantyl-based catalysts and molecules.

- 1. Bergman, R. G. et al, JACS 1997, 119, 5269.
- 2. Bochmann, M.; Wilkinson, G.; Young, G. B. J. Chem. Soc., Dalton Trans. 1980, 10, 1879.
- 3. Fürstner, A. et al. Angew. Chem. Int. Ed. 2017, 10108.
- 4. Armstrong, D.; Taullaj, F.; Singh, K.; Mirabi, B.; Lough, A. J.; Fekl, U. Dalton Trans. 2017, 46, 6212.

(S8) Impact of Ligand Design on Monolayer Electrochromic Materials using Inorganic Nanoparticle Supports

Nadia O. Laschuk, Iraklii I. Ebralidze, E. Bradley Easton, Olena V. Zenkina*

University of Ontario Institute of Technology

13:40 Saturday, DC1350

We present a straightforward method for the preparation of ultra-durable transition-metal based electrochromic materials (ECM) with high colour contrast ratios, long term redox stability, fast switching speeds, and tunable colours. This proposed fabrication requires as low as a monolayer of EC active molecules, and is significantly less time-consuming than layer-by-layer growth of coordination-based molecule assemblies. Our initial experiments show that various siloxane terminated terpyridine-based monolayers on conductive high surface area enhanced supports give access to a spectrum of colours for the resulting materials. The novel metal-oxide solid supports were optimized to maximize optical density. Overall, this work demonstrates a promising method for ECM colour tuning using manipulation of sterics and electronics of terpyridine-based ligands.



Figure 1. Different $Fe(Tpy)_2^{2+}$ complexes covalently attached to the high surface area support.

(S9) The Complexities of Homoleptic Uranium-Methyl Speciation

Jeffrey D. Sears, Michael L. Neidig

University of Rochester

14:00 Saturday, DC1350

The pursuit of homoleptic uranium species has spanned the greater part of the last century, beginning with intended isotope separation and quickly thereafter became an intriguing area of fundamental organometallic chemistry for the study of fblock bonding. Centrally, the synthesis of homoleptic species containing uranium-carbon σ -bonds has been considered a challenging area due to the inherent instability complexes containing simple alkyl and aryl substituents, whether due to the presence of β -hydrogens or a lack of significant steric bulk. We have spectroscopically elucidated the highly complex in situ speciation and successfully synthesized several highly unstable homoleptic uranium-methyl species. Correlating the spectroscopic data and isolable uranium species will provide greater clarity to the complex nature of fundamental organouranium chemistry.



(S10) Metallation kinetics of metallothionein in the msec timescale using Stopped-Flow Methods Natalie C. Korkola, Daisy L. Wong, and Martin J. Stillman

The University of Western Ontario

14:20 Saturday, DC1350

Metallothionein (MT) is a unique protein with 20 cysteine residues that can bind up to 7 divalent metals. The details of the metallation process are not well known. In this study, the kinetics of cadmium binding to $\beta\alpha$ MT were explored using stopped flow methods. Experiments were performed at pH 5 and 8 to replicate two different pathways: binding via "beads" with terminal thiolates or clusters with bridged thiolates. The denaturant GdmCl was used to study the role of the folded status of the apoprotein. Unfolding slowed down the metallation rate and the high pH beaded pathway proceeded much faster than the low pH cluster pathway. These results provide an understanding of MTs role in the homeostasis of cellular metals.

(S11) Highly Enantioselective Activated Imine Hydrogenation by an Iron P-NH-P' Catalyst

Chris S. G. Seo^a, Thibault Tannoux^b, Samantha A. M. Smith^a, Alan J. Lough^a, and Robert H. Morris^a*

a University of Toronto, b University of Rennes

15:00 Saturday, DC1350

Chiral amines are a key building blocks in synthetic chemistry due to their numerous applications in agricultural and pharmaceutical industries. Over the years, research in asymmetric imine hydrogenation has made considerable progress towards achieving highly enantiopure amines. However, carbon-nitrogen double bond reductions remain challenging, especially in the context of replacing precious metals with cheap, nontoxic, and environmentally friendly first row transition metals. Last year, we reported an unsymmetrical iron P-NH-P' catalyst that showed exceptional activity and enantioselectivity toward the reduction of aryl ketones¹, as well as preliminary results on N-phosphinylimine hydrogenation. Further optimization of the catalytic condition and an expanded substrate scope to other activated imines will be disclosed in this presentation. 1. Smith, S. A. M.; Lagaditis, P. O.; Lüpke, A.; Lough, A. J.; Morris, R. H. *Chem. Eur. J.* **2017**, *23*, 7212-7216.

(S12) Exploring pH Dependent Metalation Pathways of Metallothioneins using native ESI-MS

Amelia T. Yuan, Daisy L. Wong, Natalie Korkola and Martin J. Stillman

The University of Western Ontario

15:20 Saturday, DC1350

The cysteine-rich, metal-binding proteins metallothioneins (MT) are ubiquitous throughout Nature. MTs bind up to 8 Zn or Cd in metal-thiolate clusters. Following overexpression of recombinant human MT1a in *Escherichia coli*, we partially metallated the protein with zinc and cadmium and characterized their binding properties using native ESI-MS. Metallothionein 1a follows a pathway involving metal-thiolate cluster formation at low pH and a pathway dominated by beaded formation involving terminal thiolates at high pH. The degree to which depends on the metal bound. The different products were confirmed from metalation experiments at physiological pH using circular dichroism and ESI-MS. Using these techniques, we can classified the metal-selectivity of the metallothionein based on its functional cysteine units rather than its protein backbone.

(S13) Cathodic Electrochemistry and Identification of Catalytically Active Species for La₂CuO₄ Electrodes

A. Whittingham, R.D.L. Smith

University of Waterloo

15:40 Saturday, DC1350

Electrochemical CO₂ reduction to fuels and values added chemicals requires the fabrication of electrode materials with high current densities, selectivity and low cost. Ruddlesden-Popper oxides such as $La_{2-x}Sr_xCuO_4$ have demonstrated promise via tunable selectivity between pathways that favor either alcohol or hydrocarbon products. To date, there is no insight into the surface or bulk species that contribute to catalysis; making it difficult to infer the origin of this selectivity for rational improvements in catalyst design. In this work we map the electrochemical behavior La_2CuO_4 to make inferences about the catalytic species that are involved in the catalytic CO₂ reduction reaction.

(S14) The η^5 -Pentamethylcyclopentadienyl Pnicogen Dication [(η^5 -Cp*)Pn]²⁺ (Pn = P, As, Sb)

J. Zhou, L. L. Liu, L. L. Cao and D. W. Stephan*

University of Toronto

16:00 Saturday, DC1350

More than six decades after the discovery of the η^5 -cyclopentadienyl derivatives of iron, we uncovered the first cases of an η^5 -Cp ligand bonding to pnicogen atoms with the isolation of $[(\eta^5-Cp^*)Pn][B(C_6F_5)_4]_2$ (Pn = P[1], As, Sb) *via* a double-defluorination of Cp*PF₂ or double-dechlorination of Cp*PnCl₂ (Pn = As, Sb) strategy. The two degenerate LUMOs at the pnicogen centers prompt them to react as Pn(III)-based Lewis super acids, binding toluene, and reacting with [SbF₆]⁻ to give $[(Cp^*)PnF][B(C_6F_5)_4]$ and SbF₅. Various reactivity was also revealed by reactions of these dicationic species with different Lewis bases, including FLP ring opening of THF molecular. Furthermore, these compounds reacted with phosphines and/or diimines as pnicogen(I) cation transfer reagents.

1. J. Zhou, L. L. Liu, L. L. Cao, D. W. Stephan, *Chem.* doi.org/10.1016/j.chempr.2018.08.038.

(S15) Microwave-Assisted Solvothermal Synthesis of Upconverting and Downshifting Rare-Earth Doped LiYF₄ Microparticles

Nikita Panov, Riccardo Marin, Eva Hemmer*

University of Ottawa

16:20 Saturday, DC1350

Presented herein is a rapid (10 min *versus* \geq 12 h) microwave-assisted solvothermal synthesis of rare-earth doped (RE³⁺) LiYF₄ microparticles for light upconversion and downshifting. The importance of optimizing physicochemical reaction parameters such as the Li⁺-to-RE³⁺ ion ratio, the abundance of pH-sensitive surface-capping ligands, and the reaction temperature/time profile is discussed, and the growth mechanism by which LiYF₄ microparticles are formed is unveiled. Versatility of the developed method is highlighted by extending it towards the synthesis of other related state-of-the-art alkalimetal rare-earth fluoride materials. Thorough optical characterization of the obtained materials is presented, with special attention devoted to a single-particle optical assay of the upconverting LiYF₄ microparticles in which spatial variability of the emission intensity within individual particles is explored.



Figure 1. Optically active RE³⁺-doped LiYF₄ microparticles synthesised via the developed microwave-assisted solvothermal method.

(S16) C-F bond activation by hydridoboranes

Karlee L. Bamford,^a Saurabh S. Chitnis,^a Zheng-wang Qu,^b and Douglas W. Stephan^{a*}

a University of Toronto, b Universität Bonn

9:00 Sunday, DC1350

Hydridoboranes are classically used in hydroboration reactions of unsaturated substrates such as alkenes, alkynes, and carbonyl derivatives. Following the foundational contributions of Herbert Brown to hydroboration chemistry, borylation of functional groups has become a central transformation in the fields of both inorganic and organic chemistry. Despite this extensive body of work, we have unexpectedly found that hydridoboranes can also directly reduce C(sp³)-F bonds with or without an initiator, representing a previously unknown mode of reactivity for hydridoboranes. This fundamentally new observation opens the possibility of C-F bond functionalization with boron-containing reagents and other boron-mediated transformations. We have used this new insight to achieve the catalytic hydrodefluorination and catalyst-free dehydrofluorination of fluoroalkanes using hydridoboranes.



Figure 1. Summary of reactivity of hydridoboranes towards C(sp³)-F bonds.

(S17) Transition Metal Complexes of the 1,3,2-Dithiazolyl Radical

Dominique M. Leckie^a, Javier Campo^b, and Jeremy M. Rawson^a *a* University of Windsor, *b* University of Zaragoza, Spain.

9:20 Sunday, DC1350

The field of single molecule magnets has provided access to systems in which individual bits of data can be stored at the molecular (nm and sub-nm) scale. Most SMMs are based on 3d or 4f metal ions but the use of paramagnetic ligands (the so-called "metal/radical approach") has attracted attention to increase the spin ground state in polynuclear complexes. Extensive work by Preuss has investigated both 3d and 4f metal complexes of dithiadiazolyl radicals.¹ In comparison the related dithiazolyl radicals have been poorly studied.² Here, we present the synthesis and characterization of a series of mononuclear complexes of 4-methyl-benzo-1,3,2-dithiazolyl, MBDTA, with M(hfac)₂ (M = Mn, Co, Ni, Cu, Zn) using X-ray diffraction, EPR spectroscopy and SQUID magnetometry.The field of single molecule magnets has provided access to systems in which individual bits of data can be stored at the molecular (nm and sub-nm) scale. Most SMMs are based on 3d or 4f metal ions but the use of paramagnetic ligands (the so-called "metal/radical approach") has attracted attention to increase the spin ground state in polynuclear complexes. Extensive work by Preuss has investigated both 3d and 4f metal complexes of 4-methyl-benzo-1,3,2-dithiazolyl (the so-called "metal/radical approach") has attracted attention to increase the spin ground state in polynuclear complexes. Extensive work by Preuss has investigated both 3d and 4f metal complexes of dithiadiazolyl radicals.1 In comparison the related dithiazolyl radicals have been poorly studied.2 Here, we present the synthesis and characterization of a series of mononuclear complexes of 4-methyl-benzo-1,3,2-dithiazolyl, MBDTA, with M(hfac)2 (M = Mn, Co, Ni, Cu, Zn) using X-ray diffraction, EPR spectroscopy and SQUID magnetometry.



M= Mn, Co, Ni, Cu, Zn

1 Preuss, K. E., *Dalton Transactions* **2007**, 2357-2369. 2 Fujita, W.; Awaga, K., *J. Amer. Chem. Soc.* **2001**, *123*, 3601-3602.

(S18) Reactivity modes of Roesky Al(I) species in reaction with benzophenone and isobutyrone

Anton Dmitrienko^a, Denis Spasyuk^b, Georgii Nikonov^{*a}

a Brock University, b Canadian Light Source Inc.

9:40 Sunday, DC1350

NacNacAl (NacNac = [DippNC(Me)CHC(Me)NDipp]⁻) reacts with an equivalent of benzophenone to form a labile ketylate derivative that is readily engaged into a variety of cyclization reactions involving the benzophenone moiety. The scope of substrates includes phenyl nitrile, quinoline, isobutyrone, aldimine PhN=CPhH, triethyl phosphate, and cyclic thiourea. In contrast, a bulkier ketone, isobutyrone, reacts with the Al(I) centre with the formation of an aluminum hydride species via β -deprotonation of the ketone. The new compounds were characterized by NMR and X-ray diffraction techniques.



Figure 1. Assumed mechanism for the formation of ^{Me}NacNac^{Dipp}AI adduct with benzophenone.

(S19) Identification of key intermediates in iron-catalyzed C-H functionalization

T. Boddie^a, S. Carpenter^a, T. Baker^a, J. DeMuth^a, L. Ackermann^b, M. Neidig^{a,*}

a University of Rochester, b Georg-August-Universität

10:00 Sunday, DC1350

Significant research has been focused towards the development of non-precious base metal catalysts which directly activate and functionalize C-H bonds. Iron catalysts are particularly attractive due to their low cost, high availability, limited toxicity, and rich oxidation chemistry. Recently, iron-based catalytic systems have successfully directed C-H transformations via cross-coupling C-H bonds with organometallic reagents. Synthetic and spectroscopic techniques were utilized to elucidate the nature of in-situ iron speciation operative in Ackermann et al. iron-catalyzed arylation of aryl C(sp²-H) bonds by triazole assistance. Identification of key intermediates provided molecular level insight into the nature of the active iron catalytic species and the mechanism of the underlying iron C-H functionalization catalytic cycle.



Figure 1. Iron-catalyzed directed C-H functionalization with ⁵⁷Fe Mossbauer spectrum of in-situ speciation at 18 hours.

(S20) Synthesis of New Monoanionic Bidentate Inversely-Polarized Phosphaalkene-Enolate Ligands and their Coordination to Group 4 and 10 Metal Centres

Matthew A. Wiebe, Juan Rodriguez, Gino G. Lavoie*

York University

10:20 Sunday, DC1350

Inversely-Polarized Phosphaalkenes (1) feature a C=P double bond that has polarity opposite of what would be predicted by Pauling electronegativity. This results in a partially negative phosphorus atom and partially positive carbon atom. The electronic and steric properties of IPPs can be "dialed-in" based on the N-heterocyclic carbene fragment used in its preparation, making them ideal candidates for use in ligand design. Herein we report recent developments for the synthesis of new monoanionic-bidentate inversely-polarized phosphaalkene-enolate ligand precursors (2) and their attempted coordination to group 4 and 10 metal centres (3).





(S21) Balancing Oxidative Addition and Reductive Elimination on Palladium: Design of an Active Catalyst for **Carbonylative C-H Bond Functionalization**

Y. Liu, B. A. Arndtsen* McGill University

10:20 Saturday, DC1351

The development of metal catalyzed C-H bond functionalization reactions has had significant impact on synthetic chemistry. Our lab has recently reported an approach to apply these to carbonylations, where electron deficient palladium catalysts can allow the formation of aroyl electrophiles from aryl iodides, CO and AgOTf for reactions with arenes. We describe in this talk how balancing the ability of palladium to undergo oxidative addition with electron rich phosphines, together with steric bulk to facilitate the reverse reductive elimination, can generate broadly applicable catalysts for this reaction, including its use with aryl triflates. Overall, this provides the first example of the carbonylative C-H functionalization with aryl/vinyl triflates, occurs without stoichiometric metal additives, and opens a route to generate ketones from (hetero) arenes and CO.



(S22) Inclusion Chemistry of Thiazyl and Selenazyl Radicals in MIL-53(AI)

N. T. Stephaniuk and J. M. Rawson*

University of Windsor

10:40 Saturday, DC1351

Host-guest interactions continue to be a growing area of study within the scientific community, where the strength of binding and activity of molecular quests can be directly correlated to applications such as gas storage materials, sensors, activators, and heterogeneous catalysis. This presentation will describe the inclusion chemistry of 4-phenyl-1,2,3,5dithiadiazolyl (PhCNSSN) radical, its selenium analogue (PhCNSeSeN), and their fluorinated analogues (C₆F₅CNSSN and C₆F₅CNSeSeN), into the porous metal-organic framework host MIL-53(AI). The inclusion of these radicals into MIL-53(AI) was achieved through gas phase diffusion. The characterization of these inclusion complexes was confirmed through powder X-Ray diffraction and EPR spectroscopy. Reactivity studies of these radicals within the host framework will be discussed.



(S23) Dramatically Extended Photoisomerization Scope of Benzylideneamine N,C-Chelate Organoboron System Hai-Jun Li, Suning Wang

Queen's University

11:00 Saturday, DC1351

A series of benzylideneamine N.C-chelate boron compounds have been found to undergo rapid multistructural transformations with UV irradiation, yielding new BN-cycloocta-/cyclohepta-triene derivatives bearing a tetrasubstituted B=N unit quantitatively. The simple imine donor also lends itself to achieving photoreactivity in compounds with two non-bulky aryl group (such as phenyl and thienyl) substituents on boron, which is the first example for this type of organoboron photochemistry.



(S24) Microwave-Assisted Strategies for the Synthesis of Ultrasmall Lanthanide-doped Nanoparticles

I. Halimi^a, S. Maurizio^{a,b}, E. Boase^a and E. Hemmer^{a*} *a* University of Ottawa, *b* Current affiliation: Concordia University

11:20 Saturday, DC1351

Lanthanide-based nanoparticles (Ln-NPs) are known for their outstanding optical properties. For example, NaGdF4 doped with Yb³⁺/X³⁺ (X = Er, Tm, Ho) emits UV-vis and near-infrared (NIR) light under 980nm-excitation (UV-vis-emission due to upconversion). Particularly the use of NIR light matching the biological window (750nm-1750nm) and a remarkable photostability make such Ln-NPs promising alternatives to fluorescent dyes for bioimaging. Yet, reliable and rapid synthesis protocols for Ln-NPs in the sub-10nm-realm remains a challenge. Here, a bottom-up microwave-assisted approach was developed to yield ultra-small Ln-NPs (smallest size: 3-4nm), while ensuring crystalline phase control. The focus is set on the comparison of two different precursors - Ln-trifluoroacetates and Ln-oleates - with respect to the crystalline phase, size and photoluminescence of the resulting Ln-NPs.



Figure 1. Transmission electronic micrographs of Ln-NPs obtained from a) trifluoroacetate- and b) oleate-based precursors. Characteristic photoluminescence spectra of c) Yb³⁺, Tm³⁺ and d) Yb³⁺, Er³⁺ co-doped Ln-NPs under 980nm-excitation.

(S25) The Cluster Chemistry of mpmH – Towards Polynuclear SMMs with Large Spin Ground States

P. Abbasi, Th. C. Stamatatos and M. Pilkington*

Brock Universitv

11:40 Saturday, DC1351

Given the recent development of quantum computers, it has been proposed that the magnetic bistabilities of single molecule magnets (SMMs) can be exploited as qubits for quantum computing. To achieve this, the development of multi-functional SMMs that permit addressability of their spins states is at the forefront of the field of molecular magnetism. Our recent studies have been focused on the investigation of small, potentially chiral organic ligands for the assembly of 3d- and/or 3d/4f-metal clusters with large spin ground states to explore the interaction of light with chirality to address SMM properties. In a preliminary study, the cluster chemistry of rac-mpmH, 1, together with Mn has recently afforded the nanosize Mn₃₁, 2, with unique SMM properties.1 The synthesis, structural and magnetic properties of this polynuclear cluster will be presented.



1. P. Abbasi, K. Quinn, D.I. Alexandropoulos, M. Damjanovic, W. Wernsdorfer, A. Escuer, J. Mayans, M. Pilkington and Th.C. Stamatatos, J. Am. Chem. Soc., 2017, 139, 15644.

(S26) Exploring the Reactivity of Tetrathiocins with d-block Metals

L. K. Watanabe^a, Z. S. Ahmed^a, J. M. Rawson^{a*}, and C. L. B. Macdonald^{a,b}

a University of Windsor, b Carleton University

13:00 Saturday, DC1351

Metal dithiolene complexes exhibit intense colors, multiple oxidation states, reversible redox reactions and the ability to take on different geometric conformations, making them ideal in a variety of materials applications. To date, many dithiolate complexes contain strongly electron-withdrawing groups, such as $(NC)_2C_2S_2^{2-}$ and $(F_3C)_2C_2S_2^{2-}$, while the π -conjugated dithiolates contain commercial benzenedithiolate or toluene dithiolate ligands. More recently, it has been shown that alkoxyfunctionalized bis(benzo)-1,2,5,6-tetrathiocins are able to undergo oxidative addition to low valent group 10 metal complexes (Ni, Pd, Pt). This presentation extends the reactivity to the group 9 complex CpCo(CO)₂ with tetrathiocins. Reaction of cyclopentadienylcobalt dicarbonyl with the respective alkoxy-functionalized bis(benzo)-1,2,5,6-tetrathiocins under microwave conditions generated the mononuclear or dinuclear complexes [CpCoL]_n (1 - 4). These complexes were characterized by single crystal and powder X-ray diffraction, NMR spectroscopy, FT-IR and DSC.



(S27) Phosphinidene, Phosphanorcaradiene and Diphosphene Derived from Phosphirenes

Liu Leo Liu, Jiliang Zhou, Levy L. Cao, Douglas W. Stephan

University of Toronto

13:20 Saturday, DC1351

A room-temperature-stable crystalline 2*H*-phosphirene **1**, was synthesized by the reaction of an electrophilic diamidocarbene (DAC) with *tert*-butylphosphaalkyne.^[1] Of particular interest is that **1** is shown to react as a transient vinylphosphinidene generated via phosphirene-phosphinidene rearrangement. In addition, a room-temperature-stable crystalline phosphanorcaradiene **2** has been prepared via a C-C bond forming strategy induced by the demetalation of a phosphepine-Au complex using a Lewis base,^[2] while vinyl-substituted diphosphenes **3**, **4** and **5** featuring narrowest HOMO-LUMO gaps, relative to hitherto known carbon-substituted diphosphenes, have been synthesized via a concerted rearrangement/dimerization reaction of kinetically unstable cyclic alkyl amino carbene (CAAC) derived 2*H*-phosphirenes **6** and **7**.^[3]



[1] L. L. Liu, J. Zhou, L. L. Cao, R. Andrews, R. L. Falconer, C. A. Russell, D. W. Stephan, *J. Am. Chem. Soc.* 2018, 140, 147-150.

[2] L. L. Liu, J. Zhou, R. Andrews, D. W. Stephan, J. Am. Chem. Soc. 2018, 140, 7466-7470.

[3] L. L. Liu, J. Zhou, L. L. Cao, D. W. Stephan, in preparation.

(S28) Unusual C_{sp}³-C_{sp}³ Bond Formation Promoted by the Diverse Coordination of a Phosphine-Azaallyl Ligand Kyle M. K. Jackman^a, Benjamin J. Bridge^a, David E. Stephens^a, James M. Stubbs^a, Christopher N. Rowley^b, Johanna M. Blacquiere^a

a Western University, *b* Memorial University of Newfoundland 13:40 Saturday, DC1351

Despite their similarity to other common monoanionic functional groups 1-azaallyl ligands have been underused in catalysis. These ligands show a range of coordination modes, and when utilized in Suzuki-Miyaura coupling reactions they improved catalyst performance when compared to the analogous allyl derivative.¹ We have prepared a phosphine-azaallyl ligand through the deprotonation of a phosphine-imine. The ligand was coordinated to [PdCIMe(COD)] to afford a dimer with two Pd^{II}-Me fragments. The amides of the azaallyl moiety bridge the two Pd^{II} centres and stabilize the dimer. This bridging interaction can be easily broken by the addition of pyridine. Heating the complex results in the formation of two new palladium species, accompanied by an unusual C_{sp}^{3} - C_{sp}^{3} bond formation route and the release of ethane.



Figure 1. Reductive elimination of ethane from heating the [Pd(L-X)Me]₂ dimer in benzene.

[1] Shen, A.; Ni, C.; Cao, Y. C.; Zhou, H.; Song, G. H.; Ye, X. F. Tetrahedron Lett. 2014, 55, 3278.

(S29) Synthesis and Magneto-structural studies of 4f complexes of dibenzo15C5 macrocycles

Z. Ras Ali, M. Pilkington*

Brock University

14:00 Saturday, DC1351

In recent years the Pilkington group has been exploring the structure-directing capabilities of crown ether macrocycles together with *4f* ions for the assembly of stable SMMs with high coordination numbers and a strong axial field. The cavity sizes of smaller crowns such as 12C4 and 15C5 afford 'half-sandwich' topologies, where the metal ions are axially coordinated out of the plane of the crown and axial solvent molecules and/or anions complete the coordination geometries.^{1,2} In order to investigate further how subtle modifications to the organic framework of crown ether macrocycles affects their structure-directing properties, the synthesis, structure and magnetic properties of *4f* complexes of dibenzo15C5 will be presented. 1. E.L. Gavey, M. Al Hareri, J. Regier, L.D. Carlos, R.A.S. Ferreira, F.S. Razavi, J.M. Rawson and M. Pilkington, *J. Mat. Chem. C.* **2015**, *3*, 7738.

2. M. Al Hareri, Z.R. Ali, J. Regier, E.L. Gavey, L.D. Carlos, R.A.S. Ferreira, M. Pilkington, Inorg. Chem. 2017, 56, 7344.

(S30) Synthesis of Cationic and Neutral Dialkyl Yttrium Complexes of Rigid Cyclometallation-Resistant NON- and NNN-Donor Ligands

Aathith Vasanthakumar, David J.H. Emslie*

McMaster University

14:20 Saturday, DC1351

Group 4 post-metallocene olefin polymerization chemistry is far more established than that of group 3 transition metals.¹ This can in part be attributed to undesirable reactions such as ligand redistribution or cyclometallation that are inherent to many such complexes at elevated temperatures. To combat this, ligand design features such as high steric bulk, donor ability and rigidity may prove beneficial. To this end, the new ligand precursors, $H(AII_2)$ and $[H(XII_2)][B(C_6F_5)_4]$ have been prepared, and reactions with $[Y(CH_2SiMe_3)_3(THF)_2]$ afforded the corresponding dialkyl complexes: monocationic $[(XII_2)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ and neutral $[(AII_2)Y(CH_2SiMe_3)_2]$. The synthesis, structures, stability, and preliminary reactivity of these new ligands and complexes will be discussed.



1. Bambirra, S.; van Leusen, A.; Meetsma, A.; Hessen, B.; Teuben, J. H. Chem. Commun. 2003, 4, 522.

(S31) Characterizing Heme Biosynthesis in Staphylococcus aureus

R. Hooper^a, A. Celis^b, J. Dubois^b, M. Stillman^{a*} *a* The University of Western Ontario, *b* Montana State University

15:00 Saturday, DC1351

Heme b is essential in the human pathogenic bacterium Staphylococcus aureus. The terminal steps of the heme biosynthetic pathway, which involve insertion of iron into coproporphyrin III followed by decarboxylation forming the final heme, are of interest to us. Our goals are to characterize the rates of these reactions and the oxidation state of iron in the final product. ESI-Mass spectrometry has been shown to be an excellent tool for monitoring the rates of complicated reaction pathways as all species can be determined in real time. Magnetic circular dichroism spectroscopy is sensitive to the change in symmetry and oxidation state following iron insertion. Together, these two techniques will allow the reaction pathway to be elucidated with respect to enzymatic reactivity.



Figure 1. The heme biosynthetic pathway in Staphylococcus aureus.

(S32) Reactivity of Ga(I) with Multiple Bonds

Aisha Kassymbek, Georgii Nikonov*

Brock University

15:20 Saturday, DC1351

Activation of strong bonds on reduced main group elements is a hot topic.^[1] We have previously established the propensity of NacNacAI (NacNac=[ArN(Me)CHC(Me)NAr], Ar = 2,6-iPr₂C₆H₃) to cleave C=S and C=N bonds.^[2] However, very little is known about the reactivity of low valent gallium to multiple bonds.^[3,4] We found that reactions of NacNacGa with phenyl isothiocyanate result in the oxidative addition of the C=S bond followed by cyclization with the second equivalent of substrate. The P=S bond of triphenylphosphine sulfide can be also cleaved, albeit at higher temperature. In contrast, reactions of Ga(I) with related isocyanates and carbodiimides gave cycloaddition products. The new compounds were characterized by multinuclear NMR and X-ray diffraction.



1. Nikonov, G. I.; Chu, T. Chem. Rev. 2018, 118, 3608-3680.

2. Chu T., Vyboishchikov S.F., Gabidullin B., Nikonov G.I. Angew. Chem. Int. Ed. 2016, 55, 13306–13311.

3. Chu, T.; Vyboishchikov, S.F.; Gabidullin, B.; Nikonov, G.I. J. Am. Chem. Soc. 2017, 139, 8804-8807.

4. Zhang, W.; Dodonov, V. A.; Chen, W.; Zhao, Y.; Skatova, A. A.; Fedushkin, I. L.; Roesky, P. W.; Wu, B.; Yang, X-J. Chem. Eur. J. 2018, 24, 14994-15002.

(S33) Unprecedented CO₂ Bonding Modes Using Vanadium Aryloxide Compounds

Camilo J. Viasus,* Nicholas P. Alderman, Bulat Gabidullin and Sandro Gambarotta

University of Ottawa

15:40 Saturday, DC1351

Understanding the CO₂ linear coordination will ensure its activation to further transformation to one of the most abundant industrial waste by-products. In this work we are presenting the first End-On linear CO₂ coordination compound using a transition metal (η^1 -CO₂) and a new bonding coordination mode for CO₂ using vanadium aryloxide compound (η^2 -CO₂). These new approaches will contain the key for CO₂ reduction in a catalytic fashion.

(S34) Phosphorous(III) Dications: Unravelling the Catalytic Potential of Main Group Coordination Compounds

R. Andrews, S. Chitnis, J. LaFortune, D. Stephan*

University of Toronto

16:00 Saturday, DC1351

Due to the regulations put on trace metals left over from catalysis as a concern of their toxicity, significant attention has been focused towards the utility of main group catalysts as suitable alternatives in recent years. Recently, our group has shown that phosphorous(III) dicationic Lewis acids bearing bipyridine and terpyridine ligands are effective catalysts for hydrodefluorination and carbodefluorination of fluoroalkanes. This presentation highlights the synthesis and characterization of many achiral and chiral variants of these compounds, with a discussion of their electronic parameters. The preliminary reactivity of these compounds towards oxidative addition is discussed, as well as their use in catalytic reactions such as hydrosilylation and allyslilylation



(S35) Monitoring the Synergetic Effect of High Pressure and High Temperature on Enhancing CO₂ Adsorptive Capacity of ZIF-8 by In-Situ FTIR Spectroscopy

S. Jiang^a, J. Guan^b, Y. Huang^{*a}, Y. Song^{*a,b}

a Department of Chemistry, The University of Western Ontario, b Department of Physics and Astronomy, The University of Western Ontario

16:20 Saturday, DC1351

As one of the promising gas storage materials, ZIF-8 has been investigated for CO_2 adsorption under a wide range of pressure from conventional gas adsorption pressure to high pressure at the gigapascal level.^{1,2} Our previous investigation on CO_2 loaded ZIF-8 in a diamond anvil cell has shown that the application of high external pressure could enhance the guest-host interactions between CO_2 and ZIF-8 framework as well as the CO_2 storage capacity.^{2,3} However, the solidification of CO_2 occurs above 0.6 GPa at room temperature. This phase change severely affects the further diffusion and insertion of CO_2 into the framework at higher pressure, as solid CO_2 is less mobile. In this study, by in situ heating the diamond anvil cell, we liquefied the CO_2 solids initially residing outside the ZIF-8 framework and subsequently inserted CO_2 molecules it into the cages at high pressures. This significant improvement in CO_2 storage capacity in ZIF-8 was probed by using in-situ FTIR spectroscopy.

1. Wang, B.; Cote, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M., Nature 2008, 453 (7192), 207-11.

2. Hu, Y.; Kazemian, H.; Rohani, S.; Huang, Y.; Song, Y., Chem Commun 2011, 47 (47), 12694-6.

3. Hu, Y.; Liu, Z.; Xu, J.; Huang, Y.; Song, Y., J Am Chem Soc 2013, 135 (25), 9287-90.

(S36) Iron (II) catalysts toward gem-specific dimerization of terminal alkynes

Qiuming Liang, and Datong Song*

University of Toronto

9:00 Sunday, DC1351

1,3-Enynes are important building blocks for the syntheses of natural products, bioactive molecules, organic materials, and other complex molecules.¹ The selective dimerization of terminal alkynes is the ideal route for 1,3-enyne synthesis owing to its perfect atom economy.¹ The main challenge of alkyne dimerization is the control of regioselectivity due to the competing formation of head-to-head (E/Z) and head-to-tail (*gem*) isomers. We herein present the syntheses of a series of half-sandwich *N*-heterocyclic carbene (NHC) iron complexes and our investigations into their catalytic reactivity toward alkyne dimerization. The mechanistic details will be also discussed.



1. Modern Alkyne Chemistry (Ed.: Trost, B. M.; Li, C.-J.), Wiley, Weinheim, 2015.

(S37) Reactivity of Bis(silyl) Hydride Complexes of Manganese

Jeffrey S. Price, David J. H. Emslie*

McMaster University

9:20 Sunday, DC1351

Our group has recently reported the synthesis and characterization of bis(silyl) hydride complexes [(dmpe)₂MnH(SiH₂R)] (Ph, ⁿBu).^[1] We now report the reactions of these complexes with a variety of reagents; RSiH₃, H₂, N,N'-diisopropylcarbodiimide, CO₂, and ethylene, resulting in a variety of novel structures which were characterized in solution and (in most cases) solid state. In order to explain the divergent reactivity with different reagents, we propose that the bis(silyl) hydride complexes exist in solution in equilibrium with a low-coordinate silyl complex (via hydrosilane dissociation) and a silylene-hydride complex (via subsequent a-hydride elimination). These proposed intermediates were shown to be accessible using DFT calculations, and have been 'trapped' by reaction with isonitriles and N-heterocyclic carbenes (NHCs). Analysis of interligand Si•••H interactions in [(dmpe)₂MnH(SiH₂R)₂] and various isomers of silvl dihydride complexes [(dmpe)₂MnH₂(SiH_{3-n}R_n)], prepared from reactions of H₂ with silylene hydride^[2] or bis(silyl) hydride complexes, are also discussed.



[1] J. S. Price, D. J. H. Emslie, I. Vargas-Baca, and J. F. Britten, Organometallics, 2018, 37, 3010-3027. [2] J. S. Price, D. J. H. Emslie, and J. F. Britten, Angew. Chem. Int. Ed., 2017, 56, 6223-6227.

(S38) Probing the sequence of copper-thiolate cluster formation in metallothionein using ESI-mass spectrometry Adyn Melenbacher and Martin Stillman

University of Western Ontario

9:40 Sunday, DC1351

Copper is an essential element required for all life. Copper is necessary for central nervous system function and has been suggested to play a key role in the development of neurodegenerative diseases such as Alzheimer's disease. Critically, a cellular copper chaperone is required to alleviate the potential for dangerous redox chemistry. Metallothionein, a protein with 20 cysteines, provides protection and homeostatic control of Zn(II) and Cu(I). Electrospray ionization mass spectrometry (ESI-MS) can be used to view Cu(I) speciation in the protein. A series of Cu(I)-thiolate clusters form at physiological pH, however it is unclear which cysteines bind to the Cu(I) first. Isolated domain fragments of metallothionein have been used to determine domain preference of copper binding through detailed ESI-MS studies.

(S39) Unprecedented B-H Free Hydroborations by a Dicoordinate Borocation

Christopher J. Major, Karlee L. Bamford, Douglas W. Stephan*

University of Toronto

10:00 Sunday, DC1351

First isolated in 1981, borinium are a class of dicoordiate borocation. Although a great deal of stoichiometric and catalytic reactivity has been demonstrated for for 3- and 4-coordinate borocations, borinium chemistry has remained relatively unexplored. In particular, no reactivity studies on bisamido borinium compounds are known in the literature, despite being isolated over 35 years ago. A novel, and highly unusual, hydroboration of unsaturated substrates has been observed for the extremely Lewis acidic bis(diisopropylamido)borinium. This is the first known example of a additive-free formal hydroboration by a molecule containing no B-H bonds.



(S40) Synthesis and properties of NHC-bound gold nanoclusters

Paul A. Lummis,^a Mina R. Narouz,^a Renee Mann,^b Phillip Unsworth,^a Kirsi Salorinne,^b Shinjiro Takano,^c Ryohei Tomihara,^c Sami Kaappa,^d Sami Malola,^d Cao-Thang Dinh,^e Daniel Padmos,^a Kennedy Ayoo,^a Patrick J. Garrett,^a Masakazu Nambo,^b J. Hugh Horton,^{*a} Edward H. Sargent,^{*e} Hannu Häkkinen,^{*c} Tatsuya Tsukuda,^{*c,f} Cathleen M. Crudden^{*a,b} *a* Queen's University, *b* Nagoya University, *c* University of Jyväskylä, *d* The University of Tokyo, *e* The University of Toronto, *f*

Kyoto University

10:20 Sunday, DC1351

N-heterocyclic carbenes (NHCs) can be employed in the synthesis of highly-stable coinage metal surfaces, clusters and nanoparticles. In this talk, I will detail the synthesis and reactivity of mixed NHC-phosphine Au₁₁ nanoclusters, and discuss how the incorporation of even one NHC can dramatically improve the stability of the resultant cluster. In addition, I will also discuss to the synthesis of a new Au₆ gold nanocluster.

Poster Presentations

(P1) Boron Difluoride Hydrazonate Complexes: Substituent Effects on Optoelectronic Properties

Daniela Cappello, Joe B. Gilroy* The University of Western Ontario

Hybrid materials combine the functionality of π -conjugated organic ligands and inorganic elements and find applications in various optoelectronic devices.¹ Boron difluoride hydrazonate complexes are a subclass of these compounds known to fluoresce in the solid state.²⁻³ Herein, we present the straightforward synthesis of a new subclass of these materials and explore the effect of structural variation on optoelectronic properties. These complexes were weakly emissive in solution but exhibit enhanced emission in the solid state, which prompted us to investigate their aggregation-induced emission behaviour (Figure 1). The redox activity of these complexes were explored using cyclic voltammetry. Our recent results in these areas will be presented.



Figure 1. Aggregation-induced emission behaviour of borondifluoride hydrazonate complexes.

- 1. Salleo, A. et. al., Chem. Rev. 2010, 110, 3-24.
- 2. Aprahamian, I. et. al., Chem. Sci. 2012, 3, 610-613.
- 3. Aprahamian, I. et. al., Nat. Chem. 2017, 9, 83-87.

(P2) Oximato-Based Ligands in 3*d*/4*f*-Metal Cluster Chemistry: A Family of "Propeller"-like Cu₃Ln Complexes with Single-Molecule Magnetic Behavior

A. Worrell^a, D. Sun^b, J. Mayans^c, C. Lampropoulos^d, A. Escuer^c, Th. C. Stamatatos^{*,a}

a Brock University, b Shandong University, c Universitat de Barcelona, d University of North Florida

The organic chelating/bridging ligands 9,10-phenanthrenedione-9-oxime (phenoxH) and 9,10-phenanthrenedione-9,10dioxime (phendoxH2) were employed for a first time in heterometallic 3d/4f-metal cluster chemistry. We present a new family of Cu₃Ln (Ln^{III} = Gd (1), Tb (2), Dy (3)) complexes bearing the phenoxH ligand and possessing an oximato-bridged, "propeller"-like core. Moreover, the magnetic susceptibility data for complexes 2 and 3 were nicely fit to a Hamiltonian that accounts for parameters such as the spin-orbit coupling and the axial ligand-field component around the Ln^{III} atoms. This fitting procedure is here used for the first time to elucidate the exchange parameters for the anisotropic compounds. Complexes 1-3 are antiferromagnetically-coupled, while 2 and 3 exhibit single-molecule magnetic behaviour at low temperatures.





(P3) Intermediates in Iron- and Cobalt-Catalyzed Cross-Coupling Reactions

S. Carpenter and M. L. Neidig*

University of Rochester

Iron- and cobalt-catalyzed cross-coupling reactions have received substantial attention over the past decades. Notably, *N*-methylpyrrolidone (NMP) is an effective additive in both iron and cobalt catalyzed cross-coupling reactions, where reactivity of both cobalt and ferric salts was found to be comparable under analogous conditions. Our group has made significant contributions in the mechanistic understanding of simple ferric salt catalyzed cross-coupling reaction in the presence and absence of NMP, with both aryl and alkyl Grignard reagents. However, it is unclear if analogous reactions utilizing cobalt salts will behave similarly to iron. Recent success has shown $Fe_4(\mu-Ph)_6(THF)_4$ as an reactive species, while current efforts focus on the isolation and characterization of similar species formed during simple cobalt salt catalysis.



(P4) Mononuclear and H-Bonded Pseudo-Dinuclear Dy^{III} Single-Molecule Magnets in an "ON-OFF" State

C. Daneluik^a, M. Damjanović^b, D. I. Alexandropoulos^a, D. Sun^c, W. Wernsdorfer^b, Th. C. Stamatatos^{*,a}

a Brock University, b Karlsruhe Institute of Technology, c Shandong University

A new hexa-nucleating N_3O_3 organic chelate (L^{3-}) was synthesized and used for the preparation of low-coordinate, mononuclear Dy^{III} single-molecule magnets (SMMs). Our first attempts led to the crystallization and structural elucidation of the 7-coordinate compound $[DyL(H_2O)]$, which is singly H-bonded to its neighboring monomers, yielding isolated pseudodimers that are well-separated from one another. The H-bonded dimers show interesting magnetic dynamics mainly due to exchange-bias phenomena from the communication between the two spin systems. Chemical reactivity studies have allowed us to alter the magnetic properties of these H-bonded species through the synthesis of the non-SMM complex [DyL(THF)]. Details of synthetic aspects and rationale beyond preparation of these complexes, as well as their complete magnetic characterization, will be reported in this presentation.



Figure 1. Structure of the H-bonded pseudo-dimer [DyL(H₂O)]---[DyL(H₂O)].

(P5) Heavily-doped SrTiO₃ phases prepared via sol-gel and solid-state routes

H. Bakhshi^{a,b,*}, Y. Mozharivskyj^a, Rasoul Sarraf-Mamoory^b, Amin Yourdkhani^b

a McMaster University, b Tarbiat Modares University

In this study, solid-state synthesis was employed to introduce the Sm³⁺, Dy³⁺, and Nb⁵⁺ cations in SrTiO₃ crystal structure and replace Sr²⁺ and Ti⁴⁺. The goal is to find out structural changes upon heavy doping. Additionally, a sol-gel method was used to prepare Nb-doped SrTiO₃ nanoparticles. Dynamic light scattering (DLS) shows that the sols are stable after one month. Simultaneous thermal analysis (STA) was employed to find out the best calcination temperature for sol-gel products. Field emission scanning electron microscopy (FE-SEM) has revealed that the sol-gel particles are smaller than 50 nm. Chemical composition has been assessed by the energy dispersive spectroscopy and phase purity by X-ray powder diffraction.

(P6) Low Band Gap Polymer and Model Compounds Derived from Boron Difluoride Formazanates and Platinum Diynes

Jasveer S. Dhindsa, Ryan R. Maar, Stephanie M. Barbon, María Olivia Avilés, Zachary K. Powell, François Lagugné-Labarthet, and Joe B. Gilroy

University of Western Ontario

Organic conjugated polymers exhibit sought after optical and electronic properties due to the delocalization of π -electrons and are often semiconducting, leading to their use in a variety of organic electronic devices.¹ Incorporating platinum into the main chain of polymers through diyne units is known to afford a variety of advantageous properties such as photoluminescence, redox, and optoelectronic properties.² The general structure for platinum polyynes is a linear backbone comprised of the metal centre (Pt²⁺), supported by neutral phosphine ligands, and a spacer group. Herein, we introduce a readily accessible conjugated polymer and several model complexes based on electron-poor boron difluoride formazanate spacers and electron-rich platinum(II) diyne subunits as a promising candidate for use in organic electronics. Recent results in this area will be presented.³



1) Liu, S.-J et al. *Macromol. Rapid Commun.* **2012**, *331*, 461–480.

2) Ho, C.-L. et al. Chem. Soc. Rev. 2016, 45, 5264.

3) Dhindsa, J. S. et al. Chem. Commun. 2018, 54, 6899.

(P7) Synthesis and Characterization of Two-dimensional Layered Nickel Hydroxide Nanosheets

W. Rong, R. D. L. Smith

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Metal hydroxides with a layered, two-dimensional structure have potential applications in catalysis, energy storage, and supercapacitors. Individual nanosheets synthesized by exfoliating layered double hydroxide (LDHs) crystallites have been shown to exhibit interesting properties, but this synthetic approach offers little control over particle size. This poster will present our attempts to establish a direct synthetic approach that facilitates the preparation of individual nanosheets with control over the size and composition of each 2-dimensional nanosheets. The characterization of the nanosheets was using transmission electron microscopy (TEM), X-ray diffraction, and electrochemical analysis.



Figure 1. TEM micrograph of a Ni_{0.99}Fe_{0.01}(OH)₂ nanosheet prepared by solution-phase synthesis.

(P8) Cubic versus hexagonal – Effect of host crystallinity on the T1 shortening effect of NaGdF4 nanoparticles

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NaGdF₄ nanoparticles are promising candidates as MRI T₁ contrast agents due to the paramagnetic properties of the Gd³⁺ ion. However, to date there has been no report on how T₁ relaxivity is affected by the different polymorphs in which NaGdF₄ crystallizes: cubic (α) and hexagonal (β). We designed a microwave-assisted synthesis method that grants selective access to NaGdF₄ nanoparticles of either phase in the same size range (6.1 - 8.2 nm). T₁ relaxivity results show that cubic NaGdF₄ nanoparticles exhibit larger relaxivity (r₁) values than their hexagonal analogues. It was interpreted based on Solomon-Bloembergen-Morgan theory suggesting that cubic NaGdF₄ nanoparticles possess higher magnetization and larger hydrodynamic diameter resulting in significant inner sphere contribution to MRI T₁ relaxivity.

(P9) Unusual reactivity of a [BH] cation: moving towards intramolecular borenium-based frustrated Lewis pairs

Jolie Lam, Douglas W. Stephan*

University of Toronto

N-heterocyclic carbene boranes (NHC-boranes) have been vastly studied on their use as synthetic reagents, radical polymerization co-initiators, catalysts, and catalyst precursors.¹ Hereby, we report the synthesis of an isolable 3-coordinate [BH] borenium cation, its unusual reactivity, and our progress towards the production of an intramolecular frustrated Lewis pair.



Figure 1. Synthesis of an isolable [BH] cation.

1. Curran, D.P.; Solovyev, A.; Brahmi, M.M.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Angew. Chem. Int. Ed. 2011, 50, 10294-10317

(P10) Imino-stabilised phosphinidene and some of its derivatives

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Diiminophenyl (dimph) proved to be an excellent ligand platform to stabilise a low-valent phosphorus centre. A new phosphorus compound supported by dimph ligand was prepared by the reduction with KC8 at room temperature. The resultant compound dimphP (1), which can be rationalized as an imino-stabilised phosphinidene or benzoazaphopshole, shows remarkable chemical stability: it withstands the treatment with water and oxidizers (O_2 and pyridine oxide) and only reacts with excess strong acid (e.g. HCI) to generate the P(III) chloride (dimHph)PCI (2). The reactivity of (dimHph)PCI (2) was investigated. Surprisingly, substitution of the chloride under some nucleophilic (KOBu^t) and electrophilic conditions (Me₃SiOTf) regenerates the parent compound (1), by proton removal from the weakly acidic CH₂N position. A related species (dimH₂ph)P (4) is produced upon thermal rearrangement of the hydride (dimHph)PH (3).The addition pyridine oxide into the solution of (2) provided the formation of phosphorus chloride oxide (5) compound.



(P11) Synthesis and Catalytic Applications of Symmetrical NCN Pincer Ligand featuring an N-Heterocyclic Carbene (NHC)

Joshua A. Clarke and Georgii Nikonov*

Brock University

A novel NHC-based, bis-oxazole NCN pincer ligand (C_5H_8NO) $CH_2(C_3H_2N_2)CH_2(C_5H_8NO)$, is synthesized and employed for the preparation of new ruthenium (II) complexes characterized by NMR. The complex (NCN)RuCl₂(PPh₃) has been tested for applications in catalytic transfer hydrogenation (TH) and shown to be moderately active in the reduction of ketones and nitriles.

(P12) Novel Tridentate N,S,N-Metal Complexes of Zinc, Aluminum, Germanium and Phosphorus

J. Lortie, G. Nikonov

Brock University

Non-innocent ligands may impart significant stabilization of reaction centres during catalytic transformations. Here we report a novel pincer NSN ligand [(DIPPN=(Ph)CH)₂S]²⁻, featuring hard and soft donor atoms and designed for internal charge transfer. It can be conveniently generated by double deprotonation of (DIPPN=(Ph)CH₂)₂S by LDA or MeLi. Reactions of [(DIPPN=(Ph)CH)₂S]²⁻ with ZnCl₂, GeCl₂*dioxane, All₃, or PCl₃ yields the respective group 12-15 compounds characterized by NMR and by X-ray structure analysis for (NSN)Ge. DMAP coordination to (NSN)Zn in THF is reversible and the activation parameters have been determined. So derivatization chemistry will be discussed.



Figure 1. Novel ZnNSN and GeNSN complexes supported by a hard & soft donor NSN ligand.

(P13) Synthesis of Unstable Homoleptic Uranium Complexes

Nikki J. Wolford, Jeffrey D. Sears and Michael L. Neidig

University of Rochester

Homoleptic organouranium complexes have been of interest since the early 1940s with the start of the Manhattan project as volatile compounds for isotope separation in the uranium enrichment processes. This focus has since shifted to obtaining a fundamental understanding of the electronic structure and bonding of uranium. Previous attempts towards synthesizing these types of alkyl complexes in the absence of stabilizing ligands have been unsuccessful due to the instability of the resulting products. Previous work in our group has utilized low temperature synthesis and crystallization techniques to determine the speciation in iron-catalyzed reactions. Using these same techniques, we have been able to access several homoleptic alkyl and aryl uranium species using lithium nucleophiles.



(P14) Preparation and Reactivity of Inversely-Polarized Phosphaalkenes Containing a Lewis Acidic N-Heterocyclic Carbene Building Block

Brandon S. Khan, Gino G. Lavoie York University

Inversely-polarized phosphaalkenes (IPPs) are adducts comprised of N-heterocyclic carbenes (NHCs) and phosphinidenes ([PR]x). IPPs are of interest due to the inversely-polarized C=P bond, which results in an electron-rich phosphorus atom. This is contrary to bond polarization predicted by Pauling electronegativity. The steric and electronic properties at phosphorus can be finely tuned through the NHC and PR building blocks. This research focuses on the use of a diacylimidazol-2-ylidene **2** as the NHC fragment. As a result of the strong π -acidity of **2**, the corresponding phosphaalkene **3** is best represented by a formal C=P double bond. We herein report an improved synthetic methodology for **3a** (R=Ph) as well as progress towards the preparation of the previously unreported hydrido derivative **3b** (R=H).



(P15) Synthesis and coordination of inversely-polarized phosphaalkene derivatives for coordination to transition metal centers as bidentate ligands.

Juan Rodriguez Villanueva and Gino G. Lavoie*

York University

The use of inversely-polarized phosphaalkenes in catalysis as spectator ligands remains widely unexplored. Therefore, we are greatly interested in demonstrating the utility of this low-valent electron rich phosphorus donor in coordination chemistry. We herein report the successful synthesis of the phosphaalkeneenolate **3** through the reaction of bromoacetophenone and 1,3-bis(2,6-diisopropylphenyl)-2-phosphanylidene-2,3-dihydro-1H-imidazole producing **2**, followed by the deprotonation using NaHMDS and the silylation using trimethylsilyl chloride. The resulting complexes will be used for the homo- and copolymerization of ethylene and polar vinyl monomers.



(P16) Exploration of $bhpH_2$ for the Synthesis and Study of Heterometallic 3d/4f Single Molecule Magnets Gabriele Delle Monache, Theocharis Stamatatos and Melanie Pilkington

Brock University

Single molecule magnets (SMMs) are discrete molecules comprised of paramagnetic coordination complexes that can be magnetized in the presence of an applied magnetic field that remain magnetized when the field is removed below their blocking temperature. SMMs have potential applications as memory storage devices as each molecule can potentially store a single bit of information. In recent years pyridyl-alkoxide ligands such as pyridine-2,6-dimethanol (pdmH₂) 1 have met with good success as bridging/chelating ligands for the preparation of high nuclearity *3d* and/or *4f* clusters with SMM properties.^{1,2} We have therefore recently turned our attention to explore the cluster chemistry of the closely related 2,6-*bis*(1-hydroxyethyl)pyridine (bhpH₂) **2**, unexplored in this field to-date. The cluster chemistry of bhpH₂ with *3d*/*4f* ions where 3d = Cu(II) and 4f = La, Gd, Tb, Dy, Ho will be presented.



Figure 1. The molecular structures of $pdmH_2$ (1) and $bhpH_2$ (2).

1. D. I. Alexandropoulos, L. Cunha-Silva, L. Pham, V. Bekiari, G. Christou and Th. C. Stamatatos, *Inorg. Chem.*, **2014**, *53*, 3220–3229.

2. X.-Q. Zhao, Y. Lan, B. Zhao, P. Cheng, C. E. Anson and A. K. Powell, Dalton Trans., 2010, 39, 4911–4917.

(P17) Catalytic Hydroarylation of Alkenes with Phenols using B(C₆F₅)₃

Jordan N. Bentley, Christopher B. Caputo*

York University

We demonstrate that tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is shown to be an effective catalyst for the hydroarylation of olefins to yield substituted phenols. This system features fast reaction times, mild conditions and good yields for a select scope of olefinic substrates and various phenols, resulting in C–C bond formation. Experimental data supports two possible mechanisms, where the Lewis acid can activate the olefin or the phenol as the first step in the catalytic mechanism.



Facile catalytic hydroarylation by B(C₆F₅)₃

(P18) New Zinc Complex for Hydrosilylation of Carbonyls

Iryna D. Alshakova, Georgii I. Nikonov*

Brock University

Zinc compounds have recently attracted increased attention as catalysts for the reduction of various functional groups of organic substrates.¹ Zinc is an inexpensive, nontoxic, and earth-abundant post-transition metal, and thus is a promising surrogate for transition metal catalysts. We prepared a new zinc complex **1** supported by a chelating NNS-ligand. **1** shows good catalytic activity in the hydrosilylation of aldehydes and ketones at elevated temperatures. Interestingly, we observed that substoichiometric amounts of methanol have a very beneficial effect on the rate of the reaction and allow for significantly higher TOFs (turn over frequency) even at room temperature. Substrate screening showed that the reaction rate strongly depends on the electron properties of substituents, with electron-withdrawing groups leading to significantly faster rates of reduction.



1. C. Boone, I. Korobkov, G. I. Nikonov, *ACS Catal.* **2013**, *3*, 2336-2340; S. Enthaler, *ACS Catal.* **2013**, *3*, 150-158; K. Revunova, G. I. Nikonov, *Dalton Trans.* **2015**, *44*, 840-866; J. L. Lortie, T. Dudding, B. M. Gabidullin, G. I. Nikonov, *ACS Catal.* **2017**, *7*, 8454-8459.

(P19) Primary Coordination Sphere Optimization of Ru-PR2NR'2 Catalysts for Alkynyl Amine Cyclization

Devon E. Chapple, James M. Stubbs, and Johanna M. Blacquiere*

Western University

N-Heterocyclic compounds are important structural motifs found in a variety of compounds such as pharmaceutical drugs and natural products.¹ Transition metal catalyzed intramolecular hydroamination of C-C multiple bonds is an atom economic route to N-heterocyclic compounds. However, low catalyst turnover numbers are problematic. Metal ligand cooperative catalysts, such as $[Ru(Cp^*)(P^R_2N^{R'}_2)(MeCN)]PF_6$ (Scheme 1), are capable of mediating proton transfer steps that give increased catalytic performance. The R' substituent has a significant impact on the basicity of the pendent amine, which must be greater than the basicity of the alkynyl amine substrate.² Systematic changes to the primary coordination sphere, such as the R substituent of the phosphine, and evaluation of the subsequent impact on catalyst performance was performed.



Figure 1. 2-Ethynylaniline cyclization catalyzed with a $[Ru(Cp^*)(P_2^RN^R)(NCMe)]PF_6$ complex.

1. Vitaku, E.; Smith, D. T.; Njardarson, J. T., J. Med. Chem. 2014, 57, 10257-10274.

2. Stubbs, J. M.; Chapple, D. E.; Boyle, P. D.; Blacquiere, J. M., ChemCatChem 2018, 10, 3694-3702.

(P20) Combining Synthesis and Structure-Property Analysis to Improve Photoelectrochemical Behaviour Yutong Liu, R. D. L. Smith*

University of Waterloo

Efforts to improve the efficiency of photoelectrocatalytic reactions on semiconducting photoelectrode materials routinely focus on the analysis of photophysics, or on the fabrication of complex material architectures. The discontinuity of experimental results and mechanistic proposals found in the literature reflect a lack of detailed structural analysis, for example the analysis of specific structural defects or mixed phases. Using Fe-based photoanode materials as a prototypical material, this project aims to identify specific types of structural defects or contaminating phases and correlate their presence to photoelectrocatalytic behavior parameters. Hematite films are prepared by variation of fabrication protocols. and parameters describing their structure will be correlated to photoelectrochemical behavior to improve fundamental understanding and guide optimization of synthetic protocols.

(P21) Surface-Based Molecular Reactions for Nano-Scale Deposition of Elements

Majeda Al Hareri, David J. H. Emslie

McMaster University

Atomic layer deposition (ALD) is a technique by which surface-based reactions between a metal (or non-metal) precursor and coreagent (e.g. H₂O, O₂) in the vapour phase yield highly uniform and conformal (ultra-)thin films. The self-limiting nature of these reactions allows for the thickness of the film to be solely controlled by the number of 'precursor - purge - coreagent - purge' cycles.¹ A potential precursor molecule must display volatility, thermal stability, and high reactivity towards the chosen coreagent.¹ These criteria are experimentally investigated before proceeding towards reactor studies, which involves conducting surface-based reactions using appropriate delivery and substrate temperatures and subsequent characterization of the thin films. Precursor design and film characterizations have been conducted in this research for the development of elemental thin films by ALD at low deposition temperatures.



[1] D.J.H. Emslie, P. Chadha, J.S. Price, Coord. Chem. Rev. 2013, 257, 3282-3296.

(P22) Effect of Europium Doping and Annealing Temperature on ZnO Photocatalyt-ic Activity

F. Oussta^a, R. Marin^a, S.N. Katea^b, G. Westin^b, and E. Hemmer^{a*}

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Zinc oxide, ZnO, is a wide band-gap semiconductor that is attracting increasing interest due to the pleth-ora of structural shapes and potential applications, including energy harvesting, water splitting, and s photocatalysis. For the latter, sponge-like micro/nanostructures are promising candidates due to their large surface. The goal of this study is to assess the effect of the annealing temperature and europium-doping on the photocatalytic activity of ZnO sponges. Therefore, their optical properties were determined by photoluminescence spectroscopy, followed by an assessment of their photocatalytic activity, using Rhodamine B (RhB) as a model dye. A strong correlation between the ZnO photoluminescence and photocatalytic performance was found, which is governed by thermally-induced material's structural properties and europium-doping.



Figure 1. Under UV-excitation, undoped and europium-doped ZnO photocatalytically degrades organic model dye RhB.

(P23) An Unexpected "Step-Conjugated" Biphosphole via Unique P-P Bond Formation

Nayanthara Asok, Zisu Wang, Joshua Gaffen, Yael Gottlieb, Wenhua Bi, Chris Gendy, Roman Dobrovetsky* and Thomas Baumgartner*

York University

A convenient synthesis for P-P bridged biphospholes is reported by effective coupling from P-amino phosphole mediated by the hard Lewis acid BF₃. The dimeric species communicate electronically through a π - σ - π conjugation in step-wise fashion which is attributed to inherent pyramidal geometry of the phosphorus centers. Computational verifications were conducted to predict a suitable reaction mechanism for dimerization. The out of plane P-P σ bond and head to head conformation contributes to intriguing opto-electronic properties of these molecules, prompting their utilisation in organoelectronic applications. Functionalization of the Phosphorus center of biphosphole by oxidation was achieved to study the photophysical properties of the material.

(P24) Light and Moisture Stable Hypercoordinate Tin Polymers

Gloria D'Amaral^a, Jeffrey Pau^a, Alan J. Lough^b, Daniel A. Foucher^a

a Ryerson University, b University of Toronto

Polystannanes are a unique class of polymers that consist of a backbone of covalently linked tin atoms. These materials are inherently semi-conductive, which may be utilized for molecular wires. Unfortunately, all current examples of polystannanes display an extreme sensitivity to light and moisture. Recently we have demonstrated significant moisture and light stability improvements when an increase in electron density around the tin center is afforded via hypercoordination. This project focusses on the synthesis of two asymmetrical polystannanes prepared by transition metal-catalyzed dehydropolymerization of dihydrido(aryl)alkylstannanes. The first is a semi-crystalline light and moisture stable polystannane with NMR (¹¹⁹Sn) evidence of prominent Sn \leftarrow O hypercoordination along the polymer backbone. The second is a lower molecular weight, functionally tosylated four coordinate polystannane with no evidence of hypercoordination, but a useful polymeric intermediate to gain access to functional polystannanes.



Figure 1. Proposed structure of light and moisture stable polystannane.

(P25) Synthesis of Iron PR2NR'2 Complexes for Cyclization Catalysis

Benjamin J. Bridge, James M. Stubbs, Johanna M. Blacquiere*

University of Western Ontario

Catalysis with iron offers a significant advantage of cost and availability over precious metal counterparts. Furthermore, low toxicity allows a higher tolerance of residual iron to be present in pharmaceutical products.¹ Unfortunately, homogenous catalysis with this common metal has not yet achieved a broad scope of useful applications, especially when compared to other group 8 elements such as ruthenium. Herein we report a set of four cationic iron complexes with $P^R_2 N^{R'}_2$ -type ligands (R = Cy, Ph; R' = Ph) that are analogous to ruthenium catalysts previously developed within the group.² Preliminary evidence has shown that these homogenous iron catalysts are able to catalyze C-N bond formation through the cyclization of 2-ethynylaniline to indole.



1. Furster, A. ACS Cent. Sci. 2016, 2, 778-789.

2. Stubbs, J. M.; Chapple, D. E.; Boyle, P. D.; Blacquiere, J. M. Chem. Cat. Chem. 2018, 10, 3694-3702.

(P26) Thermoelectric Performance of (Sn,Ge)Te materials

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A series of $Sn_{1-x}Ge_xTe$ (x=0.05-0.95) compounds were prepared by melting followed by spark plasma sintering (SPS). For x i 0.5, the $Sn_{1-x}Ge_xTe$ phases adopt the cubic structure (*Fm-3m*), while for $x \ge 0$, they crystallize with the rhombohedral structure (*R3m*). Ge incorporation improves both power factor and thermal conductivity of $Sn_{1-x}Ge_xTe$. Decrease in the thermal conductivity can be explained by an increase phonon scattering caused by point defects. For the cubic phases, the maximum *ZT* value of 0.81 is achieved for $Sn_{0.8}Ge_{0.2}Te$ at 600°C, with the average ZT value being 0.35 over the 100-600°C temperature range. For the rhombohedral phases, the maximum ZT value of 0.86 is achieved by $Ge_{0.95}Sn_{0.05}Te$ at 500°C, and the average ZT value is 0.39 over the 100-500°C temperature range.

(P27) Development of Experimental Scaling Relations for Electrochemical CO₂ Reduction

E. P. Alsac, R. D. L. Smith*

University of Waterloo

In order to exploit excess electricity produced from wind and solar, electrocatalysis could be an ideal solution. Among potential electrocatalytic methods, CO₂ reduction draws attention for producing high value products like carbon monoxide, and hydrocarbons. However, ECR involves multi-electron steps, and hence there are vast numbers of possible ECR products. To increase selectivity of the catalyst, several experimental and theoretical strategies have been improved. In this study, some strategies for reinforcing the relationship between theory and experiment to guide the development of selective ECR catalysis will be shown.

(P28) Thermoelectric Properties of Quaternary Copper Chalcogenides

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Energy efficiency is vital in today's society due to the depletion of natural resources. In this regard, thermoelectric materials are valuable since they convert waste heat into electricity. A materials' thermoelectric efficiency is governed by the figure of merit (*zT*). Copper chalcogenides are among the most promising thermoelectric materials at elevated temperatures, caused by an extraordinarily low thermal conductivity because of disordered copper ions, for example in β -Cu_{2-x}Se. Unfortunately, the application of β -Cu_{2-x}Se is hindered by the migration of the Cu ions causing material decay. Therefore, additional large elements were used to impede migration. Here, we are presenting the physical properties of Ba₃Cu_{16-x}(S,Te)₁₁ with a complex crystal structure and a maximum *zT* value of 0.88 for Ba₃Cu_{15.3}Sr_{.5}Te_{3.5}.



Figure 1. Thermoelectric figure-of-merit of $Ba_3Cu_{16-x}(S,Te)_{11}$.

(P29) Thermoelectric Properties of Hot Pressed CaMnO₃

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University of Waterloo

Thermoelectric (TE) materials are functional materials that convert thermal energy and electrical energy into each other. The efficiency of TE materials can be evaluated by their dimensionless figure of merit, zT: the higher zT, the higher the efficiency. TE devices are composed of both p- and n-type TE materials; however, in general, the performance of the investigated oxidic p-type TE materials is superior to that of n-type materials so far. CaMnO₃ is considered as a potential, environmental-friendly n-type TE material. Here, we report a new method to densify CaMnO₃ powder, and compare the electrical conductivity, the Seebeck coefficient, and the power factor of the hot pressed sample to the properties of the samples densified via other methods.

(P30) Incorporation of Indium into the Zn₁₃Sb₁₀ Thermoelectric Material

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The composition of the In-substituted $Zn_{13}Sb_{10}$ phases follows the $Zn_{13-1.5x}In_xSb_{10}$ charge-balanced formula and the reduction in the Zn content is due to the In^{3+} oxidation state, compared to the Zn^{2+} oxidation state. Zn deficiency in the In-doped samples is supported by the X-ray powder diffraction, EDS elemental analyses and single-crystal X-ray diffraction. The heat capacity measurements indicate that incorporation of In suppresses the low temperature phase transitions, which could be due to the disappearance of some interstitial Zn atoms and/or difficulty in ordering the remaining ones. The thermal conductivity reveals changes in the phonon scattering pathways upon In doping; dominance of point defect scattering in $Zn_{13-1.5x}In_xSb_{10}$ vs. Umklapp scattering in the pristine $Zn_{13}Sb_{10}$.

(P31) Crystal Structure of new Magnesium Fluorogermanates

Sergei Novikov, Yurij Mozharivskyj*

McMaster University

High-temperature solid state reactions and flux growth were employed to obtain crystals of two new phases, Mg₃GeO₄F₂ and Mg₂Pb₂Ge₂O₇F₂. Single crystal X-ray diffraction showed that the Mg₃GeO₄F₂ phase adopts the orthorhombic symmetry, *Pnma*, with *a* = 10.304(2), *b* = 8.7471(17), *c* = 4.8221(10) Å, V = 434.62(15) Å³. The structure of Mg₃GeO₄F₂ is built from the GeO₄ and MgO₄F₂ polyhedra and resembles the structure of mineral norbergite, Mg₃SiO₄(F,OH)₂. The Mg₂Pb₂Ge₂O₇F₂ phase crystallize with the *Pbcn* space group, *a* = 7.2258(15), *b* = 11.139(2), *c* = 10.262(2) Å. V = 826.0(3) Å³. The Mg₂Pb₂Ge₂O₇F₂ structure is similar to that of the silicate minerals, Pb₂R^{III}₂Si₂O₉. High-temperature powder X-ray diffraction was used to investigate the reactions between Mg₂GeO₄ and MgF₂ in the 50-1200°C range.

(P32) Hydrogenase Models: Dehalogenation and Remediation

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Synthetic hydrogenase models **1H** derived from methylenetetrahydrofolate (MTHF) **2H** and Thauer's hydrogenase **3H** are capable of reducing halocarbons R-X to hydrocarbons R-H.[1]. Like dehalohydrogenase enzymes, their model compounds are promising for the remediation of halocarbons. Treatment of the notorious pesticide DDT with MTHF models produces the previously unexplained spectrum of dechlorinated metabolites.



[1]. Denk, M. K.; Milutinovic, N. S.; Marczenko, K. M.; Sadowski, N. M; Paschos, A. Chem. Sci., 2017, 8, 1883-1887.

(P33) Biomimetic 2Fe2S clusters bearing o-phenylenediamine ligands

Qiuming Liang, and Datong Song* University of Toronto

Binuclear iron–sulfur clusters $[2Fe-2S]^n$, such as those in ferredoxin- and Rieske-type proteins, are ubiquitous and multipurpose biological cofactors in nature.¹ The primary function of these clusters is one-electron transfer, which shuttles between the all-ferric $[2Fe-2S]^{2+}$ and the mixed-valence $[2Fe-2S]^{+1}$ states.² The study of biomimetic clusters helps to elucidate how simpler ligands influence the reduction potentials. The use of redox active ligands can provide facile access to the highly reduced diferrous $[2Fe-2S]^0$ state that is otherwise difficult to isolate. In this poster, we present the synthesis of a series of $[2Fe-2S]^n$ clusters (n=2+, 1+, 0) that are supported by two redox active *o*-phenylenediamide ligands.



1. H. Beinert, R. H. Holm, E. Mînck, *Science* **1997**, *277*, 653.

2. E. I. Solomon, X. Xie, A. Dey, Chem. Soc. Rev. 2008, 37, 623.

(P34) Ligand acidity constants of PF₃ and N-Heterocyclic Carbene ligands calculated by density functional theory in Iron(II) Hydride complexes

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University of Toronto

The pK_a of metal-hydride intermediates a notable characteristic in the design of catalysts. The acid dissociation constant (K_a) in THF can be approximated using the Ligand Acidity Constant (LAC) method which involves adding acidity constants, A_L, for each ligand in the conjugate base complex and correcting for its charge and the stability of the hydride complexes. Here, Density Functional Theory (DFT) is used to calculate the p K_a of 26 iron hydrides with formula [FeH(CO)_(5-x)(L)_x]⁺ (L = PF₃ or *N*-heterocyclic carbene (NHC)), yielding linear plots of p K_a of [FeH(CO)_(5-x)(L)_x]⁺ vs x from which A_L values for PF₃ and 6 NHC ligands are derived. This work explores how ligand electronics and NHC wing-tip sterics affect ligand donor strength and A_L.



Figure 1. Acidity constants for *N*-heterocyclic carbenes (NHC).

(P35) Development of Homochiral Transition Metal N-Heterocyclic Carbene Complexes for Asymmetric Hydrogenation of Ketones and Imines

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Hydrogenation of polar unsaturated bonds to afford enantioenriched products is highly sought out in the agricultural, pharmaceutical, and fine chemical industries. Recent developments in our group have uncovered a class of homochiral bidentate N-heterocyclic carbene (NHC) ligands which have seen use in extremely active ruthenium AH catalysts.² This scaffold provides interesting avenues for ligand modification to multidentate NHC ligands, which is expected to increase the structural rigidity at key catalytic sites. In addition, chiral triazolium salts have been shown to be isolable with a different synthetic protocol. The electronic and steric properties of these corresponding NHCs may play a key role in the enantiodetermining step in catalysis. Herein details progress towards homochiral transition metal NHC complexes for the AH of prochiral ketones and imines.



(1) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 13529–13530.

(2) Wan, K. Y.; Sung, M. M. H.; Lough, A. J.; Morris, R. H. ACS Catal. 2017, 7, 6827–6842.

(P36) Multidentate Ligands for Heavy Metal Sequestration

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Carbohydrate feedstocks produce several useful building blocks for commercial products. Hydroxymethylfurfural (HMF) is produced as a dehydrogenation product of fructose, however it does not see significant commercial use. Using HMF as a building block, a diverse family of multidentate ligands have been synthesized. Short and sweet synthesis of these ligands show attractive applications for large-scale production. Heavy metal binding studies with CoCl₂•6H₂O, and UO₂(NO₃)₂•6H₂O so far have shown rapid reactions with a diimine-furan ligand (NON ligand; Figure 1).



R=H, Polymer support

Figure 1. NON ligand for heavy metal sequestration.

(P37) The Reactions of Iso-Chalcogenazole N-Oxides with Pd(II)

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We have shown that it is possible to take advantage of Te...O sigma-hole interactions ("chalcogen bonds") to spontaneously assemble macrocyclic tetramers and hexamers, that exist in equilibrium in solution, from iso-tellurazole N-oxides. In spite of the electron donor ability of the oxygen atom and electron accepting ability of tellurium, these macrocyclic tetramers are capable of making complexes towards heavy d⁸ ions such as Pd(II), Pt(II).^{1,2} Benzo-iso-selenazole oxide however undergoes solvent addition and rearrangement upon reaction with Pd(II). The relative strength of the Te...O and Se...O sigma-hole interactions is a major factor in the contrasting behavior of these ligands.



1. P. C. Ho, P. Szydlowski, J. Sinclair, P. J. W. Elder, J. Kübel, C. Gendy, L. M. Lee, H. Jenkins, J. F. Britten, D. R. Morim and I. Vargas-Baca, *Nat. Commun.*, **2016**, *7*, 11299.

2. P. C. Ho, J. Rafique, J. Lee, M. L. Lee, H. A. Jenkins, J. F. Britten, A. L. Braga and I. Vargas-Baca, Dalton Trans, 2017, 46, 6570.

(P38) Halogenation of Iso-Tellurazole N-Oxides

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Iso-tellurazole N-oxides are heterocycles that self-assemble through short Te...O secondary bonding interactions (also known as chalcogen bond when centred on group-16 elements) forming macrocyclic tetramers and hexamers which exist in equilibrium in solution. These macrocycles display the properties of typical covalently-bound macrocycles, they coordinate transition metal ions, host small molecules, or form adducts with fullerenes. Here we will demonstrate that the macrocycles are stable to partial (Figure) or full halogenation of the tellurium atoms; moreover, such oxidation strengthens the chalcogen bonding interactions.



1. P.C. Ho, P. Szydlowski, P.J.W. Elder, J. Sinclair, J. Kübel, C. Gendy, L.M. Lee, H. Jenkins, J. F. Britten, D. R. Morim, I. Vargas-Baca, *Nat. Commun.*, **2016**, *7*, 11299.

(P39) Coordination Chemistry of Iso-Tellurazole N-Oxides with d¹⁰ Transition Metal Ions

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McMaster University

It is possible to take advantage of Te...O secondary bonding interactions ("chalcogen bonds") to spontaneously assemble macrocyclic tetramers and hexamers from iso-tellurazole *N*-oxides. The tetramers act as macrocyclic ligands towards d⁸ metal ions.¹ We will present the coordination complexes of iso-tellurazole *N*-oxide macrocycles with d¹⁰ coinage metal-ions. While Cu(I) binds the tetramer forming a square pyramidal complex. Ag(I) and Au(I) form binuclear complexes with the hexamer and tetramer, respectively.



R=Ph, ^tBu,3,5-(^tBu)₂C₆H₃

1. Ho, P. C.; Szydlowski, P.; Sinclair, J.; Elder, P. J. W.; Kübel, J.; Gendy, C.; Lee, L. M.; Jenkins, H.; Britten, J. F.; Morim, D. R.; Vargas-Baca, I. *Nat. Commun.* **2016**, *7*, 11299.

(P40) Optical Properties and Crystal Structures of Selenogermanates

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Noncentrosymmetric (NCS) chalcogenides have been extensively studied for applications as nonlinear optical (NLO) materials in recent years. γ -Sr₂GeSe₄was reported to adopt the NCS orthorhombic space group *Ama2*. The new crystal structure of Pb₂GeSe₄ is isotypic with the high temperature structure of Pb₂GeS₄, adopting the NCS cubic space group *I-43d*. Subsequently, the selenides Sr_{2-x}Pb_xGeSe₄ were synthesized with x = 0, 0.7, 1.75, and 2. The phases with x = 0 and 0.7 adopt the γ -Sr₂GeSe₄ structure, whereas phases with x = 1.75 and 2 adopt the high temperature Pb₂GeS₄ structure. The refractive index and second harmonic generation (SHG) tensor elements have been calculated using DFT.

(P41) Exploring P-H Bond Additions to Organic Substrates

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Organophosphines are widely used in industry as ligands for catalysis in the production of higher value chemical products. $PH_3(g)$ is used in the preparation of organophosphines and phosphonium salt derivatives, where there is a substantial market in the semiconductor and pesticides industries, however the use of PH_3 is rare in academia. Furthermore, the range of reaction partners is small and usually involves an olefin. Our current work aims to expand the scope of PH_3 chemistry towards the synthesis of new and valuable organophosphines via P-H bond addition using PH_3 promoted via addition of a Lewis acid or using radical initiators. Our methods will not only be applied to olefin bearing natural products but also to benzynes and Michael acceptors.



(P42) Monolayer Terpyridine-Based Electrochromic Materials on Fluorine-Doped Tin Oxide (FTO) Nanosurfaces: Effect of Fluorine Doping and Extended Conjugation.

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This study presents the development of a series of novel electrochromic materials (ECM's) that demonstrate excellent colouration efficiency, redox activity and significant lifetime stability. The novel ECM's were designed using monolayers of various 2,2':6',2-terpyridine (Tpy) Fe(II) complexes on fluorine-doped tin oxide nanoparticles (FTO NP's) solid supports. Each terpyridine ligand contained a 4'-phenyl pyridine-derived substituent on the 4' position including pyridin-4-yl vinyl and pyridin-4-yl ethyl substituents. The conductive thick solid supports were prepared by screen-printing FTO NP's onto FTO/glass substrates. Functionalization of the FTO solid support allowed chemisorbtion of the Fe(Tpy)₂²+ complexes onto a chlorobenzyl-terminated silane layer. Cyclic voltammetry, chronoamperometry, UV-visible spectrophotometry and spectroelectrochromic analysis were used to characterize each ECM. CV results indicate good reversibility and fast switching kinetics for the ECM's. The ECM's also showed distinct colour changes depending on the oxidation state of iron in the metal terpyridine complex.

(P43) Investigating CO Guest Interactions in SDB-based Metal-Organic Frameworks Using Solid-State Nuclear Magnetic Resonance Spectroscopy

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Metal-organic frameworks (MOFs) are promising CO capture and separation materials. SDB-based (SDB = 4,4'-sulfonyldibenzoate) MOFs are particularly attractive due to their high gas adsorption ability in the presence of moisture. Here, CO adsorption in PbSDB and CdSDB are investigated using solid-state nuclear magnetic resonance (SSNMR) spectroscopy. These MOFs readily captured CO and the adsorption mechanism was analogous to that of CO₂. Guest motions were detected, and a motional model was deduced. The motional data was compared to those reported for CO₂ in PbSDB and CdSDB. Differences in adsorption strength was observed, indicating that these MOFs can separate CO from CO₂. PbSDB and CdSDB also gave a weaker CO binding compared to other MOFs, suggesting that they can be efficiently regenerated.



Figure 1. (a) The extended crystal structure of PbSDB. (b) The experimental static ¹³C SSNMR spectrum of ¹³CO in PbSDB acquired at 293 K and 9.4 T (black trace) and the simulated spectra (green and red traces).

(P44) Exploring Bench-Stable Frustrated Lewis Pair Chemistry: Reactivity of Proazaphosphatranes and Phosphines with Boranes and Bench-Stable Carbocation Salts

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 $B(C_6F_5)_3$ and $P(MeNCH_2CH_2)_3N$ form a classical Lewis adduct, $(C_6F_5)_3BP(MeNCH_2CH_2)_3N$. Although the adduct does not exhibit spectroscopic evidence of dissociation into its constituent Lewis acid and base, products of FLP addition reactions are observed with PhNCO, PhCH_2N_3, PhNSO, and CO_2. Recently, a bench-stable trityl ion 1 (Figure 1) and P(MeNCH_2CH_2)_3N were found to form a classical "phosphonium-like" Lewis adduct. Despite not exhibiting spectroscopic evidence of dissociation, the adduct induces heterolytic splitting of H₂. When 1 and other bench-stable trityl ions were combined with $P(t-Bu)_3$ and $P(o-tol)_3$, FLPs capable of heterolytic splitting of H₂ were generated and, in at least one case, reversible activation of H₂ was observed. These recent findings open up potential avenues towards the development of bench-stable FLP chemistry.



Figure 1. Reactions of a bench-stable trityl ion 1 with different bases to generate FLPs capable of heterolytic cleavage of H₂.

(P45) A novel organic radical exhibiting magnetic bistability

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Magnetic bistability, resulting in rate-independent magnetic hysteresis, is a technologically relevant property because it imparts memory. Materials that exhibit this type of behaviour are important for possible device, sensor, and safety equipment design. We have successfully synthesized a new organic radical HbimDTDA (4-(2'-benzimidazolyl)-1,2,3,5-dithiadiazolyl) that exhibits rate-independent hysteresis via a crystal-to-crystal phase transition. The material switches between diamagnetic and paramagnetic states in response to temperature by the reversible breaking and formation of pancake bonds. Magnetic and structural data for HbimDTDA that illustrate hysteretic behaviour are presented. Initial efforts in the development of Fe(II)-based spin-crossover materials using HbimDTDA as a ligand and the preparation of a selenium for sulfur analog HbimDSDA will also be described.



Figure 1. Temperature dependence of the χ T product of HbimDTDA at an applied field of 10 000 Oe with varying rates of temperature increase.

(P46) Ligand and Electronic Effects on Copper-AryInitroso Self-Assembly as a Mimic of Cu/O2 intermediates Farshid FE. Effaty, Mohammad Sharif MSA. Askari, Xavier XO. Ottenwaelder*

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Arylnitroso species (nitrosoarenes, ArNO) are redox-active species that present great structural and electronic versatility. Their metal complexes are stable mimics of O_2 and HNO complexes transiently found in nature and in catalytic cycles. This stability allows for a systematic survey of the structure and redox state of ArNO metal complexes. Here, a series of complexes was prepared by self-assembly of copper(I) and ArNO precursors (scheme).¹ The nature of the copper(I) supporting ligand (bi-, tri- or tetradentate as well as secondary vs. tertiary amine donors) and the electronic nature of the ArNO species (electron-donating or withdrawing substituents) were varied. The stoichiometry of the reaction, the topology and the electronic properties of the adducts were characterized by means of UV-vis spectroscopy, X-ray diffraction and DFT methods. The more electron-rich ligands and the more electron-poor ArNO species lead to an inner-sphere electron-transfer and formation of copper(II)-(arylnitrosyl radical) complexes, with a linkage topology that depends on the denticity of the supporting ligand. In particular, the binuclear complex shown in the scheme is structurally and electronically similar to side-on peroxo species known in Cu/O₂ chemistry. The complex reacts with di-*tert*-butylphenolate via a unprecedented, controlled nitrene transfer.² Overall, these results provide a canvas by which to predict the outcome of similar self-assembled redox reactions.



(P47) Correlating Ion mobility and Single Crystal Structure in Na-ion Chalcogenide-Based Solid-State Fast ion conductors

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All solid-state batteries are receiving considerable attention because of their better safety and higher energy density compared to conventional Li-ion batteries. By replacing the flammable organic liquid electrolytes with inorganic solid-state electrolytes, ASSBs have the potential to overcome the safety concerns of liquid cells. Herein, we present a sodium solid electrolyte, Na₁₁Sn₂SbS₁₂, that is isostructural with Na₁₁Sn₂PS₁₂ and exhibits a very good, albeit lower ion conductivity of 0.58 mS•cm⁻¹ at 25°C. Single-crystal X-ray diffraction data reveals the existence of a partially occupied interstitial Na site in both sodium materials and identifies the reasons responsible for their two-fold difference in conductivity. The findings reveal the subtle factors that underlie fast-ion conduction and provide unique understanding for designing future fast-ion conductors.



Figure 1. Rietveld refinement of XRD data for $Na_{11}Sn_2SbS_{12}$. The black circles correspond to the data points, the red line denotes the calculated pattern, and the difference map is shown in blue. Olive vertical ticks correspond to Bragg reflections. Two unknown tiny impurity peaks (at 15° and 30°) were excluded from the refinement. The inset: View of the structure of $Na_{11}Sn_2SbS_{12}$ along [001].

(P48) N-heterocyclic carbenes as chemical etchants for Cu metal and its oxides

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Due to its high abundance, low cost and low bulk resistivity, copper metal is commonly used to produce microelectronic devices. Unfortunately, under ambient conditions copper metal is prone to oxidation, resulting in defects that reduce device performance. These defects can be removed through chemical mechanical polishing, however this technique is difficult for copper due to its high malleability. An alternative strategy is to develop molecular surfactants that lower the surface binding energies of excess metals or metal oxides, permitting atomic-level chemical etching without mechanical polishing.



(P49) Investigating highly conductive solid electrolyte materials

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All-solid-state Li-ion batteries (ASS-LIBs) implement a solid electrolyte which improves volumetric and gravimetric energy density while possessing superior safety and stability through elimination of the flammable organic solvent that is present in traditional LiBs. The development of highly efficient ASS-LIBs is greatly dependent on the identification and continued research of suitable conductive solid electrolytes, which possess high RT ionic conductivities. Various sulfide compounds have exhibited high ionic conductivity. One such ion conductor is lithium-argyrodite Li₆PS₅X (X=CI and Br). Both the high ionic conductivities (10⁻³ to 10⁻² S/cm) and the large electrochemical stability window (up to 7 V vs. lithium) of these class of materials make them a very promising candidate in ASSB.

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