49th Inorganic Discussion Weekend

November 11 – 13, 2016

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Itinerary

Friday, November 11, 2016

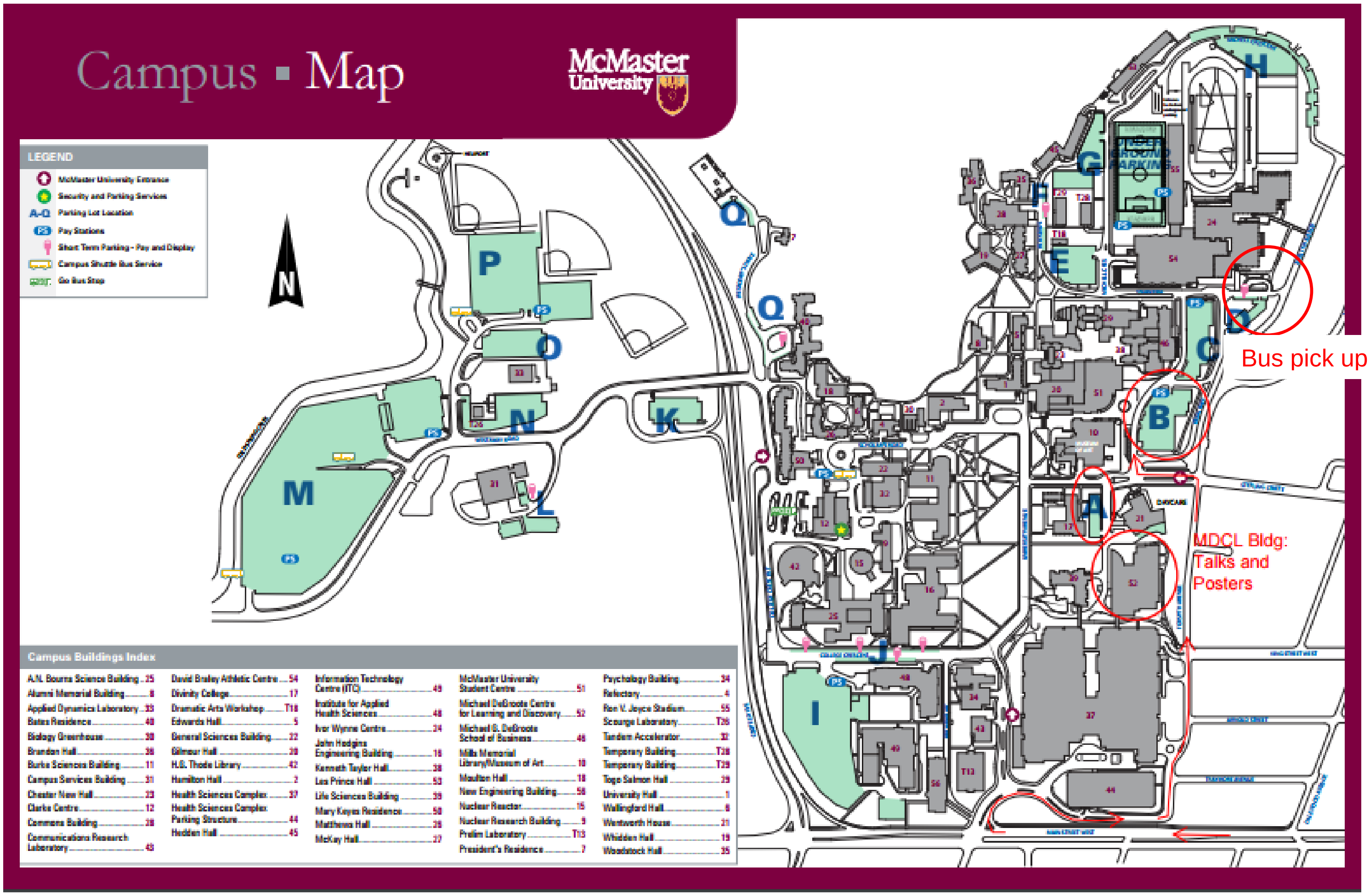
1900 - 2200	*Mixer*	*Gown & Gavel Pub* *(24 Hess St. South)*

Saturday, November 12, 2016

0800 - 0900	*Registration*	*MDCL 1305 Hallway*
0900 - 0920	*Opening Remarks*	*MDCL 1305*
0920 - 1020	*Plenary Lecture*	*MDCL 1305*
1020 - 1040	*Break*	*MDCL (Southeast Section)*
1040 - 1200	*Oral Session 1*	*MDCL 1305/1309*
1200 - 1300	*Lunch*	*MDCL (Southeast Section)*
1300 - 1420	*Oral Session 2*	*MDCL 1305/1309*
1420 - 1430	*Break (Poster Setup)*	*MDCL (Southeast Section)*
1430 - 1550	*Oral Session 3*	*MDCL 1305/1309*
1550 - 1600	*Break (Poster Setup)*	*MDCL (Southeast Section)*
1600 - 1700	*Plenary Lecture 2*	*MDCL 1305*
1700 - 1900	*Poster Session*	*MDCL (Southeast Section)*
1930 - 2200	*Banquet*	*Dundas Valley Golf and Curling Club* *(10 Woodleys Ln.)*

Sunday, November 13, 2016

0830 - 0900	*Morning Break*	*MDCL (Southeast Section)*
0900 - 1020	*Oral Session 4*	*MDCL 1305/1309*
1020 - 1040	*Break*	*MDCL (Southeast Section)*
1040 - 1200	*Oral Session 5*	*MDCL 1305/1309*
1215 - 1245	*Closing Remarks and Awards*	*MDCL 1305*

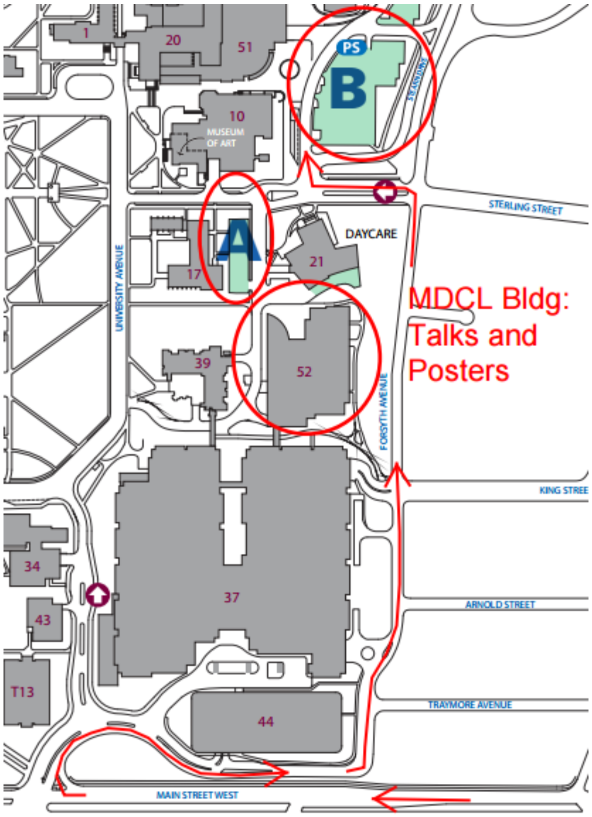


LEGEND

⇧	McMaster University Entrance
★	Security and Parking Services
A–Q	Parking Lot Location
PS	Pay Stations
📍	Short Term Parking - Pay and Display
🚌	Campus Shuttle Bus Service
🚌	Go Bus Stop

Campus Buildings Index

A.N. Bourns Science Building	25
Alumni Memorial Building	8
Applied Dynamics Laboratory	33
Bates Residence	40
Biology Greenhouse	30
Brandon Hall	26
Burke Sciences Building	11
Campus Services Building	31
Chester New Hall	23
Clarke Centre	12
Commons Building	28
Communications Research Laboratory	43
David Braley Athletic Centre	54
Divinity College	17
Dramatic Arts Workshop	T18
Edwards Hall	5
General Sciences Building	22
Gilmour Hall	20
H.G. Thode Library	42
Hamilton Hall	2
Health Sciences Complex	37
Health Sciences Complex Parking Structure	44
Hedden Hall	45
Information Technology Centre (ITC)	49
Institute for Applied Health Sciences	48
Ivor Wynne Centre	24
John Hodgins Engineering Building	16
Kenneth Taylor Hall	38
Les Prince Hall	53
Life Sciences Building	39
Mary Keyes Residence	50
Matthews Hall	28
McKay Hall	27
McMaster University Student Centre	51
Michael DeGroote Centre for Learning and Discovery	52
Michael G. DeGroote School of Business	46
Mills Memorial Library/Museum of Art	10
Moulton Hall	18
New Engineering Building	58
Nuclear Reactor	15
Nuclear Research Building	9
Prelim Laboratory	T13
President's Residence	7
Psychology Building	34
Refectory	4
Ron V. Joyce Stadium	55
Scourge Laboratory	T26
Tandem Accelerator	32
Temporary Building	T28
Temporary Building	T29
Togo Salmon Hall	29
University Hall	1
Wallingford Hall	6
Wentworth House	21
Whidden Hall	19
Woodstock Hall	35



If you are driving from the North (e.g. Toronto)

1. Take the QEW highway towards Hamilton; later, Highway 403 merges with the QEW highway.
2. After Burlington, take Highway 403 to downtown Hamilton (do not follow the QEW highway, which splits and goes east to Niagara Falls).
3. Take the Main Street West (not East) exit 69A.
4. At the traffic signal turn left onto Main Street West. Proceed to McMaster, which will be on your right.
5. Turn right onto University Avenue at the traffic light. The McMaster Hospital will be on your right (building 37).
6. Loop around the hospital and go till the Sterling Street. Turn left on the Sterling Street.
7. You can park in Lot A and B. **$7.00/day flat rate** applies for Saturday and Sunday.

Note: Avoid taking Highway 407. It is an expensive toll way.

If you are driving from theSouth/West (e.g. London)

1. Take Highway 4003towards Hamilton.
2. Take Exit 69 for Aberdeen Avenue.
3. At the traffic signal turn left (north) onto Longwood Rd S.
4 . At the traffic light turn left onto Main Street West. Proceed to McMaster which will be on your right. (Follow steps 5-7)

Plenary Lecturer – Dr. Risto S. Laitinen

Professor
Laboratory of Inorganic Chemistry, University of Oulu, Oulu Finland

Risto Laitinen received his Ph.D. in 1982 in Helsinki University of Technology (Finland). He joined University of Oulu (Finland) in 1988, first as Associate Professor of Inorganic and Analytical Chemistry, and since 1993 as Professor of Inorganic and Analytical Chemistry. He has served as Head of Chemistry Department in 1993-1999, 2003-2008, and 2010-2013. In 1984-1985 he was an Alexander von Humbold research fellow in Technische Universität Berlin (Germany). His research interests lie in synthetic, structural, and computational chemistry of sulfur, selenium, and tellurium. He has collaborated extensively with several research groups in different Canadian universities and is a constant visitor in Canada. He has long been involved in IUPAC (Member of Union Advisory Board 2004-2005, secretary, member, and national representative of Commission on Nomenclature of Inorganic Chemistry 1981-2001, and a titular member and secretary in Division of Chemical Nomenclature and Structure Representation 2015-).

Notes

Formation of Sulfur and Selenium Imides *via* Cyclocondensation and Cyclodimerization

Risto S. Laitinen

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Cyclocondensation reactions between primary amines and SCl_2 or S_2Cl_2 afford eight-membered rings, e.g. 1,3,5,7-$S_4(NMe)_4$,[1] or the six-membered rings 1,4-$S_4(NR)_2$,[2] respectively. By contrast, a complicated mixture of products is formed upon cyclocondensation of $^tBuNH_2$ with $SeCl_2$. A variety of cyclic selenium imides with the ring sizes 6-8 and 15, as well as the acyclic imido selenium dichlorides $ClSe[N(^tBu)Se]_nCl$ (n = 1-3), have been isolated from these mixtures and identified by a combination of ^{77}Se NMR spectroscopy and single crystal XRD.[3] The product distribution is dependent on the molar ratio and the concentration of the reagents.[4] $ClSe[N(^tBu)Se]_2Cl$ has been found to be a bifunctional reagent and concurrently affords 1,3-$Se_3(N^tBu)_2$ and 1,3,5-$Se_3(N^tBu)_3$ upon treatment with $^tBuNH_2$ in THF. Cyclic selenium imides are generated from this acyclic precursor either by reduction or by nucleophilic substitution.[3d] The imidoselenium dichlorides are likely intermediates in the formation of the cyclic selenium imides from $^tBuNH_2$ and $SeCl_2$.

The [2+2] cyclodimerization of chalcogen diimides $E(NR)_2$ (E = S, Se; R = alkyl, aryl) to form the dimers $RNE(\mu\text{-}NR)_2ENR$ is endergonic for sulfur diimides, approximately energy-neutral for selenium diimides, and spontaneous for tellurium diimides.[4,5] Although the monomeric structure of $Se(NAd)_2$ in the solid state has been established,[6] selenium(IV) diimides undergo thermal decomposition in solution to give a mixture of cyclic selenium imides.[3b,7] It has recently been observed that Group 12 metal dichlorides assist the cyclodimerization of $Se(N^tBu)_2$.[8] Once formed, the dimer is kinetically stable due to a relatively high energy barrier towards dissociation.

[1] (a) Stone, B. D.; Nielsen, M. L., *J. Am. Chem. Soc*. (1959), **81**, 3580. (b) Macdonald, A. L.; Trotter, J., *J. Can. Chem.* 1973, **51,** 2504.

[2] Woollins, J. D.; Williams, D. J.; Jones, R., *Angew. Chem., Int. Ed.* **1985**, *24*, 760.

[3] (a) Maaninen, T.; Chivers, T.; Laitinen, R.; Wegelius, E., *Chem. Commun.* **2000**, 759. (b) Maaninen, T.; Chivers, T.; Laitinen, R.; Schatte, G.; Nissinen, M., *Inorg. Chem.* **2000**, *39*, 5341. (c) Karhu, A. J.; Pakkanen, O. J.; Rautiainen, J. M.; Oilunkaniemi, R.; Chivers, T.; Laitinen, R. S., **2015**, *54*, 4990. (d) Karhu, A. J.; Pakkanen, O. J.; Rautiainen, J. M.; Oilunkaniemi, R.; Chivers, T.; Laitinen, R. S., *Dalton Trans.* **2016**, *45*, 6210.

[4] Schatte, G.; Chivers, T.; Tuononen, H. M.; Suontamo, R.; Laitinen, R.; Valkonen, J. *Inorg. Chem.* **2005**, *44*, 443, and references therein.

[5] Chivers, T.; Gao, X.; Parvez, M. *J. Am. Chem. Soc*. **1995**, *117*, 2359.

[6] Maaninen, T.; Laitinen, R.; Chivers, T., *Chem. Commun.* **2002**, 1812.

[7] Maaninen, T.; Tuononen, H. M.; Schatte, G.; Suontamo, R.; Valkonen, J.; Laitinen, R.S.; Chivers, T., *Inorg. Chem.* **2004**, *43*, 2097.

[8] Karhu, A. J.; Rautiainen, J. M.; Oilunkaniemi, R.; Chivers, T.; Laitinen, R. S., *Inorg. Chem.* **2015**, *54*, 9499.

Plenary Lecturer – Dr. Frédéric-Georges Fontaine

Professor
Department of Chemistry, Université Laval, Québec Canada

Dr. Fontaine received his BSc (1998) and PhD (2002) in chemistry and organometallic chemistry respectively at the Université de Montréal, the latter involving organonickel chemistry under the supervision of Dr. Davit Zargarian. He then studied the reactivity of Sc complexes with Dr. T. Don Tilley as a NSERC postdoctoral fellow at the University of California, Berkeley. Dr. Fontaine began his teaching career at Université Laval as an assistant professor in 2004, becoming an associate professor in 2009 and a full professor in 2013, including time as a guest professor at the Université de Bourgogne in 2010, a visiting professor at the University of Ottawa from 2010-2011, and an adjunct professor at Mount Allison University in 2010, a post he continues to hold.

His research group is interested in the synthesis of ambiphilic compounds containing group XIII Lewis acidic site, either as a transition metal ligand or as a metal-free catalyst in 'frustrated Lewis pair' chemistry. Among his most notable contributions is the development of highly active metal-free catalysts for the reduction of carbon dioxide and for the borylation of heteroarenes. He has published nearly 70 papers in high-impact journals including *Science*, the *Journal of the American Chemical Society*, and *Angewandte Chemie*. Dr. Fontaine's work as a professor and researcher has been honoured through numerous awards including Professor of the Year at the 36th Gala du Mérite Étudiant de l'AESGUL and has had his contributions to chemistry highlighted by Québec Science and Le Soleil as among the 'Top 10 discoveries of the year 2015'.

Notes

Ligand design in organometallic chemistry taken to the extreme: when the metal is no longer needed

Frédéric-Georges Fontaine

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Ligand design has been playing a very important role in the optimization of transition-metal catalyzed processes. In the past decade, our research group has been working on the synthesis and coordination chemistry of ambiphilic molecules having both a group XIII Lewis acid and a Lewis base within the same framework.[1] Contrarily to Frustrated Lewis Pairs (FLPs) the molecules studied do not contain significant steric bulk.[2] Along the road, we discovered that some ambiphilic molecules were more active for small molecule activation than the related coordination complexes. Indeed, as in FLP chemistry, the Lewis acid and the Lewis base can cooperate and behave similarly to a transition metal in 2-electron transfer processes, making possible some metal-free transformations that were thought to be exclusive to transition metals.[3]

By fine tuning of the steric and electronic properties of both partners in these "metal-free organometallic" species, the same way organometallic chemists design ligands for transition metals, it is possible to obtain catalytic activities that are as good, and sometime better, than traditional transition metal systems. This talk will detail the reactivity of ambiphilic molecules in the hydroboration of carbon dioxide,[4] hydrogenation of carbon dioxide,[5] borylation of heteroarenes[6] and in dehydrogenative diboration of hydroboranes.[7]

1) Fontaine, F.-G.; Zargarian, D. *J. Am. Chem. Soc.* **2004**, *126*, 8786 –8794; 2) Stephan, D. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032; 3) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A.; Rochette, É. *Coord. Chem. Rev.* **2016**, DOI: 10.1016/j.ccr.2016.05.005; 4) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326 – 9329; 5) Courtemanche, M.-A.; Pulis, A. P.; Rochette, É.; Légaré, M.-A.; Stephan, D. W.; Fontaine, F.-G. *Chem. Commun.* **2015**, *51*, 9797 – 9800; 6) Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. *Science* **2015**, *349*, 513 – 516; 7) Rochette, É.; Bouchard, N.; Lavergne, J. L.; Matta, C. F.; Fontaine, F.-G. *Angew. Chem. Int. Ed.* **2016**, *55*, 12722-12726.

Program of Events

Friday, November 11, 2016

7:00 - 10:00 pm	***Mixer (The Gown and Gabel, 24 Hess St. South, Hamilton)***

Saturday, November 12, 2016

8:00 am - 9:00	***Registration***
9:00 - 9:20	***Opening Remarks***
9:20 - 10:20	Dr. Risto S. Laitinen (***Plenary Lecture in MDCL 1305***)
10:20 - 10:40	***Break***

Oral Session 1

	Room 1 (MDCL 1305) **Chair: Jeff Price**	**Room 2 (MDCL 1309)** **Chair: Allan He**
10:40 - 11:00	**O1** Alexander E. Waked *(University of Toronto) - S(VI) Lewis Acids: Fluorosulfoxonium Cations*	**O2** Cameron M. E. Graham *(Western University) - Exploring the Reactivity of Phosphorus-Chalcogen Ring Systems*
11:00 - 11:20	**O3** Maria Zakharova *(Université Laval) - Application of Gas Oversolubility in Nanoconfined Liquids for Synthesis of Cyclic Carbonates*	**O4** Mark R. Bortolus *(McMaster Univeristy) - A New Xenon(II) Oxide Species; Synthesis and Characterization of* $[XeOXe]^{2+}$ *in the Adduct-Cation Salt,* $[CH_3CN{-}{-}{-}XeOXe{-}{-}{-}NCCH_3][AsF_6]_2$
11:20 - 11:40	**O5** John L. Lortie *(Brock University) - Zinc Hydride Catalyzed Regioselective Hydrosilylation and Hydroboration of N-heterocycles*	**O6** Maryam Abdinejad *(University of Toronto) - Structural Modulation of Cobalt-Porphyrins for Electrochemical Reduction of Carbon Dioxide*
11:40 - 12:00 pm	**O7** Mohammad A. Affan *(Queen's University) - Nickel-Catalyzed Hydrogenation of* CO_2 *in the Presence of Secondary Amines*	**O8** Levy L. Cao *(University of Toronto) - Exploring N-Heterocyclic Carbene Stabilized Boryl Radicals*

12:00 - 1:00	***Lunch***

Oral Session 2

	Chair: Ian Duffy	**Chair: John Debackere**
1:00 - 1:20	**O9** Valerie E. Fleischauer *(University of Rochester) - Insight into the Active Species and Mechanism of Alkyl-Alkyl Cross-Coupling with Iron*	**O10** Stephanie M. Barbon *(Western University) - Unusual BN Heterocycles Derived from Formazanate Ligands and Their Reduction Chemistry*
1:20 - 1:40	**O11** Samantha A. M. Smith *(University of Toronto) - Improved Synthesis of Efficient and Enantioselective Iron-based Hydrogenation Catalysts*	**O12** Konstantina Pringouri *(Univeristy of Windsor) - New Derivatives of Benzothiadiazines and their Coordination Chemistry*
1:40 - 2:00	**O13** Alex J. Veinot *(Saint Mary's University) - Metal Complexes Incorporating m-Terphenyl Substituted Cyclopentadienyl Ligands*	**O14** James T. Goettel *(McMaster University) - Xenon Trioxide and Haloxenates*
2:00 - 2:20	**O15** Manar M. Shoshani *(University of Windsor) - Unactivated C-C Multiple Bond Cleavage by a Nickel-Hydride Cluster*	**O16** Tessa M. Baker *(University of Rochester) - Magnetic Circular Dichroism Studies of Iron(II) Binding to Human Calprotectin*

2:20 - 2:30 ***Break (Poster Setup)***

Oral Session 3

	Chair: Peter Ho	**Chair: Timothy Lo**
2:30 - 2:50	**O17** Ngan Tran *(Brock University) - Methyl-Induced C-H Activation of N-Aryl Groups in Chiral NHC-Iridium Complexes*	**O18** Parisa Jafarzadeh *(University of Waterloo) - New Thermoelectric Copper Chalcogenides*
2:50 - 3:10	**O19** Fioralba Taullaj *(University of Toronto) - Organometallic Chemistry of Adamantane*	**O20** Shoushun Chen *(Western University) - Understanding Metal Doping in the Metal-Organic Framework MIL-121 Using Multinuclear Solid-State NMR*
3:10 - 3:30	**O21** Thomas Auvray *(Université de Montréal) - Electronic Properties of a Family of Light-Harvesting Polyoxometalate-Polypyridine Hybrids based Re(I) Carbonyl Complexes*	**O22** Allan He *(McMaster University) - Structure, Magnetic Properties and Magnetocaloric Effect in* $(Mn,Fe)_2(Si,P)$
3:30 - 3:50		**O23** Ernest Prack *(University of Toronto at Mississauga) - A Low-Barrier "H-M-H" Molecular Rotor*

3:50 - 4:00 ***Break (Poster Setup)***

4:00 - 5:00 Dr. Frédéric-Georges Fontaine ***(Plenary Lecture in MDCL 1305)***

5:00 - 7:00 ***Poster Session***

7:30 - 10:00 ***Banquet (The Dundas Valley Golf and Curling Club. 10 Woodleys Ln, Dundas)***

Sunday, November 13, 2016

8:30 am - 9:00 ***Morning Coffee***

Oral Session 4

	Chair: Majeda Al Hareri	**Chair: Jamie Goettel**
9:00 - 9:20	**O24** Stephanie A. Rufh *(University of Ottawa) - Intercepting Deactivation for Phosphine-Stabilized Metathesis Catalysts*	**O25** Soren K. Mellerup *(Queen's University) - Tuning the Colors of the Dark Isomers of Photochromic Boron Compounds: Four-State Color Switching*
9:20 - 9:40	**O26** Mohammadmehdi Haghdoost *(Université du Quebéc) - Do More Effective Ru(II)-Arene Catalysts Lead to Improved Anticancer Agents?*	**O27** Zitong Wang *(Western Univeristy) - Investigating Growth of the Ga-MIL-53 and PbSDB Microporous Metal-Organic Frameworks via Atomic Force Microscopy*
9:40 - 10:00	**O28** Karl Z. Demmans *(University of Toronto) - Synthesis of New Iron (II) PNNP Catalysts to Increase the Stability of a Highly Active Catalyst for the Transfer Hydrogenation of Aromatic Ketones*	**O29** John R. DeBackere *(McMaster University) - Recent Advances in the Coordination Chemistry of Krypton Difluoride*
10:00 - 10:20	**O30** Valerie Hardouin Duparc *(Université de Montréal) - Reactivity Studies of Chan-Evans-Lam Coupling using Copper(II) Complexes with Sulfonated Ligands*	**O31** Karlee L. Bamford *(Univeristy of Toronto) - Group 13 Radicals via Chelating Redox Active Ligands*

10:20 - 10:40 ***Break***

Oral Session 5

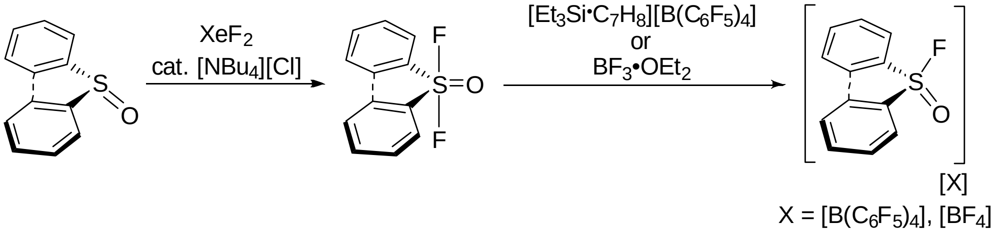
	Chair: Katia Paskaruk	**Chair: Mark Bortolus**
10:40 - 11:00	**O32** Minh Tho Nguyen *(Brock University) - Zinc and Phosphorus Complexes Supported by Bis(imino) NCN Pincer Ligand*	**O33** Alexander M. Polgar *(Western University) - Preparation of Mixed Coinage Metal Chalcogenide Clusters from Simple Precursors*
11:00 - 11:20	**O34** Jeffrey S. Price *(McMaster University) - Bis(phosphine) Adducts of Manganese Hydride Complexes*	**O35** Zeinab S. Ahmed *(University of Windsor) - Exploring the Effects of Phosphine Control on Metal Dithiolene Complexes*
11:20 - 11:40	**O36** Qiumling Liang *(University of Toronto) - Reactivity of Iron Complexes containing bidentate picoyl-NHC ligands*	**O37** Yue Zhang *(Western Univeristy) - Welcoming Gallium and Indium to the A520 MOF Family: Synthesis, Comprehensive Characterization, and CO_2 Dynamics*
11:40 - 12:00 pm	**O38** Jeremy L. Bourque *(Western University) - Synthesis of a Gallene, a Gallium-Carbon Double Bond*	**O39** Nadia O. Laschuk *(University of Ontario Institute of Technology) - Development of a Metal Ion Sensor for ppb to ppm Fe^{2+} Levels of Detection*

12:15 - 12:45 ***Closing Remarks and Awards***

O1 S(VI) Lewis Acids: Fluorosulfoxonium Cations

Alexander E. Waked,*† Fu An Tsao,† Levy Cao, Jordan Hofmann, Lei Liu, Stefan Grimme, Douglas W. Stephan
*Department of Chemistry, University of Toronto, Toronto, ON M5S 3H6, *alexander.waked@mail.utoronto.ca*

Lewis acids continue to garner attention due to in part by the advent of frustrated Lewis pair chemistry.[1] Previous research in the Stephan group has concentrated on the synthesis of Lewis acidic main group catalysts, mainly based on Group 13 (boron[2] and aluminum[3]) and Group 15 (phosphorus[4]) compounds. The current study, however, shifts the focus from Group 13- and 15-based Lewis acids to Group 16 chalcogens. In particular, a family of sulfur(VI) fluorosulfoxonium cations was synthesized and characterized spectroscopically and crystallographically, and their catalytic activity was probed in Lewis acidic hydroarylation and hydrothiolation catalysis.[5]



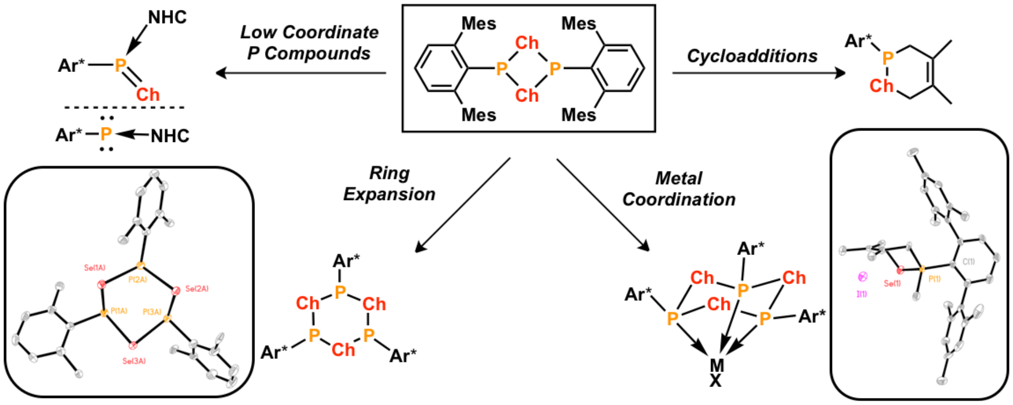
1. D. W. Stephan. *J. Am. Chem. Soc.* **2015**, *137*, 10018. **2.** T. Mahdi, D. W. Stephan. *J. Am. Chem. Soc.* **2014**, *136*, 15809. **3.** J. A. Hatnean, J. W. Thomson, P. A. Chase, D. W. Stephan. *Chem. Commun.* **2014**, *50*, 301. **4.** C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan. *Science* **2013**, *341*, 1374.
5. A. E. Waked,† F. A. Tsao,† L. Cao, J. Hofmann, L. Liu, S. Grimme, D. W. Stephan. *Chem. Commun.* **2016**, *52*, 12418.
† Equal contribution.

O2 Exploring the Reactivity of Phosphorus-Chalcogen Ring Systems

Cameron M.E. Graham, Taylor E. Pritchard, Paul J. Ragogna*
Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research, Western University, London, ON, N6A 5B7, cgraha43@uwo.ca

Main-group ring systems have long been of interest because of their unique structures, and broad applications in catalysis, incorporation in electronic components, and sequestration of metals. One subsection in this area is phosphorus-chalcogen (P_2Ch_2) ring systems with P in the +3 oxidation state. The synthesis of these P-Ch rings using bulky *m*-terphenyl ligands will be discussed. The utility of these 4-membered rings will also be addressed, including isolating low coordinate P-Ch compounds, their use in cycloadditions, expansion to larger P-Ch rings, and coordination to transition metal complexes.

(1) Henne, F.D.; Watt, F.A.; Schwedtmann, K.; Hennersdorf, F.; Kokoschka, M.; Weigand, J.J. *Chem. Commun.* **2016**, 52, 2023. (2) He, G.; Shynkaruk, O.; Liu, M.; Rivard, E. *Chem. Rev.* **2014**, 114, 7815. (3) Lensch, C.; Clegg, W.; Sheldrick, G.M. *J. Chem. Soc. Dalton Trans.* **1984**, 723.



O3

Application of Gas Oversolubility in Nanoconfined Liquids for Synthesis of Cyclic Carbonates

Maria Zakharova[a], Freddy Kleitz[*a], Faïçal Larachi,[b] and Frédéric-Georges Fontaine[*a]

[a] Department of Chemistry, Université Laval, Québec G1V0A6, Canada; [b] Department of Chemical Engineering, Université Laval, Québec, G1V0A6, Canada, maria.zakharova.1@ulaval.ca

Direct coupling between CO_2 and oxiranes has become one of the focal points in CO_2 catalysis representing an atom-efficient transformation to selectively access organic cyclic carbonates (OCC) and polycarbonates from inexpensive and readily available starting materials. OCCs have been frequently associated with numerous applications involving them as nonprotic solvents, precursors for poly(carbonate) synthesis, electrolyte solvents, and more recently as useful intermediates in organic synthesis. However, a more appropriate catalytic system is still needed to perform these reactions efficiently because of the extremely high kinetic and thermodynamic barriers that are associated with this transformation. In this contribution, efficient synthesis of cyclic carbonates from corresponding epoxides is established by applying the cooperative effect between physical phenomena, such as gas oversolubility, and catalytic behavior of nanoconfined liquids. Hybrid adsorbents based on MCM-41 and SBA-15 silica materials were used for the catalytic transformation of styrene and hexene oxides to the corresponding carbonates at room temperature and under atmospheric pressure of carbon dioxide without involving the classic metal-based catalytic systems. MCM-41 based mesoporous catalysts allowed the synthesis of OCCs in effective, durable catalytic manner.

1. Martin, E.; Escudero- Adán, E. C.; Kleij, A. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 10416.

O4

A New Xenon(II) Oxide Species; Synthesis and Characterization of $[XeOXe]^{2+}$ in the Adduct-Cation Salt, $[CH_3CN{-}{-}{-}XeOXe{-}{-}{-}NCCH_3][AsF_6]_2$

Mark R. Bortolus,* John R. DeBackere, and Gary J. Schrobilgen[†]
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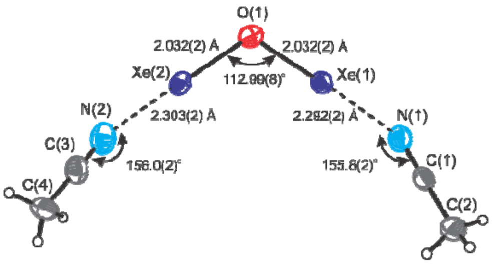
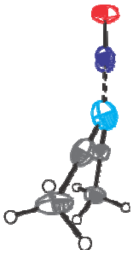
The reaction of XeF_2 with ReO_3F between –30 to –35 °C in aHF (anhydrous HF) was recently shown to yield the $[\mu\text{-}F(ReO_2F_3)_2]^-$ salt of the Xe(II) oxide dication, $[XeOXeOXe]^{2+}$, the first example of a Xe(II) oxide species and a noble-gas oxo-cation.[1] The present work reports the synthesis and characterization of the $[XeOXe]^{2+}$ dication, which provides the second Xe(II) oxide species, and the first example of a Xe(II) oxide adduct-cation. Acetonitrile displaces weakly coordinated XeF_2 from $[FXeOXe{-}{-}{-}FXeF][AsF_6]$ in aHF to form the adduct-cation salt, $[H_3CCN{-}{-}{-}XeOXe{-}{-}{-}NCCH_3][AsF_6]_2$. The $[H_3CCN{-}{-}{-}XeOXe{-}{-}{-}NCCH_3]^{2+}$ cation was characterized by low-temperature single-crystal X-ray diffraction and Raman spectroscopy. The Xe–N bonds of the adduct-cation are among the shortest for sp-hybridized nitrogen bases adducted to Xe(II). The Raman spectrum was fully assigned with the aid of ^{18}O-enrichment and calculated vibrational frequencies of the gas-phase cation. Natural bond orbital (NBO), atoms in molecules (AIM), electron localization function (ELF), and molecular electrostatic potential surface (MEPS) analyses indicate that the Xe–O bonds are polar-covalent, whereas the Xe–N bonds may be described as primarily electrostatic, σ-hole bonds.[2]





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O5

Zinc Hydride Catalyzed Regioselective Hydrosilylation and Hydroboration of N-heterocycles

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There is significant interest in developing zinc catalysis due to the natural abundance, low cost, and low toxicity of this metal compared to traditional late-transition metal catalysts [1,2]. Our group has previously reported chemoselective hydrosilylations of nitriles catalyzed by the zinc hydride ^{Ar}NacNacZnH (NacNac = [ArNC(Me)CHC(Me)NAr]$^-$ and Ar = 2,6-Pr$^i_2$C$_6$H$_3$) [2]. We then reckoned that the less sterically protected, xylyl-substituted zinc hydride ^{Xy}NacNacZnH (NacNac = [XyNC(Me)CHC(Me)NXy]$^-$ and Xy = 2,6-Me$_2$C$_6$H$_3$) should be more reactive and likely applicable to catalytic reduction of *N*-heterocycles to value added products used by pharmaceutical and agrochemical industries. Herein we report 1,2-regioselective catalytic hydrosilylation and hydroborations of quinolines and pyridines with this NacNacZnH compound. Similarly, the reductions of acridine and even more challenging substrate, 1,10-phenanthroline, were also accomplished. Monitoring the stoichiometric reaction of quinoline and NacNacZnH by ^{1}H-NMR spectroscopy reveals fast coordination, 1,2-insertion of quinoline into the Zn-H bond followed by isomerization to the 1,4-insertion product. Kinetics studies showed that the catalytic reaction is first order in silane and first order in the substrate. Labelling experiments demonstrated the reversibility of hydrosilylation. The crystal structure of the 1,4-insertion product, NacNacZn[DQH][quinoline], was elucidated X-ray structure analysis.

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O6

Structural Modulation of Cobalt-Porphyrins for Electrochemical Reduction of Carbon Dioxide

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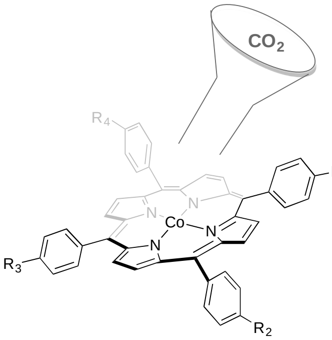
Carbon dioxide (CO$_2$) is the primary greenhouse gas emission, released by both natural and human activities.[1] The conversion of CO$_2$ to value-added organic chemicals is thus of importance to reduce carbon footprint. Metalloporphyrins, such as Fe(0) and Co(I) porphyrins show great promise as catalysts for CO$_2$ reduction. [2] Also, due to the strong ligand metal interaction, functional groups on porphyrins have a substantial impact on electron configuration on the metal center. It has been shown the amino functional groups allow manipulation of absorption and conversion of CO$_2$.[3] Therefore, in this contribution, the redox activity of a series of cobalt-amino porphyrin molecules was studied. The catalyst efficiency for the entire synthesized molecule will be reported as well.



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O7

Nickel-Catalyzed Hydrogenation of CO_2 in the Presence of Secondary Amines

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Catalytic hydrogenation of CO_2 is an efficient and selective way to form value-added chemicals, but most of the highly active catalysts have required precious metals. In this regard, we are interested in the hydrogenation of CO_2 to formic acid derivatives by nickel-dmpe catalysts. Nickel complexes have been extensively studied for cross-coupling reactions but less explored for the hydrogenation of CO_2 to formic acid derivatives. Herein, we describe the syntheses of Ni(II) complexes such as $[Ni(dmpe)_2X]X$; $[Ni(dmpe)X_2]$; $[\{Ni(Me_2(O)P(CH_2)_2P(O)Me_2)(acac)_2\}\cdot CHCl_3]_n$; $[\{Ni(acac)_2\}(MeO)_2(MeOH)_2]_2$; and $[Ni(PNN)X]X$ (X= Cl^-, $acac^-$, dmpe = 1,2-bis(dimethylphosphino)ethane); PNN = $C_{19}H_{35}N_2P$. The synthesized Ni(II) complexes were also studied as homogeneous catalysts for the hydrogenation of CO_2 to formic acid derivatives using morpholine and dimethylamine as bases in DMSO. With the appropriate selection of catalyst and reaction conditions, >90-96% conversion of amine was achieved to the formamide. In this study, the effect of the changing the metal to amine ratio has been investigated.

O8

Exploring N-Heterocyclic Carbene Stabilized Boryl Radicals

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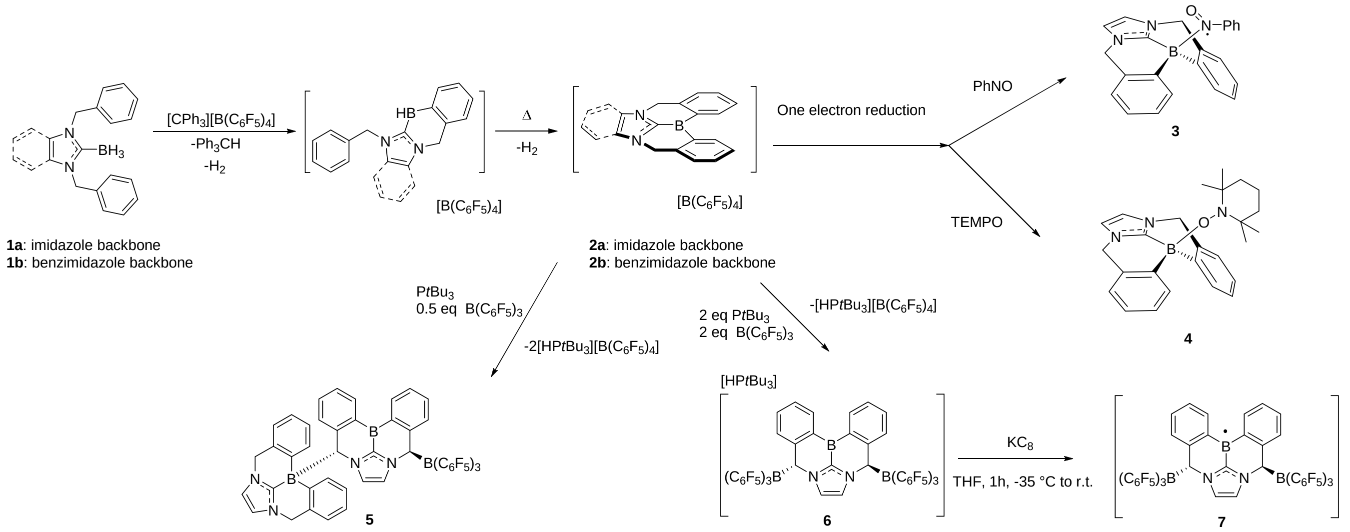
Recently, the Stephan group has reported a new protocol for an effective synthesis of planar N-Heterocyclic Carbene (NHC) borenium ion (**2a**), which can be prepared from hydride abstraction of the carbene-borane adduct (**1a**), followed by heating.[1] One electron reduction of **2a & 2b** generated an NMR active species which can be intercepted by reaction with PhNO or TEMPO. Reaction of **2a** with varying stoichimetries of tBu_3P and $B(C_6F_5)_3$ afforded **5** and **6**. Electrochemical and EPR studies are consistent with a reversible one-electron reduction of **6** generating the radical dianion **7**.[2]



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O9

Insight into the Active Species and Mechanism of Alkyl-Alkyl Cross-Coupling with Iron

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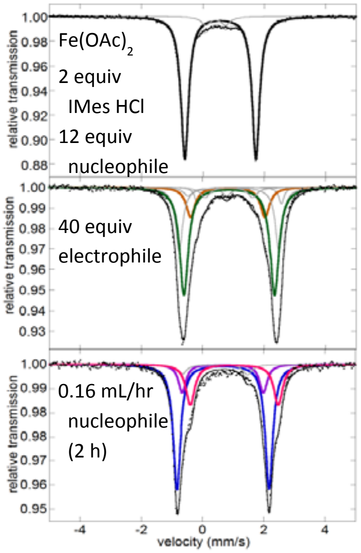
*Department of Chemistry, University of Rochester, Rochester, NY 14603, *vfleisc2@ur.rochester.edu*



Recently there has been rapid growth of efficient iron-based catalyst systems using co-solvents, ligand additives, and well defined iron complexes. However, little is known about the mechanisms of these systems in comparison to more well developed precious metal catalysis. Using inert atmosphere synthesis, inorganic spectroscopic methods, and density functional theory my co-workers revealed mechanistic details regarding relevant *in situ* formed species in iron-mesityl cross-coupling not previously known. Mössbauer spectroscopy, magnetic circular dichroism (MCD), electron paramagnetic resonance (EPR), and density functional theory (DFT) are a powerful group of tools to use for iron systems that contain mostly paramagnetic species that are difficult to study using traditional techniques. This presentation will demonstrate the value of these methods as applied to alkyl-alkyl cross-coupling with iron.

O10

Unusual BN Heterocycles Derived from Formazanate Ligands and Their Reduction Chemistry

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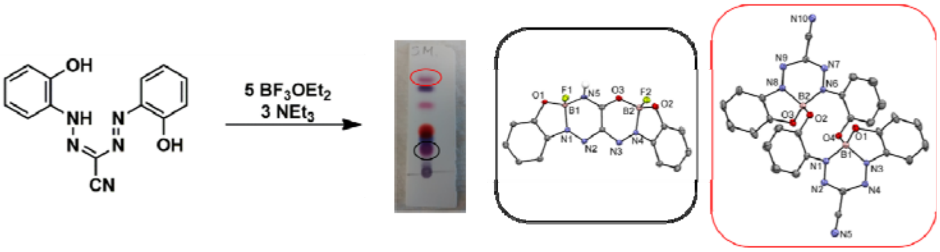
Reaction of a potentially tetradentate $N_2O_2^{3-}$ formazanate ligand with boron trifluoride diethyl etherate yielded a variety of novel BN heterocycles, which could be separated by column chromatography and crystallized. The five monomeric and dimeric compounds which were identified all contain boron-nitrogen and boron-oxygen bonds, and anywhere from 0 to 3 fluorine atoms. These compounds have interesting optical and electronic properties, including high molar absorptivities and can be electrochemically reduced reversibly.

Prompted by the interesting electrochemistry, we investigated the reduction chemistry of two of the reaction products. Reduction with one or two equivalents of cobaltocene yielded stable radicals, di-radicals and anions, that were characterized crystallographically, and their properties were compared to the parent heterocycles.

This presentation will discuss in detail the identification of the novel BN heterocycles isolated, and their reduction chemistry. Spectroscopic and electrochemical properties will be discussed during this presentation.



O11

Improved Synthesis of Efficient and Enantioselective Iron-based Hydrogenation Catalysts

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**robert.morris@utoronto.ca*

The Morris group has been focused on the design of iron-based catalysts for the asymmetric hydrogenation of polar double bonds for years. In 2014, our group published the synthesis of asymmetric direct hydrogenation catalysts that were highly active and enantioselective for the reduction of a number of ketones.[1] This family of catalysts required harsh activation using LiAlH4 which not only activated the catalyst but also formed other iron-containing species. An improved synthesis of chiral ligands and their corresponding iron complexes (Figure 1) has been achieved. Their application in asymmetric direct hydrogenation has been preliminarily tested and has so far shown that they can be highly enantioselective (>90 %ee) and can also perform in base-free conditions.

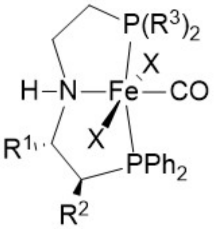

Figure 1

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O12

New Derivatives of Benzothiadiazines and their Coordination Chemistry

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The family of 1,2,4-benzothiadiazines in various oxidation states have attracted attention for both materials and pharmaceuticals applications.[1] The development of polydentate N-donor ligand sets with tuneable coordination chemistry is highly desirable for the construction of new functional materials.[2] We have developed a range of derivatives of the ligand in which the group at the C(3) position is varied to include pyridyl and pyrimidine rings (Fig. 1). Their reactivity towards first row transition metal ions is discussed.

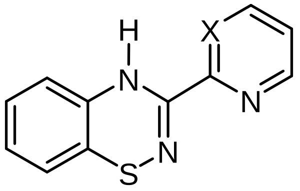

Fig. 1 Molecular structure of 1,2,4-benzothiadiazine, where X = CH, N.

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O13

Metal Complexes Incorporating *m*-Terphenyl Substituted Cyclopentadienyl Ligands

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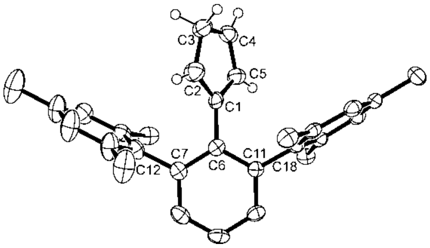
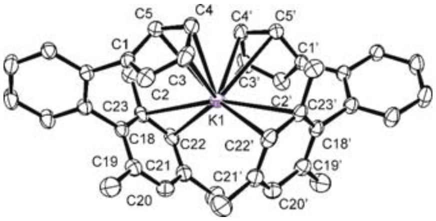
Sterically hindered cyclopentadienyl (Cp) ligands are valued for their ability to stabilize highly reactive metal centres, allowing for the isolation of molecules with novel bonding environments and reactivity. While many examples of bulky Cp ligands functionalised with alkyl or relatively small aryl groups are known, to date there is only one example of an *m*-terphenyl substituted Cp ligand. These ligands are of particular interest because the flanking aryl groups of the terphenyl could potentially participate in bonding with the metal centre, allowing for the observation and potential trapping of reactive intermediates or new molecular structures.

A new synthetic route to highly tunable, bulky, and chelating cyclopentadienyl ligands featuring *m*-terphenyl substituents was developed, and several metal complexes were prepared and characterised both structurally and spectroscopically. Using structural information obtained from single crystal X-ray diffraction data, it was determined that significant interactions between the flanking aryl groups of the *m*-terphenyl and metal centres do indeed occur in some cases.





O14

Xenon Trioxide and Haloxenates

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Xenon trioxide is a shock-sensitive, thermodynamically unstable, and strong oxidizing compound, which was first discovered in 1963. It is synthesized by the hydrolysis of XeF_6 or XeF_4. The crystal structure of an orthorhombic phase of XeO_3 was previously reported. Fluoroxenates were discovered by Selig in 1965 and chloroxenates were discovered shortly after in 1967. The compounds were characterized by elemental analysis and vibrational spectroscopy. The structures of $K[F(XeO_3)]$, $M_9[(XeO_3)Cl_2]_4Cl$ [M = Cs, Rb], and more recently, $Cs_2[F(XeO_3)_2(HF_2)]$ have also been reported. However, the structures of $M_9[(XeO_3)Cl_2]_4Cl$ were severely disordered. Two new low-temperature (LT) phases of XeO_3, β-XeO_3 ($R3$), and γ-XeO_3 ($R3c$), have now been obtained and were characterized by LT single-crystal X-ray diffraction and Raman spectroscopy. A variety of room temperature-stable fluoroxenate salts were synthesized and their crystal structures determined. The reaction of XeO_3 with $[N(CH_3)_4]Br$ and $[N(C_2H_5)_4]Br$ gave two different cluster anions ($[Br_3(XeO_3)_3]^{3-}$ and $[Br_4(XeO_3)_4]^{4-}$; Figures 1 and 2) which provide conclusive evidence for the first Xe−Br bonds. Their chlorine analogues have also been obtained.

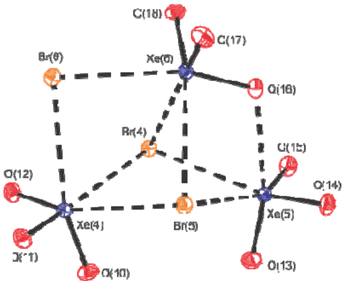

Figure 1

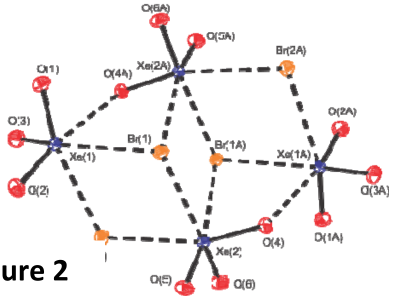

Figure 2

O15

Unactivated C-C Multiple Bond Cleavage by a Nickel-Hydride Cluster

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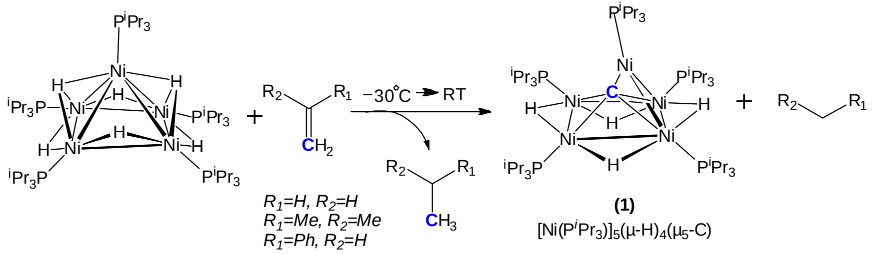
C-C bond activation and cleavage has been an area of interest for its potential in functionalization of hydrocarbons for industrial processes and synthesis.[1,2] Only few examples of unactivated and unstrained C-C bond cleavage have been reported due to the thermodynamic challenges of breaking C-C bonds. The pentanuclear Ni hydride cluster, $[(^{i}Pr_3P)Ni]_5H_6$, C-H bond activates ethylene and subsequently cleaves the C-C bond, which results in the formation of methane at temperatures as low as −30 ˚C. The reaction provides $[Ni(P^{i}Pr_3)]_5(\mu\text{-}H)_4(\mu_5\text{-}C)$ (**1**), a new pentanuclear nickel hydride cluster bearing a 5-coordinate carbide. The reaction of $[(^{i}Pr_3P)Ni]_5H_6$ with several alkenes result in the formation of **1**, and in some cases, observable intermediates. These intermediates, along with ^{13}C labelling studies were used to offer insight into the mechanism of C-C bond cleavage.



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O16

Magnetic Circular Dichroism Studies of Iron(II) Binding to Human Calprotectin

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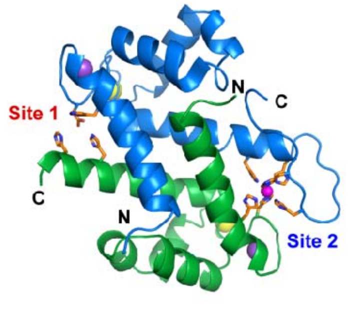

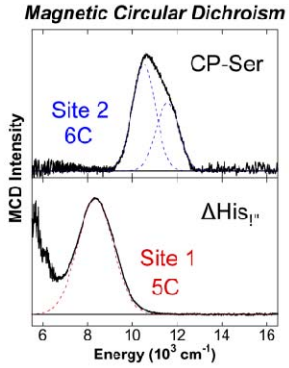

Calprotectin (CP) is an abundant metal-chelating protein involved in host defense, and the ability of human CP to bind Fe(II) in a calcium-dependent manner was recently discovered. In the present study, near-infrared magnetic circular dichroism spectroscopy is employed to investigate the nature of Fe(II) coordination at the two transition metal-binding sites of CP that are a His_3Asp motif (site 1) and a His_6 motif (site 2). Upon the addition of sub-stoichiometric Fe(II), a six-coordinate (6C) Fe(II) center associated with site 2 is preferentially formed in the presence of excess Ca(II). Analysis of CP variants lacking residues of the His_6 motif supports that CP coordinates Fe(II) at site 2 by employing six His ligands. In the presence of greater than one equiv of Fe(II) or upon mutation of the His_6 motif, the metal ion also binds at site 1 of CP to form a five-coordinate (5C) Fe(II)-His_3Asp motif that was previously unidentified in this system. Notably, the introduction of His-to-Ala mutations at the His_6 motif results in a mixture of 6C (site 2) and 5C (site 1) signals in the presence of sub-stoichiometric Fe(II). These results are consistent with a reduced Fe(II)-binding affinity of site 2 as more weakly coordinating water-derived ligands complete the 6C site. In the absence of Ca(II), both sites 1 and 2 are occupied upon addition of sub-stoichiometric Fe(II), and a stronger ligand field 5C is observed for the 5C site, suggesting that Ca(II)-binding influences Fe(II) coordination at the His_3Asp motif.

O17

Methyl-Induced C-H Activation of *N*-Aryl Groups in Chiral NHC-Iridium Complexes

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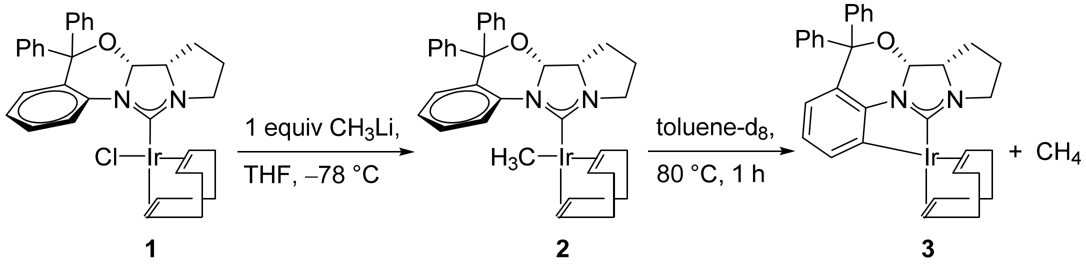
Iridium(I)(cod)Cl complexes with L-proline-derived *N*-aryl NHC ligands (**1**) undergo C-H activation at the *ortho*-aryl positon upon chloride substitution with methyllithium (**2**) to give putative iridacycles (**3**) with concomitant loss of methane. The generality of this reaction is currently under investigation with both *N*-phenyl[1] and planar chiral *N*-ferrocenyl[2] analogues. The ability to selectively deuterate the *ortho*-aryl position of the preceding ligands serves as a kinetic probe to investigate mechanistic aspects of this process, which may shed light on whether the reaction is concerted or step-wise. Recent results related to the generality and potential applications of this transformation may also be presented.



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O18

New Thermoelectric Copper Chalcogenides

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Copper chalcogenides are among the most promising thermoelectric materials when exposed to environments higher than room temperature. β-$Cu_{2-x}Se$ has a extraordinarly low lattice thermal conductivity, and an outstanding *figure-of-merit* of $zT = 1.5$ at 1000 K. Unfortunately, the application of β-$Cu_{2-x}Se$ is hindered due to the migration of copper ions throughout the material causing material decay.[1,2]

Aiming to prevent copper ion migration by adding large Ba^{2+} cations, we developed several new Ba-Cu-chalcogenides, including $BaCu_{6-x}STe_6$ and $BaCu_{6-x}SeTe_6$.[3] The presence of Ba and Te impedes the copper ion migration from one Cu cluster to the next, which leads to increased material stability.

Our first measurements indicated that $BaCu_{5.9}SeTe_6$ exhibits better thermoelectric performance than its S-containing counterpart.[4] With this contribution, we present the results of our attempts to optimize these properties via doping, for example with K^+ on the Ba^{2+} site.

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O19

Organometallic Chemistry of Adamantane

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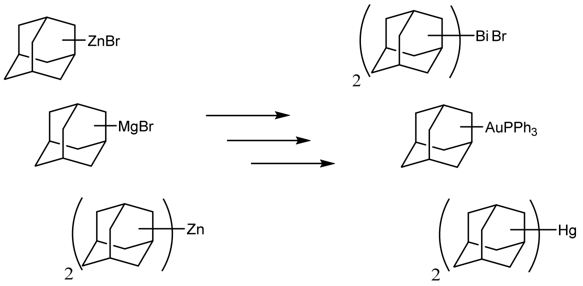
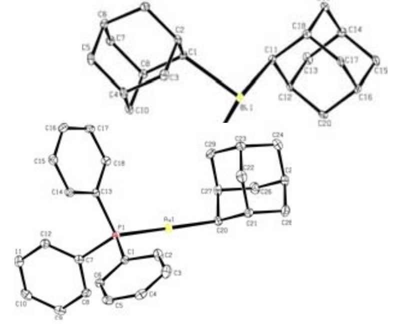
The chemistry of adamantane remains limited due to the inherent difficulty of directing substitution on the adamantane cage. Synthetic procedures for selective functionalization of adamantane at multiple sites are rare and commonly limited to the bridgehead positions. Substitution at multiple bridge positions with any degree of selectivity is challenging yet highly desirable. Synthesis of a single face tri-substituted adamantane could present pathways to novel ligands, materials, and potential drug molecules. Our group is focused on directing adamantyl substitution through C-H activation. Recent work in the group has led to reliable synthetic procedures for adamantyl anion equivalents required for transmetallation. Synthesis of the first gold, bismuth and mercury adamantyls will be presented. Future work is focused on using metal 2-adamantyl complexes for directed C-H activation.





O20

Understanding Metal Doping in the Metal-Organic Framework MIL-121 Using Multinuclear Solid-State NMR

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Department of Chemistry, University of Western Ontario, London, ON N6A 5B7, schen548@uwo.ca

Metal-organic frameworks are next-generation porous materials that can incorporate a variety of metal centres and organic linkers and can assume a wide array of geometries and pore sizes.[1] To increase guest adsorption performance or to introduce catalytically-active reaction sites, the introduction of metal atoms to the MOF pores from an external source is often explored.[2] In many instances, powder X-ray diffraction patterns of the doped and pristine MOFs are similar, and thorough characterization of the doped MOF is quite challenging.

We have employed solid-state NMR (SSNMR) techniques to investigate the local structure and environment of several nuclei in metal-doped MIL-121 MOFs;[3] in particular, dopant metals from the *s*-block and *d*-block such as Li, Na, Ca, Zn, and Cd have been investigated. Using ^{13}C, ^{1}H, and multinuclear metal SSNMR, we have successfully obtained information on both the dopant location and doping level in MIL-121. Metal SSNMR spectra reveal that the doped metal centres are chemically bound within the pores to the organic linkers. Extending this work to other MOF systems and dopant metal centres should be quite useful for characterizing other doped MOF systems and understanding the origins of their unique properties and applications.

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O21

Electronic Properties of a Family of Light-Harvesting Polyoxometalate-Polypyridine Hybrids based Re(I) Carbonyl Complexes

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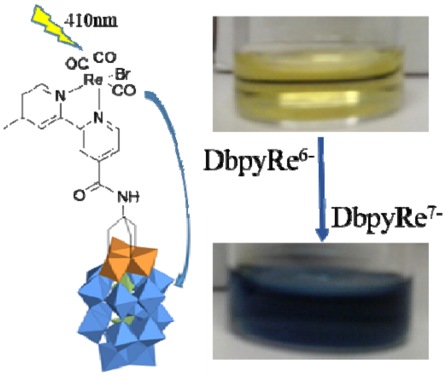
A family of hybrids based on the tri-substituted Dawson polyoxometalate (POM) $[P_2V_3W_{15}O_{62}]^{9-}$ functionalized with remote polypyridine coordination site has been extended[1] and used as ligand for the neutral $\{Re(CO)_3Br\}$ moiety. These Re(I)-hybrids were characterized by various analytical techniques, including luminescence spectroscopy and electrochemistry. These hybrids exhibits several redox processes on a wide range of potentials with reductions centered on V(V), W(VI) and the organic ligand. Both units, the POM and the Re(I) complex, retain their intrinsic properties in the different hybrid and display photosensitization in the near UV, tailing in the high energy visible region. The excited state of the Re(I) complex, known to be emissive, is however quenched and an electron transfer to the POM is observed. This electronic process will be discussed in the talk, so will its use in photocatalytic reaction such as hydrogen production.



[1] M.-P. Santoni, A.K. Pal, G.S. Hanan, M.-C. Tang, A. Furtos, B. Hasenknopf, *Dalton Trans.*, **2014**, 43, 6990–6993

O22

Structure, Magnetic Properties and Magnetocaloric Effect in $(Mn,Fe)_2(Si,P)$

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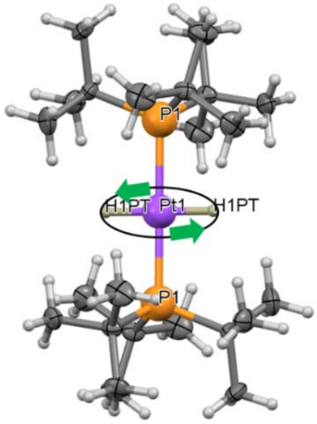
The magnetocaloric effect (MCE) has quickly found its place in many research labs across the world after the discovery of a large cooling effect in the $Gd_5(Si,Ge)_4$ alloys.[1] The research undertaken paved the way for the development of magnetic cooling technology that offers a more efficient, eco-friendly and quieter alternative to vapor-based refrigeration. Just this year in February 2016, Japan and the US jointly launched a new X-ray astronomy satellite ASTRO-H (renamed to Hitomi) and the onboard adiabatic demagnetization is used to obtain temperatures around -273.1°C for operation of a soft x-ray spectrometer.[2] $(Mn,Fe)_2(P,Si)$ phases are seen as the most promising MCE systems because of their magnetostructural transitions around room temperature. The low cost and abundance of starting materials, easy tunability of both Curie temperature and hysteresis make them a desirable system to work with. In recent years, ball-milling followed by sintering was the primary synthetic technique for the Fe_2P- based materials,[3][4] however impurities such as cubic $(Mn,Fe)_3Si$ were common[3][5][6]. Presented here is a new synthetic method capable of obtaining phase-pure samples. It features a conventional solid-state approach that is easily reproducible and impurity-free.

[1] Pecharsky, V. K.; Gschneidner Jr., K.A. *Phys. Rev. Lett.* **1997**, *78*, 4494-4497. [2] Porter, F. S.; Fujimoto, R.; Kelly, R. L.; Kilbourne, C. A.; Mitsuda, K.; Ohashi, T.; Astro-H/SXS collaboration. *AIP Conf. Proc.* **2009**, 1185, 91. [3] Thanh, D. T. C.; Brück, E.; Trung, N. T.; Klaasse, J. C. P.; Buschow, K. H. J.; Ou, Z. Q.; Tegus, O.; Caron, L. *J. Appl. Phys.* **2008**, *103*, 07B318. [4] Yibole, H.; Guillou, F.; Zhang, L.; van Dijk, N. H.; Brück, E. *Journal of Physics D: Applied Physics*. **2014**, *47*, 075002. [5] Dung, N. H.; Zhang, L.; Ou, Z. Q.; Brück, E. *Appl. Phys. Lett.* **2011**, *99*, 092511. [6] Dung, N. H.; Zhang, L.; Ou, Z. Q.; Zhao, L.; van Eijck, L.; Mulders, A. M.; Avdeev, M.; Suard, E.; van Dijk, N. H.; Brück, E. Physical Review B. **2012**, *86*, 045134.

O23

A Low-Barrier “H-M-H” Molecular Rotor

Ernest Prack[†], Christopher A. O’Keefe[‡], Jeremy K. Moore[§], Angel Lai[†], Alan J. Lough[″], Peter M. Macdonald[†], Mark S. Conradi[§], Robert W. Schurko*[‡], and Ulrich Fekl*[†]
[†]University of Toronto, Mississauga Campus, Mississauga, ON L5L 1C6, ernest.prack@mail.utoronto.ca
[‡]University of Windsor; [§]Washington University, St. Louis; [″]University of Toronto, St. George Campus



Inspired by nature’s fascinating molecular machinery, current research is developing functional parts for future human-made molecular machines. A quintessential molecular rotor is nature’s ATPase which harnesses cellular energy in the form of ATP to drive rotational motion and convert it to work necessary for cellular metabolism. The challenge lies in emulating nature. A good starting point is identifying molecular systems with low barriers to rotation. A new class of low-barrier molecular rotors, metal *trans*-dihydrides, is suggested here. A known complex, *trans*-$H_2Pt(P^tBu_3)_2$, was experimentally studied using solid-state nuclear magnetic resonance (SSNMR) and computationally modelled: We found this complex to exhibit rapid rotation ($v_{ex} > 10^7$ Hz), even at 120K; the highest barrier to rotation was estimated to be ~3 kcal mol^{-1} (experimentally) and ~4.9 kcal mol^{-1} (DFT). Moreover, this synthetic molecular rotor does not stop spinning until ~30K. We expect this new class of rotors will help expand the field of the world’s smallest machines.

O24

Intercepting Deactivation for Phosphine-Stabilized Metathesis Catalysts

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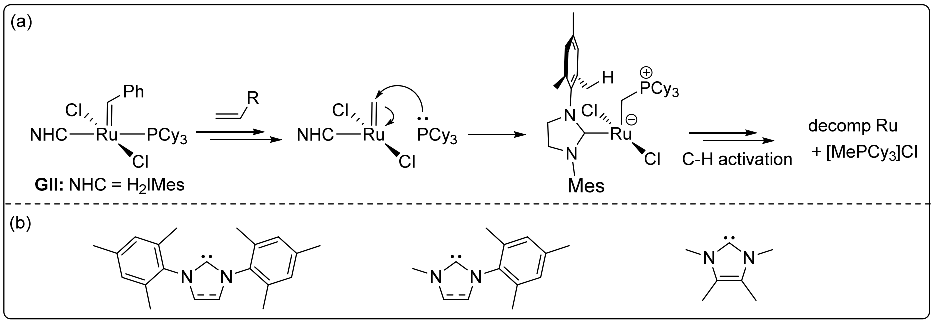
Phosphine-stabilized metathesis catalysts continue to dominate olefin metathesis, in part because of cost advantages relative to their phosphine-free analogues. However, such catalysts – including the widely-used second-generation Grubbs catalyst, **GII** – suffer from a common deactivation pathway. Free PCy_3 abstracts the methylidene ligand via a two-step process, involving first nucleophilic attack on the methylidene carbon, then elimination of the σ-alkyl moiety by C-H activation of the NHC ligand (**Figure 1a**; NHC = *N*-heterocyclic carbene). Here we examine the impact of increasing the donor power of the NHC ligand, while simultaneously truncating the *N*-substituents. **Figure 1b** depicts ligands examined, in which some have either one or both mesityl groups replaced with a methyl substituent. The impact on catalyst decomposition in the presence of nucleophiles will be described.

Figure 1. a) Known deactivation pathway for 2nd generation phosphine-stabilized metathesis catalysts. b) NHC ligands examined.



O25

Tuning the Colors of the Dark Isomers of Photochromic Boron Compounds: Four-State Color Switching

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Combining a three-coordinated boron ($BMes_2$) moiety with a four-coordinated photochromic organoboron unit leads to a series of four new diboron compounds that can undergo four-state reversible color switching in response to stimuli of light, heat, and fluoride ions (Figure 1). Thus, these hybrid diboron systems allow both convenient color tuning and state switching of such photochromic systems, as well as visual fluoride sensing by color or fluorescent emission color change.

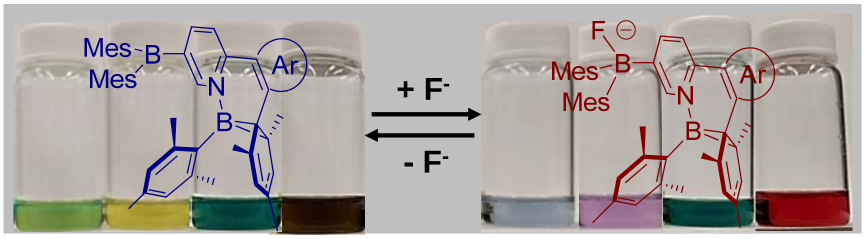

Figure 1. Impact of fluoride on the colors of the dark isomers

O26

Do More Effective Ru(II)-Arene Catalysts Lead to Improved Anticancer Agents?

Mohammadmehdi Haghdoost, Juliette Guard, Sylvain Poulet, Golara Golbaghi and Annie Castonguay*
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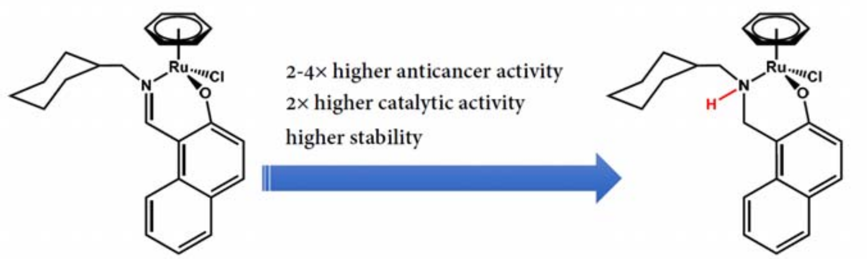
Ruthenium complexes are promising candidates to replace platinum-based drugs, as they tend to exhibit high activity against *cis*-platin resistant cell lines and induce a lower occurrence of side effects than platinum-based complexes, possibly due to their different mechanisms of action. Notably, the potential of ruthenium complexes to catalyze reactions inside cells represents an exciting new chemical tool for modulating their biological activity. Of particular interest are catalysts that can alter the redox status of human cells, as they might offer new effective mechanisms for the treatment of some diseases. For instance, a ruthenium(II) sulfonamide ethyleneamine complex was recently reported to catalytically reduce NAD+ to NADH in human ovarian cancer cells, using a non toxic dose of formate as a hydride donor (Sadler *et al*., 2015). This catalytic reaction seems to alter the redox status of cells, causing cancer cell death *via* reductive stress. This presentation will focus on the synthesis and characterization of Ru(II)-arene complexes, our results regarding their *in vitro* anticancer activity against cancer cells, and their catalytic activity for the reduction of NAD+ to NADH in biological settings.



O27

Investigating Growth of the Ga-MIL-53 and PbSDB Microporous Metal-Organic Frameworks *via* Atomic Force Microscopy

Zitong Wang*, Heng-Yong Nie, and Yining Huang*
Department of Chemistry, University of Western Ontario, London, ON N6A 3K7, zwang452@uwo.ca

Metal-organic frameworks (MOFs) are hybrid crystalline microporous materials that have drawn much attention in recent years for their potential applications in many fields of chemistry. These materials are composed of secondary building units (SBUs) containing metal centers or clusters that are joined by organic linkers to construct a 3-D porous network.[1] Unfortunately, the mechanisms of how these frameworks self-assemble during crystallization are not fully understood. A useful technique for investigating such processes is atomic force microscopy (AFM).[2] We have studied two MOFs, Ga-MIL-53 and PbSDB, which both exhibit strong absorption of CO_2 yet feature different metal centers and ligands.[3-4] The surfaces of those two materials were found to grow through the “birth and spread” crystal growth mechanism, with rectangular shaped growth hillocks evident due to anisotropic growth. By exploring possible termination structures on the surfaces, we can also probe the fundamental growth units as they self-assemble to form these 3-D microporous frameworks.

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2. Shoaee, M.; Agger, J. R.; Anderson, M. W.; Attfield, M. P. *CrystEngComm* **2008,** *10* (6), 646-648.
3. Zhang, Y.; Lucier, B. E.; Huang, Y. *Phys. Chem. Chem. Phys.* **2016,** *18* (12), 8327-8341.
4. Chen, S.; Lucier, B. E.; Boyle, P. D.; Huang, Y. *Chem. Mater.* **2016,** *28* (16), 5829-5846.

O28

Synthesis of New Iron (II) PNNP Catalysts to Increase the Stability of a Highly Active Catalyst for the Transfer Hydrogenation of Aromatic Ketones

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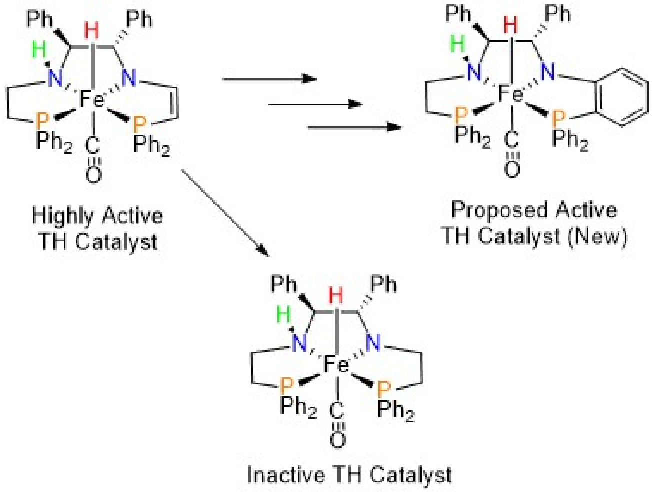
A possible degradation pathway of a highly active iron (II) P-NH-N-P precatalyst will be discussed alongside the targeted approach to synthesizing new iron precatalysts with the goal of forming a more stable active species. This lecture will be focused on the synthesis of these new PNNP ligands with preliminary catalysis results of multiple variations of the PNNP framework to see the effect on the transfer hydrogenation (TH) of acetophenone.



O29

Recent Advances in the Coordination Chemistry of Krypton Difluoride

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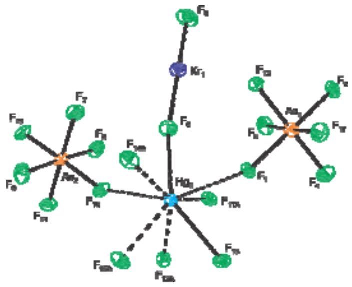
The noble-gas difluorides, NgF_2 (Ng = Kr, Xe), undergo fluoride ion abstraction in the presence of strong Lewis acid pentafluorides to form salts that may be formulated as $[FNg][MF_6]$ (M = As, Sb, Bi) and $[FNg][M_2F_{11}]$ (M = Sb, Bi). In the case of weak to moderate strength Lewis acids, NgF_2 may act as a ligand. Numerous examples of XeF_2 molecules coordinated to s- and d-block cations have been documented, but only two examples in which the superoxidant KrF_2 is coordinated to Lewis acid centers are known, namely $[BrOF_2][AsF_6]\cdot 2KrF_2$ [Brock *et al.*, *JACS*, **2010**, *132*, 3533–3542] and $Hg(OTeF_5)_2\cdot 1.5KrF_2$ [DeBackere *et al.*, *JACS*, **2014**, *136*, 3888−3903]. In the present work, the terminally coordinated KrF_2 adducts $[Hg(KrF_2)(HF)](AsF_6)_2$ **(1)**, $[Hg(KrF_2)_2](AsF_6)_2$ **(2)**, $[Hg(KrF_2)_4(HF)_2](SbF_6)_2$ **(3)**, and $[Hg(KrF_2)_5](AsF_6)_2$ **(4)** have been synthesized and structurally characterized by low-temperature X-ray diffraction, Raman spectroscopy, and quantum-chemical calculations. The present work provides a significant extension of the little studied coordination chemistry of KrF_2 and provides the first structurally characterized examples of KrF_2 terminally coordinated to a d-block metal cation.



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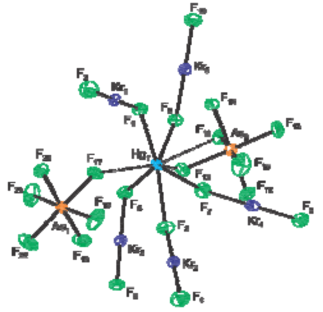

(4)

O30

Reactivity Studies of Chan-Evans-Lam Coupling using Copper(II) Complexes with Sulfonated Ligands

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Centre en Chimie Verte et Catalyse,
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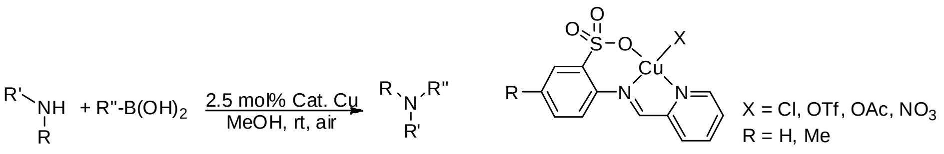

The Chan-Evans-Lam coupling is a well-known cross-coupling reaction between an aryl or alkyl boronic acid and an alcohol, an amine or other nucleophiles. Discovered in 1998, an oxidative coupling is performed under air to form the C-O or C-N bond in presence of a copper(II) species, typically $Cu(OAc)_2$. Environmentally friendly, atom-economic, and typically not in need of harsh conditions, the Chan-Evans-Lam coupling could be very interesting for industrial processes and research applications. However, even with substrates as similar as anilines and amines, reaction conditions have to be optimized for each substrate. This commonly includes the choice of solvent, presence of base, presence of oxygen, heating, removal of water, and sometimes stoichiometric amounts of copper. We recently prepared several new copper complexes, stable under air and against water, which bear a tridentate ligand with a coordinated sulfonate part and a dissociable anion. These compounds were active in the Chan-Lam couplings for a large variety of amine reagents under identical, mild conditions. Further investigations showed that coupling occurs at room temperature under air, without the requirement of additional base. Neither heating, nor removal of water proved to be necessary.

O31 Group 13 Radicals *via* Chelating Redox Active Ligands

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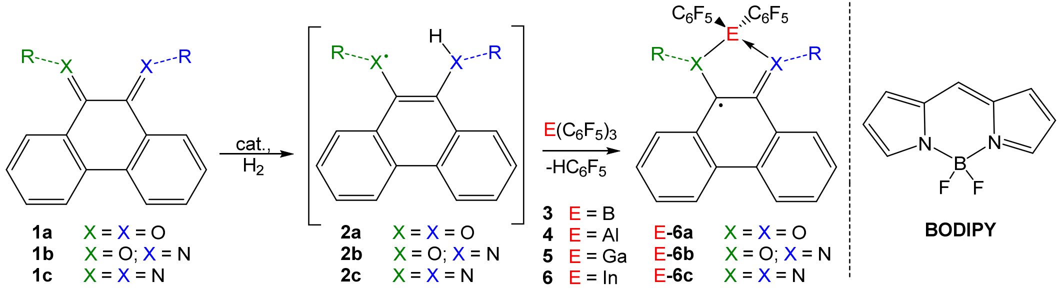
We are interested in developing new main group-centered radicals. Recently, commercially available 9,10-phenanthrenquinone (**1a**) was found to react with $B(C_6F_5)_3$ in the presence of H_2 to give a remarkably air- and moisture-stable dioxoborocyclic radical (**3a**).[1] Building upon this synthetic methodology, we have targeted oxazaborocyclic and diazaborocyclic radicals from related *o*-iminoquinone (**1b**) and α-diimine (**1c**) ligands, which have notable redox activity in transition metal complexes and are promising precursors to quinhydrone-like intermediates (**2b-c**).



Mechanistic features of the formation of these radicals have been ascertained through NMR studies, X-ray crystallography and DFT calculations. Recent results from this work show that a large library of radicals containing other main group centers (*e.g.* E = Al, Ga, In; **3-6**) and a diversity of substituents bound to those elements in place of C_6F_5 (*e.g.* halogen, aryl, alkyl) may be easily accessed, providing new handles for tuning electronic and fluorescence properties. The E-heterocyclic framework of these radicals is structurally reminiscent of the popular fluorescent dye **BODIPY**, but their open-shell electronic configuration is expected to confer novel photophysical properties that are inaccessible to closed-shell analogues.

O32 Zinc and Phosphorus Complexes Supported by Bis(imino) NCN Pincer Ligand

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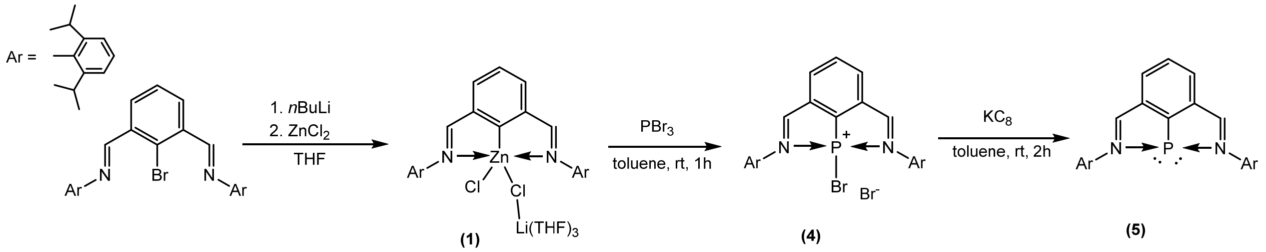
Pincer ligands received significant attention in transition metal chemistry but are much less studied in the main group chemistry. Here we report preparation of new zinc and phosphorus compounds supported by a NCN diimine pincer ligand. The complexes 2,6-(2,6-$^iPr_2C_6H_3N{=}CH)_2C_6H_3ZnCl_2Li(THF)_3$ (**1**) and 2,6-(2,6-$^iPr_2C_6H_3N{=}CH)_2C_6H_3ZnBu$ (**2**) were prepared by lithiation of the starting bromide followed by a zinc/lithium metathesis. The reaction of complex **1** with $LiHBEt_3$ resulted in the hydride transfer to the C=N imine group, affording an unusual zinc dimer (**3**). A salt elimination reaction between **1** and PBr_3 gave 2,6-(2,6-$^iPr_2C_6H_3N{=}CH)_2C_6H_3P(III)Br_2$ (**4**). The reduction of **4** by potassium graphite furnished the phosphorus (I) compound **5**. All complexes were characterized by NMR spectroscopy, compounds **1-3** and **5** were determined by X-ray crystallography.



O33

Preparation of Mixed Coinage Metal Chalcogenide Clusters from Simple Precursors

Alexander M. Polgar*, John F. Corrigan
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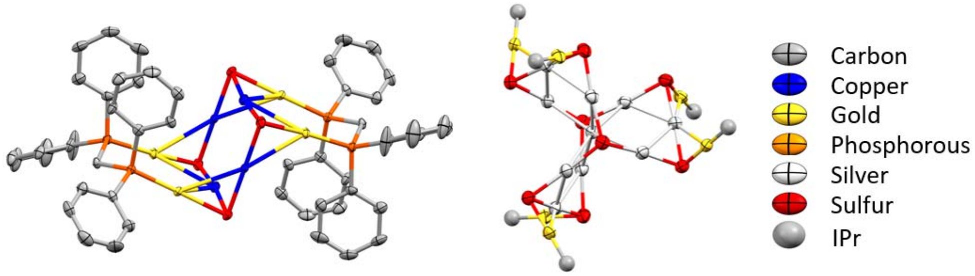
Coinage metal chalcogenide clusters have fascinated inorganic chemists for decades owing to their impressive structural diversity and optoelectronic properties. Recent developments have shown that the "alloying" of two different metals in the cluster core can enhance these qualities, especially with regard to the tuning of photoluminescence. Despite this promise, there are currently few methods for the controlled assembly of mixed-metal (ternary) chalcogenide clusters. In this talk, the directed synthesis of a gold(I)-copper(I) sulfido cluster $[Au_4Cu_4S_4(dppm)_4]$ (**1**; dppm = bis(diphenylphosphino)methane) from the gold trimethylsilylthiolate $[Ph_3PAuSSiMe_3]$ (**2**) will be presented. Recent work has shown that the thermal instability of reagents like **2** may be avoided through replacement of the ancillary phosphine with an N-heterocyclic carbene (NHC). This is demonstrated through the synthesis of $[(IPr)AuESiMe_3]$ (**3**; E = S, Se, Te; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), all of which exhibit good thermal stability in solution and the solid state. The utility of these new reagents is demonstrated through the preparation of the novel gold(I)-silver(I) sulfido clusters $[Au_4Ag_4S_4(IPr)_4]$ (**4**) and $[Au_6Ag_{10}S_8(IPr)_6]$ (**5**).



O34

Bis(phosphine) Adducts of Manganese Hydride Complexes

Jeffrey S. Price* and Dr. David J. H. Emslie
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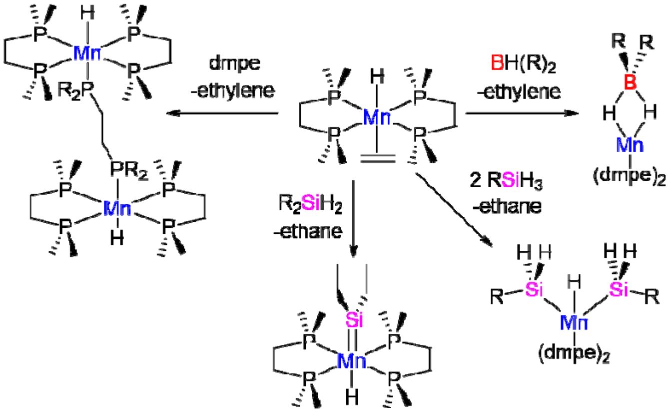
With a view towards the development of new precursors for Chemical Vapour Deposition (CVD) of elemental manganese and manganese-containing thin films, the structural, spectroscopic, and physical properties of novel manganese hydrides are reported. $[Mn(H)(ethylene)(dmpe)_2]$ (**1**), first reported by G. Wilkinson,[1] is used in this work as a precursor for the preparation of a wide variety of silyl-, silylene-, and phosphine- manganese hydride complexes. Also prepared from this complex are a series of manganese(I) hydroborate compounds. A number of these complexes display good volatility and thermal stability, which are key characteristics of any CVD precursor. Reactivity of mixed silyl-hydride complexes with a variety of reagents is also reported. This work demonstrates the versatility of complex **1** as readily prepared, thermally stable precursor to a variety of manganese hydride complexes.



[1] G. Girolami, C. Howard, G. Wilkinson, H. Dawes, M. Thornton-Pett, M. Motevalli, and M. Hursthouse, *J. Chem. Soc. Dalton Trans.* 1985, 921.

O35

Exploring the Effects of Phosphine Control on Metal Dithiolene Complexes

Zeinab S. Ahmed*, Justin D. Wrixon, Muhammad U. Anwar, Yassine Beldjoudi, Nabila Hamidouche, John J. Hayward and Jeremy M. Rawson
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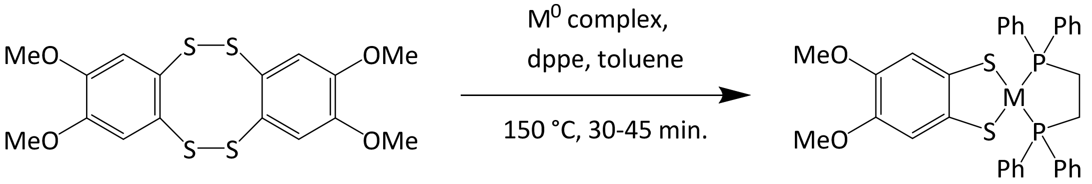
Transition metal dithiolene complexes act as useful building blocks to such diverse materials applications as organic light emitting diodes, solar cell technology, next-generation quantum computing applications, and as models for the active sites of biologically important enzymes. In the past, our group has explored the oxidative addition of a benzo-fused 1,2,5,6-tetrathiocin to zero-valent transition metals in the presence of 1,2-bis(diphenylphosphino)ethane as a new approach to making these complexes.[1]



M^0 = Ni(COD)$_2$, Pd$_2$dba$_3$ or Pt(PPh$_3$)$_4$

In this presentation we explore the effect of the phosphine co-ligand used on the structure of the resultant complexes, affording a range of poly-nuclear complexes which were characterized by NMR spectroscopy and X-ray diffraction.

[1] J.D. Wrixon, J.J. Hayward, O. Raza and J.M. Rawson, *Dalton Trans.*, 2014, **43**, 2134-2139.
[2] J.D. Wrixon, J.J. Hayward and J.M. Rawson, *Inorg.Chem.*, 2015, **54**, 9384 – 9386.
[3] J. D. Wrixon, Z. S. Ahmed, M. U. Anwar, Y. Beldjoudi, N. Hamidouche, J. J. Hayward and J. M. Rawson, *Polyhedron*, 2016, **108**, 115 -121.

O36

Reactivity of Iron Complexes containing bidentate picoyl-NHC ligands

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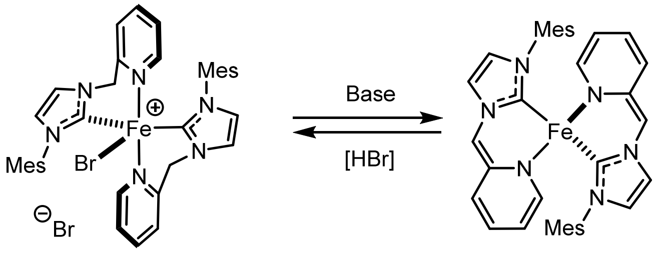
Metal-ligand cooperation is an area of great interest as it enables fascinating reactivity patterns in bond activations. An interesting mode of metal–ligand cooperation involving dearomatization–rearomatization of pyridine/acridine based tridentate ligands have been extensively studied and applied to many stoichiometric and catalytic processes (hydrogenation, water-splitting, etc.). Comparing to pincer-based ligands mentioned above, bidentate picolyl-containing ligands rarely show parallel reactivity where the removal of pyridylic proton dearomatizes the pyridine ring. Meanwhile, the development of iron-based catalysts has attracted very much attention due to its obvious advantages, including high abundance on earth, low price, low toxicity, and unique catalytic characteristics. In this presentation, the synthesis and reactivity of picolyl-NHC iron complexes will be discussed, including the reversible dearomatization/rearomatization process.



O37 Welcoming Gallium and Indium to the A520 MOF Family: Synthesis, Comprehensive Characterization, and CO_2 Dynamics

Yue Zhang,* Bryan E. G. Lucier, Sarah M. Mckenzie, Joel W. Reid, Victor V. Terskikh, Yining Huang
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Metal-organic frameworks (MOFs) are constructed from metal centers and organic linkers, with the eventual MOF properties and applications strongly dependent on the nature of building blocks employed and the final crystal structure.[1] Basolite A520 (Al-A520) is a reported porous MOF that incorporates aluminum centres along with fumarate linkers,[2] and is a very promising candidate for applications in fields such as gas adsorption (*e.g.*, CH_4, CO_2);[3] incorporation of an alternate metal center into this motif may modify these properties and unlock additional features. Furthermore, the adsorption locations, motional rates, and motional angles of guest molecules are critical to increasing adsorption capacity and selectivity, yet remain unknown in this system.

We will present the synthesis and detailed characterization of the new gallium and indium fumarate MOFs known as Ga-A520 and In-A520. Using a combination of powder X-ray diffraction, Rietveld refinements, solid-state NMR (SSNMR) spectroscopy, infrared spectroscopy, and thermogravimetric analysis, the structures of Ga-A520 and In-A520 are revealed to be analogues of Basolite A520 (Al-A520). Both MOFs exhibit an affinity for CO_2, but Al-A520 exhibits superior CO_2 adsorption performance versus Ga-A520 and In-A520 at 1 bar and 273 K. Static ^{13}C and ^{1}H-^{13}C cross-polarization SSNMR experiments yield rich details of CO_2 motion within both Ga-A520 and In-A520 MOFs, along with the CO_2 adsorption site locations and relative adsorption strengths.

(1) Zhou, H. C.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5415. (2) Alvarez, E.; Guillou, N.; Martineau, C.; Bueken, B.; Van de Voorde, B.; Le Guillouzer, C.; Fabry, P.; Nouar, F.; Taulelle, F.; de Vos, D.; Chang, J.-S.; Cho, K. H.; Ramsahye, N.; Devic, T.; Daturi, M.; Maurin, G.; Serre, C. *Angew. Chem. Int. Ed.* **2015**, *54*, 3664. (3) Gaab, M.; Trukhan, N.; Maurer, S.; Gummaraju, R.; Müller, U. *Micropor. Mesopor. Mat.* **2012**, *157*, 131.

O38 Synthesis of a Gallene, a Gallium-Carbon Double Bond

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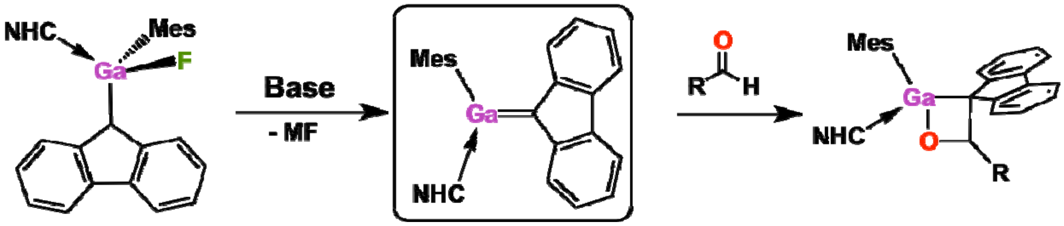
The study of the chemistry of unsaturated main group compounds, specifically those involving double bonds of heavy Group 14 elements (M=E; M = Si, Ge; E = C, Si, Ge), has been of much interest for many years. Silenes (Si=C) and germenes (Ge=C) have been shown to activate a wide range of small molecules, including aldehydes,[1] alkynes[2] and organometallic reagents.[3] Tetrelenes are reactive toward a wide range of substrates and have been shown to be useful in the synthesis of unique inorganic compounds, in particular ring systems.[4] Although these silenes and germenes have been well-studied, there are no reports in the literature describing the synthesis of a compound containing a gallium-carbon double bond. The presence of a Lewis acidic gallium centre within a multiply bonded system may lead to new and exciting reactivity. The synthetic route used to synthesize the first double bonded gallium-carbon compound, **1**, and reactions with organic substrates will be described.

(1) Baines *et al.* *Organometallics* **2011**, *30*, 3010-3017. (2) Baines *et al.* *Can. J. Chem.* **2014**, *92*, 462-470. (3) Baines *et al.* *Organometallics* **2015**, *34*, 3748-3755. (4) Baines *et al.* *Chem. Soc. Rev.* **2015**, DOI: 10.1039/c5cs00522a.



O39

Development of a Metal Ion Sensor for ppb to ppm Fe^{2+} Levels of Detection

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The most abundant transition metal in the human body is iron, and it plays a vital role in oxygen transport. Iron deficiencies lead to anemia but an abundance of iron is also dangerous; it can provoke cancer and Alzheimer's because excess iron generates free radicals within our bodies. Zinc is the second most common transition metal in the body. It is significant for cellular metabolism, yet a surplus is hazardous as well. Zinc in excess may lead to Alzheimer's, prostate cancer, and even death if it accumulates in the cells.[1] Therefore there is a need for detection and quantification of analytes such as Fe^{2+} and Zn^{2+} in biological and environmental samples. Current methods of analyte detection such as AAS, ICP, and in some cases MS require expensive and sophisticated equipment. In contrast, chemical ion sensors offer a solution because with correct development, they can be selective and cheap to prepare.[2]

We have created a water soluble chemosensor, 2,2′:6′,2″-terpyridin-4′-ylphosphonic acid (**L**), which selectively detects for ppb to ppm levels of Fe^{2+} and Zn^{2+} in competing ion solutions. Fe^{2+} with **L** experiences a colour change to pink (>30s), which is observable to the naked eye, and through the use of fluorimetry, Zn^{2+} may also be detected.[1] **L** functionalized on porous TiO_2 nanoparticles in the presence of Fe^{2+} also exhibits distinct colour changes. With the benefit of the phosphoric group, **L** was deposited on screen-printed films resulting in reusable Fe^{2+} detecting strips (Figure 1). The intensity of the colour depends on the nature of the particles, film thickness, and Fe^{2+} concentration. It is regenerated with EDTA.[3] The high affinity between **L** and Fe^{2+} makes it suitable for environmental and biological systems.

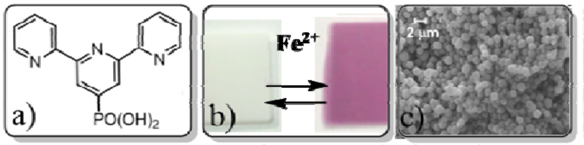

Fig 1: a) Structure of **L**, **b)** Colorimetric recognition of Fe^{2+} ions by **L** on screen-printed TiO_2/glass surfaces, and c) TiO_2 nanoparticles

[1] N. O. Laschuk, I. I. Ebralidze, D. Spasyuk, O. V. Zenkina, *Eur. J. Inorg. Chem.* **2016**, *2016*, 3530-3535.
[2] H. Sharma, N. Kaur, A. Singh, A. Kuwar, N. Singh, *J. Mater. Chem.* **2016**, *4*, 5154-5194.
[3] N. O. Laschuk, I. I. Ebralidze, S. Quaranta, S. T. W. Kerr, J. G. Egan, S. Gillis, F. Gaspari, A. Latini, O. V. Zenkina, *Mater. Des.* **2016**, *107*, 18-25.

P1

Heavy Metal Cage Match: The Organometallic Chemistry of Adamantane

Bijan Mirabi*, David Armstrong, Fioralba Taullaj, Kamalpreet Singh, Alan Lough, Ulrich Fekl**
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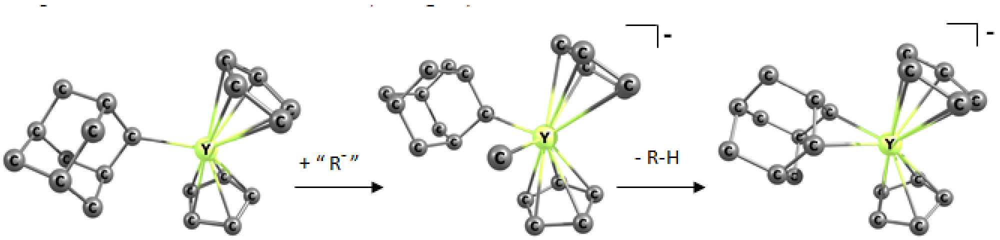
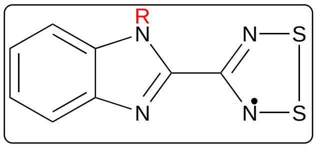
Progress in the chemistry of adamantane has been limited due to the difficulty associated with selective functionalization of the adamantane cage. Reliable high yielding synthetic procedures for directed multi-substitution of adamantane are rare, and they are commonly limited to the bridgehead position. Methods for selective substitution of multiple bridge positions of adamantane are highly desirable for applications in materials chemistry, pharmaceuticals, and catalysis. C-H activation is a promising approach to directing substitution on adamantane; however, synthesis of appropriate precursors is challenging. Recent work in our group has led to high yielding procedures for synthesis of adamantyl anion equivalents (Grignard, alkyl zinc, dialkyl zinc). These adamantyl anion precursors were used in the synthesis of the first adamantyl complexes of gold, bismuth, and mercury. We are currently working on the synthesis of ruthenium, zirconium, and yttrium complexes with potential for C-H activation. The first experimental evidence for a short lived yttrium adamantyl complex will be presented. Experimental evidence was complimented with DFT calculations (see figure).

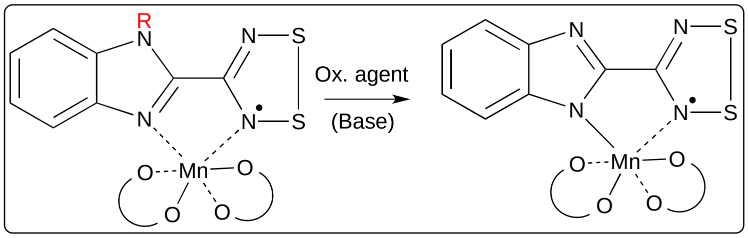


P2

Synthesis of benzimidazole-DTDA radicals and oxydation of Mn(II) in Mn(III) complexes

Tobie Wohlhauser*, Kathryn Preuss
*Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1,*twohlhau@uog.ca*





1,2,3,5-Dithiadiazolyl ligands have been reported and have been used to design molecular materials with interesting magnetic properties, (Fatila, E. M.; Clérac, R.; Rouzières, M.; Soldatov, D.; Jennings, M.; Preuss, K. E. "High-Spin Ribbons and Antiferromagnetic Ordering of a MnII-Biradical-MnII Complex" J. Am. Chem. Soc. 2013, 135, 13298-13301). Previously, our group reported a paramagnetic Mn(hfac)$_2$ complex of 4-(benzoxazol-2'-yl)-1,2,3,5-DTDA with antiferromagnetic coupling between the radical ligand and the metal center of a neighboring molecule, thus providing a large spin ground state.

This work reports the synthesis of a benzimidazole DTDA radical which will potentially allow the stabilization of a Mn(III) metal center. The trimethyl-silylated radical analogue can avoid the use of a base during the oxidation of the complex. The Mn(II) metal center will potentially provide interesting magnetic properties because of its d^5 electronic configuration but a Mn(III) center can lead to the possibility to obtain single molecule magnet.

P3

[Ru(triphos)(NCMe)$_3$](OTf)$_2$ as a homogeneous catalyst for the conversion of non-food biomass-derived substrates to value added products and fuels

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University of Guelph, Guelph, ON, Can, N1G 2W1, elatifi@uoguelph.ca, mschlaf@uoguelph.ca

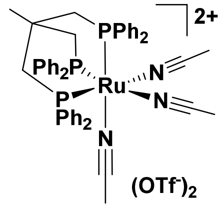

Figure 1: Ru-triphos HDO catalyst

Biomass-derived carbohydrates are a renewable carbon source, but have high oxygen content in the form of polar OH functionalities. To be used for the production of renewable fuels or chemicals, this high oxygen content must be reduced. Using conventional heterogeneous catalysts to decrease oxygen content via hydrodeoxygenation (HDO), the removal of oxygen using hydrogen, often results in rapid catalyst deactivation by coking and fouling, i.e., the formation of caramelized sugars and humins on the catalyst's surface. Homogeneous catalysts on the other hand are not susceptible to fouling or coking, but instead often suffer from lower temperature stability than heterogeneous systems. [Ru(triphos)(NCMe)$_3$](OTf)$_2$ (Figure 1), with a chelating triphosphine ligand anticipated to provide high temperature stability, was prepared and evaluated as a homogeneous HDO catalyst. The biomass-derived substrates 2,5-hexanedione and 2,5-dimethylfuran were successfully hydrodeoxygenated to value-added 2,5-hexanediol (a potential, renewable polymer linker) and 2,5-dimethyltetrahydrofuran (a fuel additive and solvent). The catalyst was stable up to 150 °C, but decomposed to an inactive insoluble cluster species above this temperature.

P4

Bistridentate ruthenium complexes with non-symmetrical Hpp ligands: Efficient chromophores for light-harvesting applications

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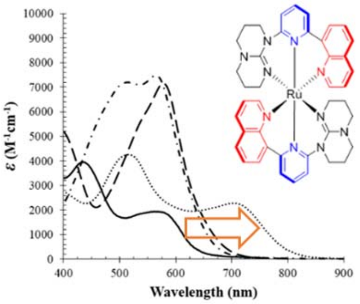
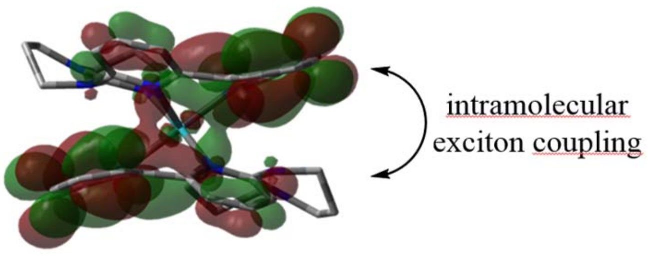
Six ruthenium complexes were synthesized based on three non-symmetrical tridentate ligands bearing the strongly electron-donating group 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*α*]pyrimidine (hpp), **bpyG** (**bpyG** =2,2′-bipyridyl-6-hpp), **phenG** (**phenG** =2-hpp-1,10-phenanthroline) and **QpyG** (**QpyG** = 2-hpp-6-quinolylpyridyl). The *fac-*/*mer-*conformation of the homoleptic species has a dramatic effect on the optical properties, where the *fac*-isomer absorption is red-shifted by 150 nm, thus reaching the near-IR at approximately 850 nm. Owing to the interesting structural effect on the optical properties, density functional theory (DFT) and time-dependent DFT calculations have been implemented to enlighten the experimental data and prove that exciton coupling is at the origin of the observed shift. The electronic properties have been investigated and, as corroborated by electrochemical data, the presence of the hpp ligand strongly affects the oxidation potential of the ruthenium metal ion, which allows facile fine-tuning of the electronic properties. The luminescence properties of all the compounds have also been investigated (λ_{max} emission = 781–817 nm) and the complexes have longer excited-state lifetimes at room temperature than the parent bis(2,2′:6′,2″-terpyridine)ruthenium(II) by 10 to 30 times.





P5

Mechanistic Studies of Iron-Catalyzed C-H Functionalization

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C-H functionalization is employed in nature, and is often catalyzed by iron-containing enzymes.[1] Many synthetic and catalytic laboratories aim to develop iron-catalysts that mimic these C-H functionalization reactions found in nature. The ability to functionalize C-H bonds would aid in difficult natural and unnatural product syntheses by circumventing the current multi-step syntheses. Iron-catalysts for C-H activation have increased in popularity in recent years; iron is abundant in nature, environmentally benign, and inexpensive compared to precious metal catalysts.[1] While there are many reports of iron catalyzed direct C-H functionalization, react developments have focused on iron-catalysts for the cross-coupling of a C-H bond with either Grignard reagents or organozinc reagents.[2-9] This class of direct C-H functionalization was first reported in 2008, where iron salts catalysts were used in the cross-coupling aryl C-H bonds with a phenylzinc reagent.[2] Since then, catalytic reactions using the same motif have increased in popularity across many different research groups.[2-8] These systems include arylation, alkylation, and amination in both C(sp^2)-H and C(sp^3)-H activation.[10] While there has been success with iron-catalyzed direct C-H functionalization, *in-situ* generated iron species have yet to be identified and mechanistic understanding of these systems is limited to a few detailed proposals. Current efforts have been placed on understanding these currents systems, as it is believed these systems will provide insights on studying more complex C-H functionalization systems.

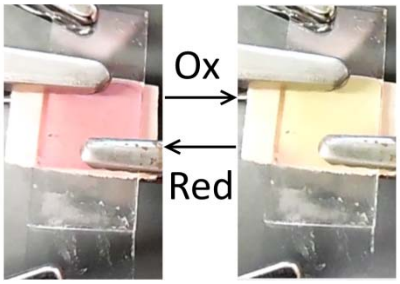
(1) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev. (Washington, DC, U. S.)* **2011**, *111*, 1293. (2) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5858. (3) Gu, Q.; Al Mamari, H. H.; Graczyk, K.; Diers, E.; Ackermann, L. *Angewandte Chemie International Edition* **2014**, *53*, 3868. (4) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E. *Angewandte Chemie International Edition* **2009**, *48*, 2925.

(5) Ilies, L.; Asako, S.; Nakamura, E. *Journal of the American Chemical Society* **2011**, *133*, 7672. (6) Fruchey, E. R.; Monks, B. M.; Cook, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 13130. (7) Shang, R.; Ilies, L.; Matsumoto, A.; Nakamura, E. *Journal of the American Chemical Society* **2013**, *135*, 6030.

(8) Sekine, M.; Ilies, L.; Nakamura, E. *Org. Lett.* **2013**, *15*, 714. (9) Matsubara, T.; Asako, S.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2014**, *136*, 646. (10) Sun, Y.; Tang, H.; Chen, K.; Hu, L.; Yao, J.; Shaik, S.; Chen, H. *J. Am. Chem. Soc.* **2016**, *138*, 3715.

P6

Novel Electrochromic materials



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We recently have reported on the development of a novel highly sensitive TiO_2-based screen printed material that was developed to detect metal ions in water.[1] The titania 2-6 μm thick films were screen printed on hydrophilic surfaces and then functionalized with water soluble 2,2':6',2''-terpyridin-4'-ylphosphonic acid (p-terpy). The TiO_2-anchored p-terpy receptor is able to coordinate to iron and ruthenium. The addition of iron (II) to the p-terpy functionalized material leads to a distinct colour change from white to magenta, while the addition of ruthenium (III) to the material results in a distinct colour change from white to peach. Here we report on the design of new materials based on semiconducting nanoparticles such as TiO_2, ITO, and ZnO/Al_2O_3 that were screen printed on conductive transparent ITO- and FTO- covered glass plates. Functionalization of these high surface area substrates with p-terpy followed by the formation of the corresponding Fe (II) and Ru (III) metal complexes leads to the formation of intensively colored materials. Since optical properties of electrochromic materials depend in a continual but reversible manner on the applied voltage, the materials were characterized using cyclic voltammetry. Indeed, the change of the metal oxidation state results in the drastic colour change of the material. The materials demonstrates long-term redox and photochemical stability, high contrast ratios, and high color homogeneity.

1. Laschuk, N. O.; Ebralidze, I. I.; Quaranta, S.; T. W. Kerr, S.; Egan, J. G.; Gillis, S.; Gaspari, F.; Latini, A.; Zenkina, O. V. *Mater. Des.* **2016,** *107*, 18-25

P7

Iron Pincer Ester Hydrogenation Catalysts: Synthesis and Preliminary Activity

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Since their recent emergence, ester hydrogenation catalysts utilizing a more earth-abundant metal such as iron with competitive activity to their heavy-metal counterparts have been sought after. The synthesis and preliminary catalytic activity of an iron(II) ester hydrogenation catalyst supported by an asymmetric P-NH-P' pincer ligand (Fig. 1) is described herein.

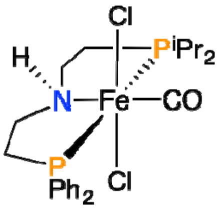

Figure 1: Fe(II) ester hydrogenation catalyst

P8

Multitasking Ru (II) & (III) Complexes Bearing Aromatase Inhibitors: Synthesis, Characterization, *in vitro* Antiproliferative Activity and *in vivo* toxicity assessment

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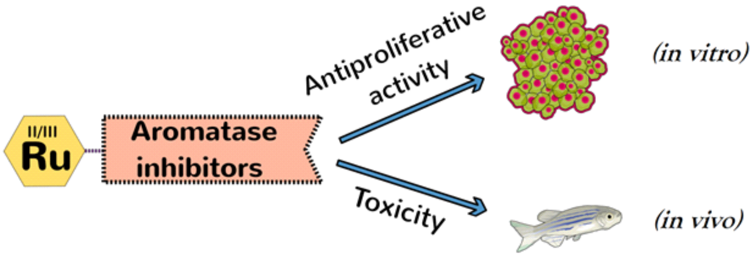
Ruthenium complexes are presently an object of great attention in the field of medicinal chemistry, as antitumor agents with selective antimetastatic properties and low systemic toxicity. Interest in Ru anticancer drugs has been growing rapidly since NAMI-A and KP1019 have successfully entered phase II clinical trials. Besides, some ruthenium complexes are active against platinum resistant cells and also display less side effects. Our goal is to create a series of multitasking ruthenium complexes bearing aromatase inhibitors currently used for estrogen receptor positive breast cancer (ER+) therapy. Ruthenium can act as a cell-killing agent through various modes of action, whereas aromatase inhibitors such as Letrozole and Anastrozole can act as anticancer agents by linking to aromatase, blocking the activity of the enzyme responsible for the production of estrogens in postmenopausal women. In this presentation, we report the synthesis of a series of ruthenium-Letrozole and ruthenium-Anastrozole complexes as well as their characterization using various techniques, including nuclear magnetic resonance spectroscopy, X-ray crystallography and high resolution mass spectrometry. In addition, we report their *in vitro* human breast cancer cell antiproliferative and antimigratory activities, which were assessed by MTS and wound healing assays, respectively. Furthermore, the results of *in vivo* toxicity test of the complexes on zebrafish embryos are also discussed.



P9

Exploring the utility of an iodide-functionalized Merrifield resin as a "phosphine sponge" in the synthesis of ruthenium metathesis catalysts

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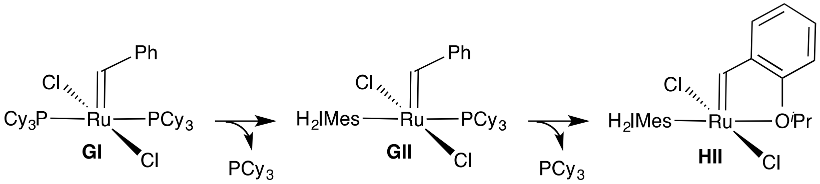

Olefin metathesis has received significant attention in recent decades for its power and versatility in the assembly of new carbon-carbon bonds. The advent of relatively robust, readily handled ruthenium catalysts has transformed organic synthesis in academia, and the first industrial processes using such catalysts are now coming on stream.[1] Most widely used are the second-generation Grubbs and Hoveyda catalysts **GII** and **HII** (Figure 1). Several years ago, our group developed convenient, high-yield routes to these catalysts, using the commercially available sulfonic acid resin Amberlyst® 15 to scavenge the PCy_3 byproduct (Figure 1).[2] Despite its utility, the high reactivity of this resin was found to present some challenges to storage and use under glovebox conditions. We were therefore intrigued by the potentially higher selectivity of an iodide-functionalized Merrifield resin (chloromethylpolystyrene-divinylbenzene)[3] as an alternative "phosphine sponge". Here we describe the utility of this material in the synthesis of **GII** and **HII**, and in studies of the reactivity of **GII**.

(1) Higman, C. S.; Lummiss, J. A. M.; Fogg, D. E. *Angew. Chem., Int. Ed.* **2016**, *55*, 3552. (2) van Lierop, B. J.; Reckling, A. M.; Lummiss, J. A. M.; Fogg, D. E. *ChemCatChem* **2012**, *4*, 2020. (3) Zhao, X.; Ivanova, N.; Hadzovic, A.; Zimmer-De Iuliis, M.; Lough, A. J.; Morris, R. H. *Organometallics* **2008**, *27*, 503.

P10

Transfer hydrogenation with 2-propanol and ethanol catalyzed by ruthenium (II) complexes supported by a pyrazole-phosphine ligand

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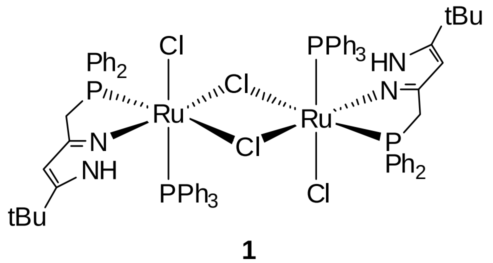
Ruthenium (II) complexes have been successfully applied to catalytic hydrogenation (HY) and transfer hydrogenation (TH) of various unsaturated substrates, mainly carbonyl compounds. The TH utilizes sources of hydrogen, other than the dihydrogen gas, which helps to overcome the main drawbacks oftheHY, such as (i) the storage and application of the potentially dangerous dihydrogen gas, (ii) the high pressures required by most reaction conditions, and (iii) consequently, the requirement of a special equipment. Most commonly used hydrogen donors for the TH are 2-propanol or formic acid, which are readily available, cheap, convenient in manipulation, and provide excellent results in the catalytic reduction of unsaturated substrates.



1

We would like to present our finding obtained during the study of the TH with 2-propanol catalyzed by the recently designed ruthenium (II) complex **1** which was found to be efficient catalyst for the TH of heterocyclic compounds, nitriles, and olefins; as well as to demonstrate new opportunities of esters reduction by catalytic TH in ethanol.

P11

Hydrodefluorination of Fluoroaromatics by Isopropyl Alcohol Catalyzed by a Ruthenium NHC Complex. An Unusual Role of the Carbene Ligand

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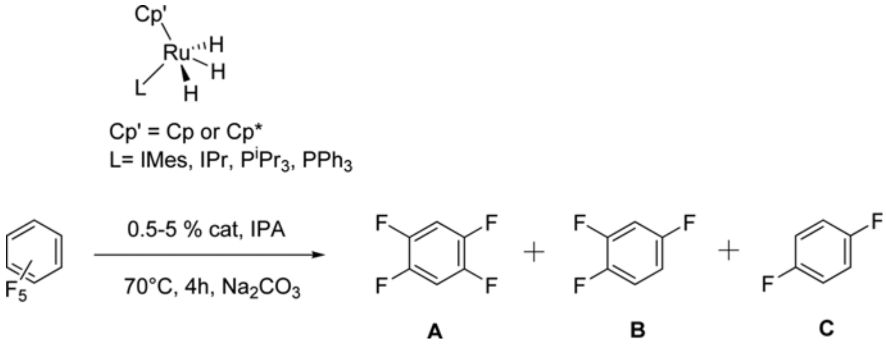
A series of new NHC (NHC = N-heterocyclic carbene) ruthenium complexes Cp'(NHC)RuH_3 were synthesized, which showed the interesting reactivities toward the catalytic hydrodefluorination of aromatic fluorides at 70 °C with isopropyl alcohol as the reducing reagent. The reaction is selective for aromatic fluorides, while there is no activity for substrates bearing C(sp^3)-F. Kinetic studies and crossover experiments suggested a new mechanism based on the elimination of NHC, the reversible substrate coordination, followed by the coordination of the alcohol.



P12

Supramolecular photochemistry with Ru and Co towards artificial photosynthesis

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The development and well-being of our society rely on innovative research concerning sufficient clean energy resources. Nowadays, with global warming issue, new alternatives to fossil fuels are based on carbon neutral energies. In the field of molecular artificial photosynthesis, photo-catalytic systems are developed to oxidize water in order to reduce CO_2 or protons [1]. Mimetic system for hydrogen generation was initiated by Lehn and Al.[2]: a system with a sacrificial electron donor such as triethanolamine, a photosensitizer $Ru(bipy)_3^{2+}$ and ' cobaloxime ' catalyst produce some hydrogen under blue light irradiation. Efficiency of photo-systems PS/Cat linked by coordination bonding is explored in literature [3]. Recently in our group, development of polynuclear supramolecular architecture Ru/Co proves greater efficiency as compared to $Ru(bipy)_3^{2+4}$. In this following work, a heteroleptic photosensitizer $[Ru(L)X(bipy)3\text{-}X]^{2+}$ (L= 4,4'-Bis(phenyl)aminocarbonyl] -2,2'-bipyridine) are investigated in different photo-reaction conditions (various wavelengths of irradiation, various concentrations, organic or aqueous media). In this case, a other supramolecular approach by halide recognition of amide pocket and the chloride of cobaloxime are evaluated for photo-catalysis. Additionally, cyclohexyl oxime Co derivative catalysts are experimented for hydrogen generation. Ru[(diphenyl-[4,4'-Bis(phenyl)aminocarbonyl]-2,2'-bipyridine)$(bipy)_2$][PF_6]$_2$ and Co$(chg)_2$ClDMAP(chg=cyclohexane1-2dione oxime) enhance interesting performances compared to references. Herein, photo-physical, electrochemical measurements, and photo-catalytic activities of the new species are discussed.

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P13

Synthesis and reactivity of 4-coordinate cobalt(III) complex containing bis(amido)pyridine ligand

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Bis(amido) pyridine, a tridentate dianionic ligand, was utilized to isolate a cationic 4-coordinate cobalt(III) complex, which was characterized by NMR and x-ray diffraction. Cyclic voltammetry studies showed that the complex undergoes two reversible 1-electron redox processes. DFT calculations (B3LPY/LANL2DZ) were performed to understand the nature of the second oxidation observed at higher potential. The 4-coordinate cobalt(III) complex is stable to air and moisture. Reactivity studies with Grignard reagents, super-hydride, isopropoxide, and phenoxide are presented. The cationic Co(III) complex is currently being investigated as precursor to a neutral bis(amido)pyridine cobalt hydrocarbyl complexes, for application in alkene polymerization.

P14

When crystallography can use help from Mössbauer spectroscopy

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Crystallography is the best method for getting detailed structural information about solids. However, there are cases when crystal structure solving by X-ray/neutron diffraction encounters difficulties. In such cases, information from other techniques can be helpful. Tin-119 Mössbauer spectroscopy can be very helpful, even essential, for some tin(II) containing materials. Divalent tin has an electron pair in its valence shell, not used for bonding, called "non-bonding electron pair" or "lone pair". The lone pair can be either on the *5s* native (i.e. unhybridized) orbital or on a hybrid orbital. An unhybridized *s* orbital is spherical, and it is said to be "non-stereoactive" since it does not change the stereochemistry of tin. In such a case, tin is present in the form of the Sn^{2+} stannous ion and bonding to tin is ionic, the tin coordination number is high and undistorted or only weakly distorted. A hybridized lone pair is axial since it is located on a hybrid orbital, and therefore it occupies space in the tin coordination sphere, reducing its coordination number and strongly distorting the shape of the polyhedron of coordination, hence it is said to be stereoactive. Tin-119 Mössbauer spectroscopy gives the tin oxidation number and also a unambiguous answer about bonding type and whether the lone pair is stereoactive. Since tin(II) can have only one lone pair, the site(s) that tin occupies in a crystal must not have symmetry elements that will generate extra lone pairs on tin. This fact has been used (i) to show that the crystal structure of $\alpha-\mathrm{SnF2}$ could have been solved 12 years earlier and much wasted efforts on a model that could not work would have been saved, and (ii) to help solve the crystal structures of disordered $M_{1-x}Sn_xF_2$ and of the very challenging doubly disordered $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution, and it showed that the latter contains a hitherto unknown form of disorder.

P15

The preparation and characterization of a novel Ni(0) compound

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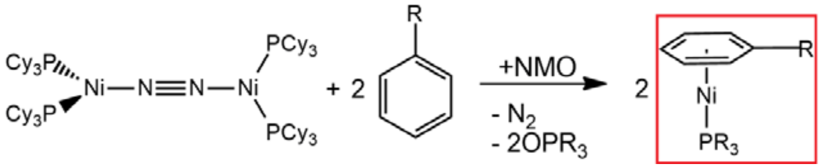
The activation and functionalization of C(sp^2)—O bonds has attracted significant interest in the past decades in the field of organic synthesis, pharmaceutic synthesis as well as sustainable fuel. It's an ideal alternative to aryl halides in organic synthesis because of the low toxicity, various derivatives, high nature abundance as well as low cost. It can be applied to produce green fuel from the lignin of plants. Economical Ni precatalysts, using bulky, strong σ-donating ligands such as PCy_3 (Cy = cyclohexyl), have been reported to activate C(sp^2)—O. Based on computational studies, it has been proposed that the active species in the C—O bond cleavage step is Ni^0PCy_3 moiety , but the existence theses monophosphine species has never been experimentally proven.

Our group has developed a novel method of preparing a Ni^0L compound, $(Cy_3P)Ni(\eta^6\text{-aryl})$, from a dinitrogen compound $(\mu\text{-}N_2)[Ni(PCy_3)_2]_2$. Jolly first prepared $(\mu\text{-}N_2)[Ni(PCy_3)_2]_2$ in 1968, however, despite its frequent use, nobody has reported that it reacts with aromatics, producing $(Cy_3P)Ni(\eta^6\text{-aryl})$ as a product and N_2 gas and PCy_3 as byproduct. This equilibrium reaction can be driven by oxidizing the PCy_3 to $OPCy_3$ using *N*-methylmorpholine *N*-oxide (NMO). We have isolated a series of $(Cy_3P)Ni(\eta^6\text{-aryl})$ (aryl = toluene, mesitylene, trifluoromethylbenzene, anisole). The reactivity of these $(Cy_3P)Ni$ sources in inert bond activation is being studied.



P16

A Palladium Catalyzed C-H Carbonylative Functionalization of Arenes

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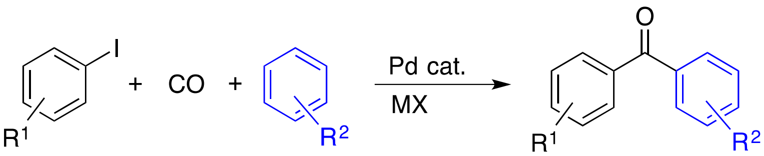

The ability to functionalize inert hydrocarbons represents one of the most potentially useful transformations in synthetic organic chemistry. Transition metal catalysis has proved quite fruitful in this area with the ability to activate C-H bonds and directly install useful functionality. These reactions usually proceed through a carboxylate assisted CMD pathway, which normally requires directing groups, an intramolecular reaction, or very specific substrates with weaker C-H bonds. An alternative approach to this widely used strategy, would be to use transition metal catalysis to make highly reactive organic fragments that could be used to functionalize a C-H bonds. In this regard, carbonylation chemistry, and in particular palladium catalyzed carbonylation chemistry, has seen growing use in the construction of esters, amides, ketones and other products and could thus be useful for the synthesis of potent carbonylated electrophiles. We have recently exemplified this approach by using palladium catalysis to functionalize electron rich heteroaromatics through the generation of a putative aroyl iodide intermediate. In this work, an efficient method for the carbonylative functionalization of unactived arenes (benzene and benzene derivatives) has been developed. This reaction proceed through an unusual, highly electrophilic aroylating intermediate.

P17

A Palladium-Catalyzed Synthesis of (Hetero)Aryl-Substituted Imidazoles from Aryl Halides, Imines and Carbon Monoxide

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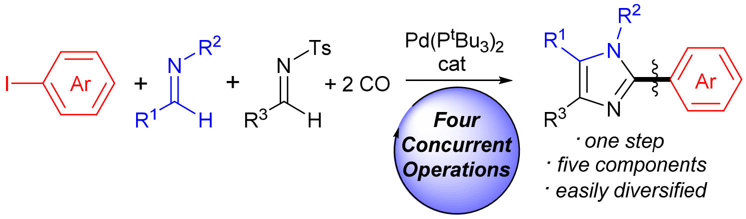
We describe here a tandem catalytic route to prepare imidazoles in a single operation from aryl iodides, two electronically distinct imines and CO. The reaction involves a catalytic carbonylation of aryl halides with imines to form 1,3-dipoles, which undergo spontaneous 1,3-dipolar cycloaddition. Overall, this offers an alternative to coupling reactions to construct the (hetero)aryl-imidazole motif, where variation of the building blocks can allow the synthesis of broad families of imidazoles with independent control of all substituents on the imidazole ring. The details of this reaction, catalyst development, mechanism and substrate scope will be discussed.



P18

Oxygen Reactivity of a NiCl(π-allyl)(NHC) Species

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Hydrocarbons are by-products of gas refinement, and converting the C-H bonds of these hydrocarbons to carbonyl groups through a direct, selective process is desirable. A direct oxidation process would produce less waste and provide an economical pathway to high value commodity and fine chemicals from these hydrocarbon feedstocks. One strategy is to use a catalyst with a toxic and/or expensive oxidant.[1] An alternative oxidant is O_2, as it is cheap, abundant, and has limited health hazards. However, O_2 can react through reduced oxygen species, which can lead to decreased selectivity.[2] Therefore, an efficient catalyst should control the selectivity of the oxidized products. A class of candidate species are NiCl(π-cinnamyl)*N*-heterocyclic carbene complexes that selectively oxidize the cinnamyl to phenyl vinyl ketone and cinnamaldehyde on exposure to O_2. [3] The NHC ligand has been altered to include a pendent amine in the secondary coordination sphere of the complex. These complexes react to O_2, mimicking the reported reactivity. Analyses of the decomposition products and the synthesis of stable intermediates have been conducted. Ligand rearrangement was observed, indicating a multistep decomposition pathway. Lastly, attempts at forming a stable intermediate has been performed by salt metathesis with sodium azide, with results indicating the successful installation.

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P19

Nickel Catalyzed Silylation of Aryl C-H Bonds

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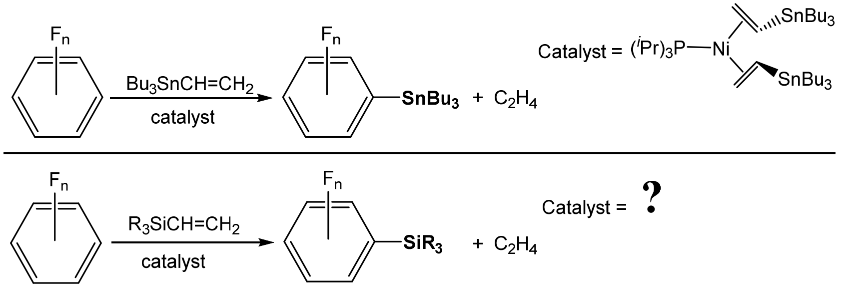
The catalytic functionalization of C–H bonds via transition metal compounds has extensive applications towards the synthesis of organic compounds bearing versatile functional groups. These reactions are commonly performed with 2nd and 3rd row transition metal complexes, whereas more abundant and economic 1st row metal complexes have not been as thoroughly studied. Our group has previously reported the nickel catalyzed C−H bond stannylation of partially fluorinated aromatics.[1] A series of mechanistic studies and tuning of the nickel catalyst have been investigated to move towards silylation of aryl C–H bonds as a facile route towards organosilicon compounds that are desired due to their economy, ecology, non-toxicity, and utility in silicon based cross coupling reactions.



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P20

Supported Transition Metal Catalysts For Use In Microwave-Assisted Continuous-Flow Organic Synthesis

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Microwave-assisted continuous-flow organic synthesis (MACOS) is the combination of microflow synthesis with microwave heating for organic reactions. MACOS has shown application in a large scope of reactions as a clean and fast synthetic method. Metal films coated on the walls of the capillary have been employed as heterogeneous catalysts in MACOS, but present several technical problems in their use; the occurrence of laminar flow allows for only a small proportion of the reaction solution to come into contact with the catalyst, and metal films are highly conductive, which can cause thermal runaway under microwave irradiation, damaging both the film and the reactor. In order to overcome the problems associated with metal films as catalysts in MACOS, metal nanoparticle-impregnated silica macrospheres were prepared and used as microwave-transparent catalyst support beds.

Macrosphere diameter is controlled through preparation conditions, up to 1.3 mm. The macrospheres can be loaded *in situ* with Pd or other desired metals, up to 4.3 wt.% Pd. The nanoparticles were confirmed to be Pd^0 nanoparticles, dispersed through the macrosphere structure. The Pd-loaded macrospheres do not afford significant heating under microwave irradiation, and act as a mixer within the capillaries, overcoming many of the problems associated with bulk metal films in MACOS. The *in situ* Pd-loaded macrospheres as a supported catalyst in MACOS for Heck cross-coupling reactions provided good yield over repeated uses of the catalyst with little leaching of Pd from the support.

The preparation of inorganic/organic hybrid macrospheres with metal coordinating functionality allowed for selective loading of Pd onto the surface of the macrospheres in higher quantity than obtainable for *in situ* loading while using significantly less total Pd. The Pd-loaded hybrid macrospheres show catalytic activity towards Heck cross-coupling reactions in MACOS, although with lower activity than the Pd nanoparticle-loaded macrospheres. The Pd-loaded hybrid macrospheres can also be converted to Pd nanoparticle-loaded macrospheres with high selective Pd nanoparticle loading on their surface.

P21

The Influence of the Transmetallating Reagent in Difficult Coupling Reactions: Control in the Selectivity of C–F Bond Activation by Ni(0) Complexes in the Presence of $AlMe_3$

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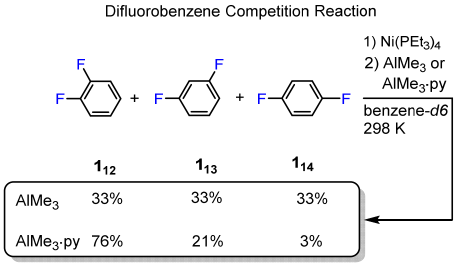
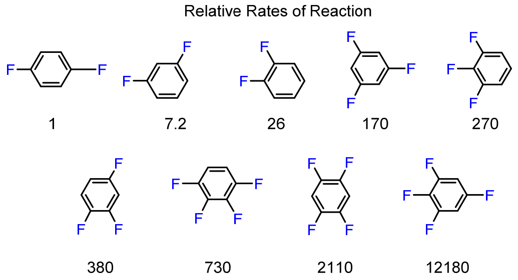
Fluorinated organics have unique properties which have led to their use in a wide variety of applications. Examples include pharmaceuticals, and materials applications such as n-type semiconductors.[1,2] Simple nickel catalysts such as $Ni(PEt_3)_4$ have shown the ability to singly activate highly fluorinated aromatics hexafluoro- and pentaflurobenzene, but struggle to activate the tetrafluorobenzenes. The tri- and difluorobenzenes do not activate at all with just a nickel catalyst. The addition of a lewis acid such as trimethylaluminum to the reaction successfully activates the di- tri- and tetrafluorobenzenes immediately upon addition. Additional difficulties arise due to ring whizzing and diactivation of the fluorobenzenes. In an attempt to slow down diactivation, pyridine was added to the reaction. This new reaction allowed for greater mono activation of the fluorinated aromatics. Competition reactions were carried out to better understand the mechanism for mono activation.





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P22

Radical labelled Au Nanoparticles; Synthesis and surface modification

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The synthesis of organic ligand-protected inorganic nanoparticles (NP) have attracted considerable attention in recent years due to their optical, electronic, and chemical properties in many applications. In 2002, gold nanonparticles (AuNPs) functionalized with organic radicals were first reported and have opened up a new field leading to potential applications such as oxidation catalyst for organic synthesis, mediators for controlled polymerization and electro-oxidation of alcohols. The idea of this project is to use alkyl thiols, which are particularly good at stabilizing AuNPs, which also support a terminal TEMPO radical. This poster describes the synthesis and characterization of TEMPO-functionalized AuNPs by EPR, UV-Vis, IR, Raman Spectroscopy and SEM microscopy. These studies reveal 25 nm diameter AuNPs which can be isolated from the solution and re-dissolved, and can be easily characterized in solid state.

P23

Simple Copper Catalysts for the Aerobic Oxidation of Amines: Counterions as a Selectivity Control Element

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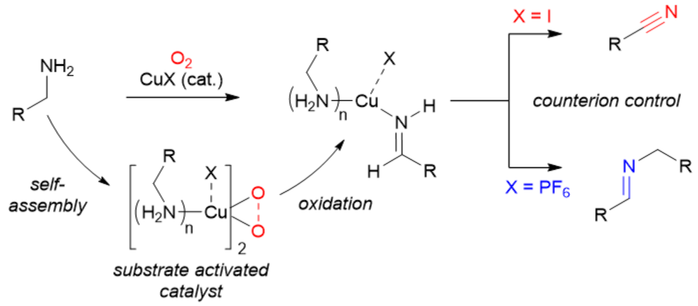
We describe the use of simple copper-salt catalysts in the selective aerobic oxidation of amines to nitriles or imines. These catalysts are marked by their exceptional efficiency, proceed at ambient temperature and pressure, and allow the oxidation of amines without expensive ligands or additives. This work highlights the significant role counterions can play in controlling selectivity in catalytic aerobic oxidations. The reaction details including scope, mechanism and counterion effects will be discussed.



P24

BODIPY dyes as non-innocent π-spacer for Dye Sensitized Solar Cells

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Owing to their intense absorption and sharp emission (exhibiting high quantum yields) properties, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes) dyes have also been extensively used in material applications. BODIPYs are synthetically versatile and can be readily tuned using a variety of synthetic techniques. Likewise, shape-persistent phenylacetylene macrocycles have been explored in a number of optoelectronic and light-harvesting applications, including two-photon absorption. Combining these two architectures could presents a derivative where a BODIPY is contained orthogonally within the phenylacetylene-macrocycle. This structure was inspired by photosystem II antennae complexes where energy is absorbed by antennae complexes and funneled down to a reaction centre. Specifically, this family of molecules uses the phenylacetylene macrocycle to harvest the light and transfer it to the BODIPY core, and this has been observed by examining the fluorescence emission from the BODIPY. This novel dye design if coupled to a donor (**D**) and acceptor (**A**) capable of anchoring to TiO_2 could be modified to become a π-spacer (*i.e.* D-π-A motif) for dye-sensitized solar cells (Figure 1) resulting in panchromatic absorption, and ultimately more efficient devices.

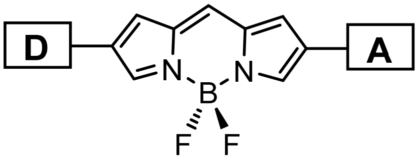

Figure 1. D-π-A Dye motif with BODIPY as π-spacer

P25

Synthesis and Characterization of Side- and Main-Chain Boron Difluoride Formazanate Polymers

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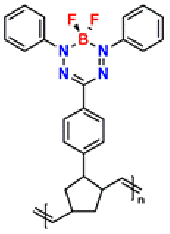
Boron difluoride (BF_2) formazanate complexes have been shown to possess interesting tunable spectroscopic properties, moderate to high fluorescence quantum yields, and unusual redox activity.[1] Their incorporation into side-chain polymers (*e.g.,* **1**) through ring-opening metathesis polymerization (ROMP) preserved the unique properties of the complex, and mechanistic studies showed the controlled nature of the polymerization.[2] Furthermore, main-chain copolymers based on BF_2 complexes and fluorene derivatives (*e.g.,* **2**) were synthesized by alkyne-azide cycloaddition chemistry.[3] These copolymers exhibited a red-shift in their absorption and emission spectra due to the extended π conjugation associated with the triazole rings. Both the main-chain and side-chain BF_2 formazanate polymers show potential as light-harvesting materials. Recent results surrounding the synthesis, characterization, and materials-based applications of BF_2 formazanate polymers will be presented.



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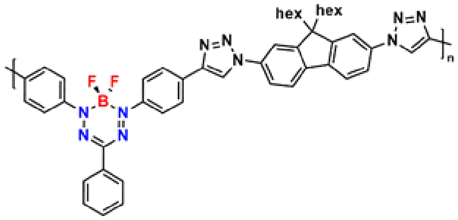

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P26

Exploring dye stability utilizing BODIPY dyads

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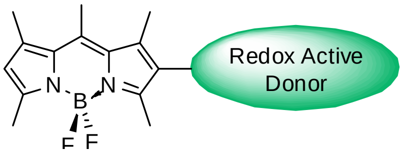
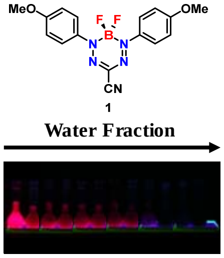


Figure 1. BODIPY dyads

Donor-π-spacer-acceptor architectures are a favourable motif in the design of dyes for light harvesting applications. There is an endless selection of molecules that can be consolidated into this motif. Previous work in the group exploring ferrocene-BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) dyes has demonstrated that there is a significant incompatibility between electron rich donors and BODIPY chromophores in terms of dye stability. To explore this further, we have designed a series of BODIPY-redox active donor dyads (Fig. 1). Implementing electron withdrawing and electron donating groups onto these redox active donors allows for tuning of the HOMO energy; these modifications alter the redox stability and electron transfer within the dyads and can give insight about charge separation. Current work on the synthesis and structure-property relationships of these dyads will be reported.

P27

Exploration of the Aggregation-Induced Emission Enhancement in Boron Difluoride Complexes of 3-Cyanoformazanates



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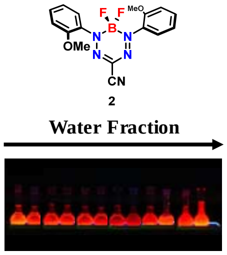

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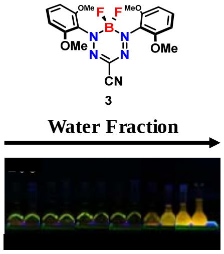

3

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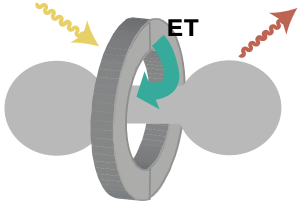
Upon aggregation, organic fluorophores generally experience attenuated emission intensity due to intermolecular π-π interactions, which leads to excimer formation.[1] This phenomenon is known as aggregation-caused quenching and is detrimental to many applications. In 2001, the diametrically opposite phenomenon of aggregation-induced emission (AIE) was discovered by Tang and co-workers.[2] AIE-active molecules are non-emissive in dilute solutions but highly emission in the aggregated state. Since its discovery, AIE-active compounds have garnered significant attention due to their applicability to the fields of organic electronics, chemical sensing, and fluorescence cell imaging.[3] The Gilroy group has demonstrated that boron difluoride (BF_2) complexes of 3-cyanoformazanates possess tunable spectroscopic and electrochemical properties through substituent choice[4] and substitution pattern.[5] This poster presentation will describe the first examples of BF_2 formazanates that demonstrate aggregation-induced emission enhancement by controlled addition of water to THF solutions of compounds **1–3**.[6]

(1) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970. (2) Luo, J. *et. al. Chem. Commun.* **2001**, 1740. (3) Mei, J. *et. al. Chem. Rev.* **2015**, *115*, 11718. (4) Barbon, S. M. *et. al. Chem. Eur. J.* **2014**, *20*, 11340. (5) Maar, R. R. *et. al. Chem. Eur. J.* **2015**, *21*, 15589. (6) Maar, R. R. *et. al. J. Mater. Chem. C.* **2016**, *4*, 6478.

P28

Exploring BODIPY-phenylacetylene rotaxanes as artificial photosynthetic systems



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*Department of Chemistry and Biology, Ryerson University, Toronto, ON M5B 2K3, *sahana.sritharan@ryerson.ca*

Attempts to mimic nature, and create artificial photosynthetic systems has transformed from an active chemical curiosity to a full-blown research pursuit, owing to our need for clean and sustainable energy generation. To this end, our program has focused primarily on study and modification of the *demi-porphyrin* dye, BODIPY (4-4'-difluoro-4-bora-3a,4a-diaza-*s*-indacene). BODIPY dyes have gained considerable attention owing to their highly desirable properties, such as strong absorption, fluorescence quantum yields, good chemical and photo-stability. These desirable physiochemical properties have led to materials that can be used for chemosensers, biological labeling agents, fluorescent switches, laser dyes, and organic sensitizers. Recently, we have examined BODIPY-based dyes in dye-sensitized solar cells (DSSCs), and within supramolecular energy transfer motifs where the BODIPY is contained within a phenylacetylene macrocycle. From this work we have gained considerable insight into collecting and harvesting light using this dye family. Building from these studies we are now interested in designing BODIPY-based rotaxanes. As a compliment to our previously reported work, rotaxanes would permit the study of through space energy transfer providing insights into the requirements of light-harvesting antennae and dye stability. This presentation presents our recent efforts in the synthesis of BODIPY-phenylacetylene rotaxanes for light-harvesting applications.

P29 Construction of Alternating Polymers of Sn & Si

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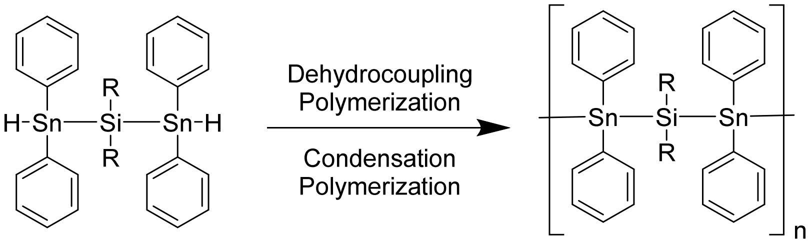
Polystannanes are great materials for semiconducting materials with their low bandgap energy and delocalized σ backbone. However, these materials have limited application due to their instability to light and moisture. This may be overcome with the inclusion of silanes within the polymer backbone. The addition of the silane moiety increased the polymer's stability to light and moisture. The dehydrocoupling polymerization or condensation polymerization of alternating stannylsilyl monomers may be used to synthesize the target polymer. The use of various substituents on the stannanes or silanes may tune the bandgap of the polymer.



P30 Intramolecular π-complexation on the Reactivity of Transient Alkenylgermylene and Alkynylgermylene

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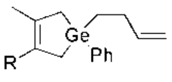
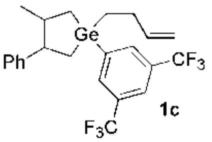
The photolysis of a potential GeH_2 precursor in solution, 3-methyl-4-phenyl-1-germacyclopent-3-ene, was found to afford a novel intramolecular germylene alkene π-complex, detected as a short lived transient species by laser flash photolysis.[1] As an extension of this work, a study of the chemistry of 3-butenylphenylgermylene (GeBuPh) from the photolysis of 1-(3-butenyl)-3,4-dimethyl-1-phenylgermacyclopent-3-ene (**1a,** R = Me) has been undertaken. The direct detection of the germylene in solution by laser flash photolysis requires the use of the more strongly absorbing analog, **1b** (R = Ph), however; the species exhibits a UV-Vis absorption spectrum (λ_{max}= 490nm) and reactivity toward selected germylene substrates that are similar to those exhibited by the model alkylphenylgermylene, GeMePh.[2] These results thus indicate that GeBuPh no significant indications of intramolecular π-complexation. With this in mind we have synthesized and studied the photochemistry of compounds **1c - e,** designed to produce a greater propensity for intramolecular complexation with the remote C=C bond and C≡C bond. Intramolecular germylene alkene π-complexes have been successfully detected for 1c, d in hexane solution by laser flash photolysis. Rate constants have been determined for reaction with some representative germylene substrates, and report on effects of intramolecular π-complexation on the reactivity of the Ge(II) center.

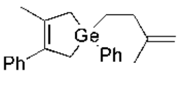
1. Billone, P. S.; Beleznay, K.; Harrington, C. R.; Huck, L. A.; Leigh, W. J., Journal of the American Chemical Society **2011,**133, 10523.



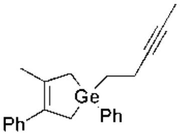
R = Me **1a**
R = Ph **1b**



1c



1d



1e

P31

Engineered Designer Monomers: The Path to Light and Moisture Stable Polystannanes

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This work continues an investigation into the utility of covalently attached light absorbing chromophores to protect the light sensitive backbone of a polystannane. The UV absorbing azobenzene antenna is incorporated into a polymerizable tin-dihydride monomer that may lead to interesting homo- and copolymer materials. Additionally, the flexible nature of the attached UV chromophore is such that it can adopt 5-coordinate geometry at Sn to further protect the sensitive Sn-Sn polymer bonds from nucleophilic attack. In this work, we present the syntheses of a series of azostannyl precursor compounds, such as the mono- and di-chlorinated species, and the polymerisable dihydride azostannane. Efforts to polymerize these materials and the final successful route for the polymerization will also be described. All precursor species were confirmed by NMR (^{1}H, ^{13}C, ^{119}Sn, HSQC), HRMS and in three cases structurally characterized by X-ray crystal structure analysis. The orientation of both the mono- and dichlorinated tin species reveal an interesting 3-center-4 electron dative interaction. The behavior of the azo-stannyl compounds and polymers were also probed by UV-Vis spectroscopy. It was observed that the cis-(n-p*) and trans-(p-p*) light switching characteristics of azobenzene are preserved in all stannyl compounds. Both polymers were also characterized by fluorimetry. Characterization of the polymers by Triple detection GPC show broad, high molecular weight ($0.8\text{-}8.0 \times 10^{5}$ Da) film forming copolymers in a 1:1 ratio (PDI = 4.12) and 8:2 ratios (PDI = 4.06).

P32

Mechanistic Study of an Asymmetric Disilene

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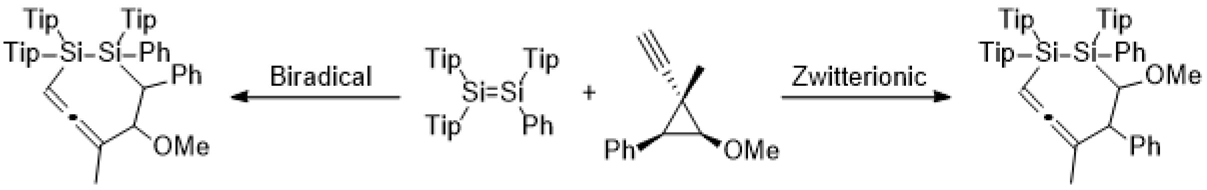
The chemistry of disilenes have been extensively studied for 35 years. Since their discovery, cycloaddition reactions have been a fundamental reaction even though it was not until 15 years ago that progress into understanding the mechanism began. The Baines group has developed cyclopropyl mechanistic probes to determine whether a biradical or zwitterionic pathway is taken upon reactions of alkyne and aldehyde functional groups with disilenes.[1] When Scheschkewitz synthesized an asymmetric disilene in 2007 a major question arose: Will the lack of symmetry change the mechanism?[2] Utilizing cyclopropyl mechanistic probes, the mechanism of cycloaddition to Scheschkewitz's disilene has been investigated.

[1] Milnes, K. K.; Pavelka, L. C.; and Baines, K. M.; *Chem. Soc. Rev.*, 2016, **45**, 1019-1035

[2] Bejan, I.; and Scheschkewitz, D.; *Angew. Chem. Int. Ed.*, 2007, **46**, 5783-5786



P33

Mechanistic Aspects of Silylenes with Carbonyl Compounds in Solution

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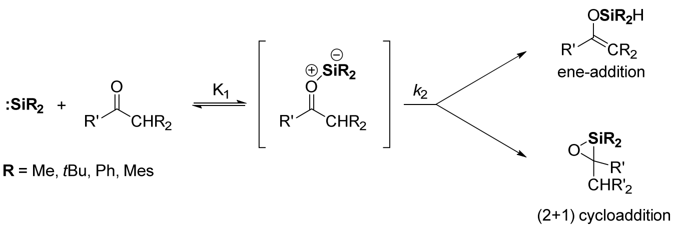
There has been considerable interest in the reactions of silylenes with carbonyl compounds, which can proceed via either an ene-addition or (1+2)-cycloaddition pathway depending on whether the carbonyl substrate is enolizable or not. These reactions are thought to proceed via a sila-carbonyl ylide intermediate, which is supported by low temperature matrix isolation[1] and computational studies.[2] The present work describes the results of fast kinetics studies of the reactions of transient dialkyl- ($SiMe_2$ and Si*t*-Bu_2) and diaryl ($SiPh_2$ and $SiMes_2$) silylenes with various enolizable and non-enolizable ketones in hexanes solution by laser flash photolysis, and our attempts to detect sila-carbonyl ylide intermediates directly and characterize their reactivity.



(1) Ando, W., Hagiwara, K., Sekiguichi, A. Organometallics, **1987**, 6, 2270.
(2) Ishida, S., Iwamoto, T., Kira, M. *Organometallics*, **2010**, 29, 5526-5534.

P34

Synthesis and Characterization of Push-Pull Polystannanes

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Until now, polystannanes are the only characterized polymers with a backbone of covalently bonded metal atoms. Polystannanes have extensive σ-conjugation due to their metallic character, which causes a pronounced optical absorption band. The σ-conjugation can be further influenced by the nature of substituent bonded to tin. Despite having potential advantages, these polystannanes are challenging to synthesize and are sensitive to moisture and light. The focus of this research is to counter-act this problematic property by incorporating light absorbing aryl groups onto the tin backbone. A series of new CH_3O phenylated tetra-aryl, monochloro-, dichloro-, and dihydride stannanes have been synthesized and characterized by NMR (^1H, ^{13}C, ^{119}Sn, HSQC) spectroscopy. An X-ray structure determination of the previously unknown tin dichloride, $(MeOC_6H_4)_2SnCl_2$ was also successfully carried out in our group. Recent synthesis and characterization work will be reported.

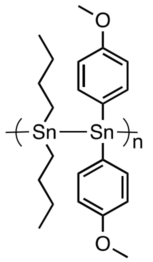

Figure 1. Target alternating polymer

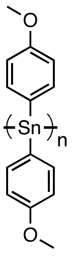

Figure 2. Target homo polymer

P35

Laser Flash Photolysis Studies of Transient Stannylenes in Solution

Ian Duffy*, Dr. William Leigh
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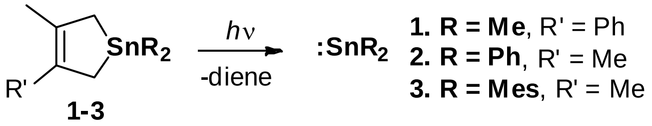

1-3

1. R = Me, R' = Ph
2. R = Ph, R' = Me
3. R = Mes, R' = Me

Stannacyclopent-3-enes **1-3** each undergo clean and efficient photocycloreversion to afford the respective transient stannylenes in solution: $SnMe_2$, $SnPh_2$ and $SnMes_2$. Flash photolysis experiments allow the direct detection of the transient stannylenes by UV-visible spectroscopy, with $SnPh_2$ and $SnMes_2$ having been detected for the first time under any set of conditions. The stannylenes dimerize at close to the diffusion controlled rate; the corresponding dimers of $SnMe_2$ and $SnMes_2$ adopt a doubly bonded distannene structure ($R_2Sn{=}SnR_2$), while dimerization with $SnPh_2$ proceeds to the stannylstannylene ($Sn(SnPh_3)Ph$).[1] Lewis acid-base complexation with aliphatic O, N, and S donors proceeds rapidly and reversibly, generating the corresponding stannylene-donor pairs. Bimolecular rate constants (k_Q) of these reactions fall within a factor of four of the diffusional limit in all cases, while equilibrium constants (K_{eq}) suggest a Lewis acidity order $SiR_2 > SnR_2 > GeR_2$ (R = Me, Ph) and $SnMes_2 > SiMes_2 > GeMes_2$ for more sterically hindered tetrylene derivatives. Reflecting the differences of stannylenes to their lighter Si and Ge homologues, reaction with tributyltin hydride and C-C unsaturated compounds also proceed with characteristics of reversible complexation, affording short-lived Lewis acid-base products exhibiting absorption maxima between 375 - 430 nm. Furthermore, the reaction with acetic acid and $SnPh_2$ proceeds entirely via arene elimination, while with $SnMe_2$; the products are derived from two independent pathways, elimination of methane and O-H insertion. σ-bond insertion with organotin chlorides generally furnishes the formal Sn-Cl insertion product, the proposed intermediate stannylene-donor pair is observed between $SnPh_2$ and Bu_3SnCl as a short lived absorption band with $\lambda_{max} = 410$ nm.

Duffy, I. R.; Leigh, W. J. *Organometallics* **2015**, *34*, 5029

P36

Coordination complexes of d^8 metal ions with macrocycles self-assembled from iso-tellurazole *N*-oxides

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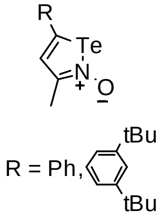
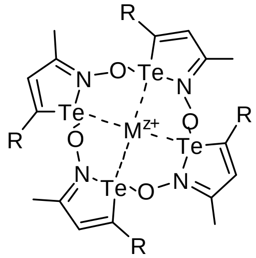
*Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4M1, *hopc2@mcmaster.ca*





M=Pd, Pt, z=2;
Rh, Ir, z=1

The sulfur and selenium analogues of crown ethers and their metal complexes have been known for long time but the tellurium equivalents remain elusive. Synthetic difficulties are one important reason, on top of which is the instability of the Te-C bond after coordination of a metal ion to the chalcogen. Recently[1] it was shown that it is possible to take advantage of Te···O secondary bonding interactions ("chalcogen bonds") to spontaneously assemble macrocycles from iso-tellurazole *N*-oxides capable of acting as tetradentate ligands towards Pd(II). Here we present the coordination complexes of Pt(II), Rh(I) and Ir(I). Those are the first examples of ions of these elements coordinated exclusively to four neutral tellurium atoms.

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.

P37

Synthesis, stability and structure of Sb(III, V) and Bi(III, V) organometallic compounds

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Antimony, bismuth, and their compounds have found increased industrial use over the past few decades. Sb is used in alloys and as an n-dopant in semiconductors, while its oxides are commonly employed as flame retardants. Bi has seen niche applications as a non-toxic substitute for lead in alloys and in medicine such as Pepto-Bismol.

The aim of this project is to synthesize substituted aryl organometallic compounds of Sb and Bi and study their physical and chemical stability for a larger molecular materials project. We are particularly interested in how these properties are affected by the size and shape of functional groups (in both axial and equatorial positions), the metal centre (Sb or Bi) and the oxidation state (III or V). For example, Bi(V) compounds tend to be less chemically stable than their Sb counterparts, presumably due to the inert pair effect and relativistic effects. Molecular geometry around the metal centre and oligomerization (e.g. monomeric vs. dimeric oxides) are also of interest. Our primary characterization methods are X-ray diffraction, thermogravimetric analysis, infrared spectroscopy and ^{1}H NMR.

Synthesis of these materials involves an aryl Grignard or aryllithium step followed by oxidation by a (pseudo)halogen. Alternatively, a metathesis reaction of a Sb(V) or Bi(V) dihalide with the appropriate ionic salt can also yield the desired Sb/Bi(V) product. Although these syntheses are relatively simple, side reactions and unpredictable reactivity often complicate the process. Several unexpected side products have been isolated and characterized by the above-mentioned methods and will also be presented.

P38

Annulated Iso-Chalcogenazole N-oxides

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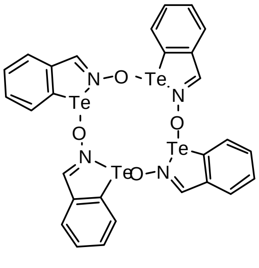
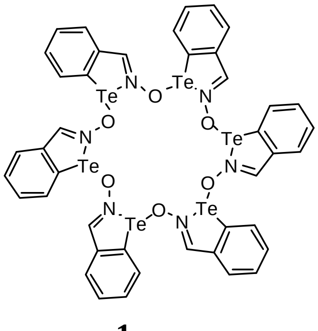
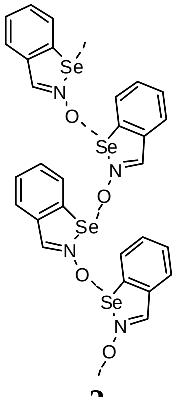
Iso-tellurazole N-oxides[1] and their benzo-annulated derivatives spontaneously assemble macrocyclic aggregates (**1_4**, **1_6**) through Te$\cdots$O secondary bonding interactions ("chalcogen bonds"). The recently isolated selenium derivative (**2**) also features strong Se$\cdots$O chalcogen bonds, as shown by a crystal that features infinite polymeric chains. However, its structure is in sharp contrast with the only other crystallographic determination of an iso-tellurazole N-oxide (**3_2**) in which dimers are formed by Se$\cdots$O interactions trans to carbon, not nitrogen. The relative stabilities of these structures will be discussed based on the results of DFT-D3 calculations.



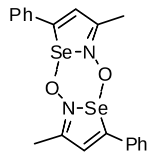
1_4



1_6



2_∞



3_2

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

Heterodinuclear complexes of a macrocyclic compartmental ligand for the design of Single Molecule Magnets

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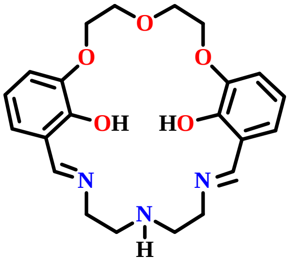
Single molecule magnets (SMMs) are molecules which are magnetized in the presence of an external magnetic field and retain their magnetization once the field is removed. This slow relaxation is due to an ‘energy barrier’ U to reversal of the magnetization which depends on *D,* the magnetic anisotropy and *S* (for transition metals) or *J* (for lanthanides). For Ln-based SMMs, the intrinsic anisotropy of their coordination complexes can be enhanced by targeting the preparation of complexes with an appropriate ligand field. In recent years we have employed N_3O_2 and N_5 Schiff-base macrocycles to confer D_{5h} symmetry on Ln(III) ions which has afforded a new family of Ln-SMMs.[1,2] Extending this concept we are currently investigating the coordination chemistry of the compartmental ligand, **H_2L** which contains two discrete N_3O_2 and O_5 binding pockets that can support pentagonal bipyramidal coordination geometry. The synthesis and coordination chemistry of this ligand with first row transition metal and lanthanide ions will be presented together with magnetic and *ab initio* studies of selected complexes.



H_2L

1. E.L. Gavey, Y. Beldjoudi, J.M. Rawson, T. Stamatatos, M. Pilkington, *Chem. Commun*. **2014**, *50*, 3741.
2. E.L. Gavey, M. Pilkington, *Polyhedron,* **2016**, *108*, 122.

P40

Ferromagnetic ordering of Ln(III) coordination polymers of selenazyl radicals

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Our group has developed a family of radical ligands that offers extensive possibilities for coordination studies and investigation of diverse properties, with the goal of designing molecular materials with controllable magnetic properties. One such radical ligand, 4-(benzoxazol-2′-yl)-1,2,3,5-dithiadiazolyl (boaDTDA), forms coordination polymer chains when coordinated to $Ln(hfac)_3$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato; Ln = La-Eu, excluding Pm). The La complex exhibits ferromagnetic (FM) coupling between radicals within the chain,[1] and the Nd and Sm[2] complexes exhibit FM ordering below 2.2K and 3K respectively, indicative of FM coupling *between* chains. Intermolecular contacts between sulfur atoms on the thiazyl ring and carbon atoms of the aryl ring of a neighboring chain are thought to be responsible for the FM coupling between chains, via the McConnell 1 mechanism.[3] The selenazyl analogue of the boaDTDA radical, boaDSDA (4-(benzoxazol-2′-yl)-1,2,3,5-diselenadiazolyl), forms coordination polymers with $Ln(hfac)_3$ (Ln = La-Nd) that are isostructural to the boaDTDA species. $La(hfac)_3$(boaDSDA) exhibits similar FM coupling between radicals in the chain to the DTDA analogue. The Nd complex exhibits FM ordering, but the onset of ordering occurs at a higher temperature than in $Nd(hfac)_3$(boaDTDA). The incorporation of the heavier chalcogen allows for increased orbital overlap in inter-chain contacts, supporting the McConnell 1 mechanism as the source of coupling between chains. Magnetic data and single crystal XRD will be presented.

(1) Fatila, E. M.; Clérac, R.; Rouzières, M.; Soldatov, D. V.; Jennings, M.; Preuss, K. E. *Chem. Commun.*, **2013**, *49*, 6271.; (2) Fatila, E. M.; Maahs, A. C.; Mills, M. B.; Rouzières, M.; Soldatov, D. V.; Clérac, R.; Preuss, K. E. *Chem. Commun.*, **2016**, *52*, 5414.; (3) McConnell, H.M. *J. Chem. Phys.*, **1963**, *39*, 1910.

P41

Syntheses and Studies of Ln(III) Crown Ether Complexes with Emissive and/or SMM Properties

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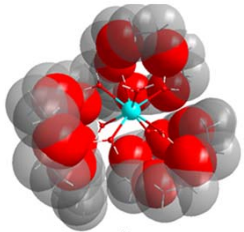
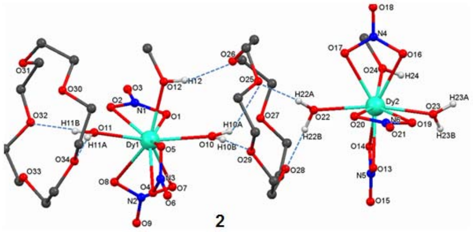
Many lanthanide ions display great potential in the field of molecular magnetism due to their high intrinsic anisotropies which can be enhanced by an appropriate coordination environment. However, many of the ligand systems employed to date require multi-step syntheses, affording complexes which are unstable to air or moisture[1]. Our approach has been to make use of the inherently oxophilic nature of Ln(III) ions together with stable, tuneable, crown ether ligands for the synthesis of mononuclear single molecule magnets (SMMs). In our first study we employed 15C5 and 12C4 macrocycles for the preparation of sandwich type complexes.[1] Modification of the organic framework of the crown ether macrocycles and/or the counter ion of the metal salt has afforded a range of new structural topologies with interesting magnetic and optical properties. We report herein the synthesis and detailed studies of three new complexes, the supramolecular capsule **1**[2] and two H-bonded chains **2**.[3]



1



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P42

Ligand Design for Chiral Single Molecule Magnets

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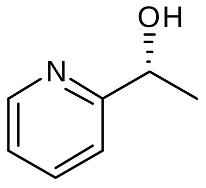
Single-Molecule Magnets (SMMs) are coordination complexes of paramagnetic metal ions that display slow relaxation of magnetization below their blocking temperature that are currently intensively researched due to their potential applications as memory storage devices. The introduction of chirality into this family of molecules creates opportunities for new properties such as magnetochiral dichroism (MChD), as well as potential applications in the field of multiferroics. In recent years we have developed synthetic strategies to chiral organic ligands for the assembly of chiral spin crossover complexes.[1] We have now extended this approach to target the preparation of small chiral, organic ligands with functionality suitable for the self-assembly of polynuclear clusters. Following this strategy, the synthesis of the chiral mpmH ligand (**1**) and its preliminary coordination chemistry together with select first row transition metal ions will be presented, as a first step towards the discovery of a new family of chiral SMMs.



mpmH (1)

1. Q. Wang, S. Venneri, N. Zarrabi, H. Wang, C. Desplanches, J.-F. Letard, T. Seda, M. Pilkington, *Dalton Trans*, **2015**, *44*, 6711.

P43

(1-Methyl-3,5-diaryl-pyridine-4(1H)-ylidene)amide, a new monoanionic nitrogen donor ligand

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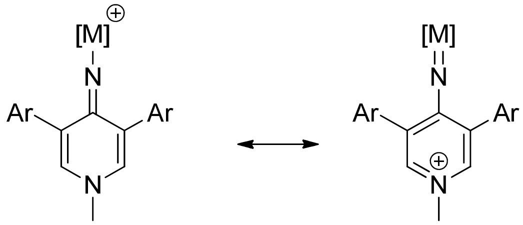
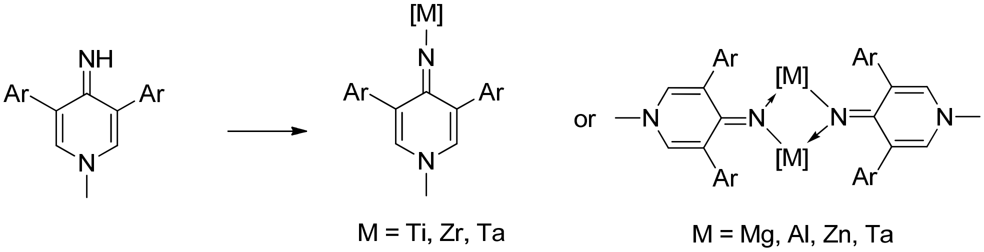
Imido-type ligands are known as ancillary ligands in a number of homogeneously catalyzed reactions (alkene polymerization, alkyne metathesis, etc). As well, they stabilize transition metals in high oxidation states and reactive cationic species by virtue of strong σ- and π-donation, and also by positive charge delocalization. For the case of our ligand, this charge delocalization is especially efficient due to ring aromatization. As well, charge delocalization decreases strong cation/anion pairing at the metal centre.



The synthesis of 1-methyl-3,5-diarylpyridin-4(1H)-imines and subsequent preparation of various metal complexes, as well as their structures and chemical properties will be discussed.



P44

Ligand-ligand charge transfer in thiazyl-metal complexes

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Thiazyl radicals offer extensive possibilities for coordination studies[1] and the investigation of diverse properties such as ordering and conductivity[2]. Previous work in the synthesis and coordination to metal ions of 1,2,3,5-dithiadiazolyl (DTDA) radical ligands has yielded interesting magnetic results. Complexes of DTDA radical ligands coordinated to $Y(hfac)_3$, $Zn(hfac)_2$ and $La(hfac)_3$ metal centers display vibrant colours despite their electronic configurations prohibiting d – d and f – f transitions, LMCT (in the case of Zn), and MLCT (in the case of La and Y). Preliminary Gaussian calculations suggest a ligand-ligand charge transfer occurring between the auxiliary beta-diketonate and radical ligand as the source of colour. This transition may also be useful in explaining the observed magnetic behavior of thiazyl radical – Ln(III) coordination polymers[3]. To investigate this transition a series of thiazyl-metal complexes composed of pymDTDA (4-(2'-pyrimidyl)-1,2,3,5-dithiadiazolyl), pymDSDA (4-(2'-pyrimidyl)-1,2,3,5-diselenadiazolyl) and two similar beta-diketonate ligands have been prepared. Preliminary UV-VIS, XRD and magnetometry data will be presented.

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P45

DFT calculations toward the development of the ligand-acidity constant method of predicting pK_a values of metal-hydrides

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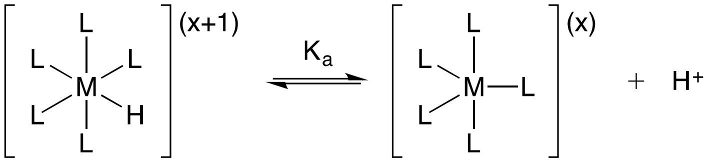
In 2013, the Morris Group reported a simple method of predicting the acidity of metal-hydride complexes. It was observed that each ligand contributes a constant value to the pKa regardless of how the ligands around the metal are arranged. These ligand additivity constants (LAC) have now been derived for a variety of ligands, and can consistently predict pKa values for metal hydrides within a margin of 3 pKa units. This predictive method can serve to help elucidate catalytic cycles and support DFT and kinetic studies. It can also be used to streamline the process of catalyst design by providing a general idea of whether a proposed catalyst would be able to facilitate a reaction efficiently. This work will present recent work that shows that DFT calculations can be used to support the highly additive nature of the LAC method.



$$\mathbf{pKa(M\text{-}H) = \sum A_L + C_{charge} + C_{nd} + C_{d6}}$$

P46

A Facile Controlled Preparation Method of Multifunctional Core-Shell Magnetic Nanoparticles by Thiol-ene Click Reactions, and Their Potential Use in Microfluidic Separations

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Surface-functionalized monodisperse iron oxide magnetic nanoparticles (IONPs) promise great advancement for aqueous microfluidic separations and catalysis. The IONPs present the interesting physical property of superparamagnetism at sizes below 50 nm. Each nanoparticle bears a significant magnetic moment when exposed to an external magnetic field, yet does not permanently magnetize once the field is removed. The large surface-to-volume ratios can be exploited for facile heterogeneous reactions at surface functionalities to be used in magnetic separation processes and recyclable dispersed catalytic supports.

One approach to introduce functionality onto the IONPs is making core-shell IONPs by surface capping in a reverse microemulsion system. The shell functionalization typically involves complicated multi-step procedures and polymerizations, which are time-consuming and labor intensive. Therefore, less complex synthetic routes towards functionalized magnetic nanoparticles are desirable. Our method prevents aggregation of IONPs and allows for the simple preparation of target-specific surface modified magnetic nanoparticles which can be used for separation and isolation of biological or chemical agents.

Our project is focused on a facile one-pot synthesis of multifunctional core-shell magnetic nanoparticles with tunable shell thickness. Efforts have been made to obtain core-shell IONPs comprising a silica coating onto a single magnetic core. We have demonstrated the potential applicability of our products in microfluidic separations using a magnetic field to separate IONPs and adsorbed targets from bulk solution.

P47

Study of the synthesis of cathode materials for lithium-ion batteries

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In order to insure energy supply of electric vehicles, lithium-ion batteries are an excellent option considering their energy storage efficiency and their durability. As a cathode component of the battery, metal complexes in solid state structures represent a good material choice due to the stability of their crystalline structure, that allow transport of lithium ions to and from the redox active complex. The overall target of my work is to examine how some redox elements can increase the energy density while maintaining the critical ionic transport.

The objective of this project is to study the solid-state synthesis of cathode materials. First, reagents have been characterised by thermogravimetric analysis (TGA) with the aim of both examining the decomposition temperature and the exact stoichiometry. Following the synthetic procedures, structural analysis of the products was made by powder X ray diffraction (XRD) to permit comparison between different compositions. Further analysis included transmission electron microscopy (TEM) and attenuated total reflectance infrared spectroscopy (ATR-IR) to examine the local structure/defects as well as inductively coupled plasma atomic emission spectroscopy (ICP-AES) to examine the stoichiometry of the final product.

P48

Improvements of the Thermoelectric Material $Zn_{13}Sb_{10}$ Through Incorporation of Dopants

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In our research, attempts were made to dope β-$Zn_{13}Sb_{10}$ with a variety of elements, on both the zinc and antimony sites. Samples were prepared by melting starting materials in an evacuated sealed silica tubes. X-ray Powder Diffraction (PXRD) and Scanning Electron Microscopy – Energy-Dispersive X-ray Spectroscopy (SEM-EDS) were used to confirm the purity of the samples. This poster discusses the In-doped $Zn_{13}Sb_{10}$ materials, which was an attempt to synthesize an n-doped $Zn_{13}Sb_{10}$ material.

The unit cell volumes of In-doped β-$Zn_{13-x}In_xSb_{10}$ changed from ~1611 Å^3 to ~1616 Å^3 for $x = 0.5$. However, the sample with this loading composition had elemental Zn as an impurity phase in addition to the major phase $Zn_{13}Sb_{10}$. This is due to the 3+ oxidation state of In, which is higher than 2+ of Zn. Prior to synthesis, we speculated that the introduction of electron-rich In on the Zn site would yield an n-doped material. Results of the synthesis and subsequent analysis suggest that replacement of Zn with In leads to the occupation of the conduction band by an extra electron. But since the states in the conduction band are antibonding, the impurity phase is therefore formed.

Subsequent samples with In were made with a lower Zn content. Several samples found to be pure were then cut into bars for Seebeck coefficient and electrical conductivity measurements. The calculated ZT value of $Zn_{12.3}In_{0.5}Sb_{10}$ achieves 0.97 at 561 K, which is greater than 0.89, the ZT value of the control sample $Zn_{13}Sb_{10}$, using $\kappa = 0.65$ W m^{-1}K^{-1}. The In-doped samples were analyzed for stability, by applying currents through the bar. The application of the 3A current for a week led to the formations of Zn on the surface of the bar sample. This test suggests that the In-doped $Zn_{13}Sb_{10}$ is not a suitable candidate for thermoelectric applicaitions.

P49

Monitoring Adsorption and Host-Guest Interactions in a Flexible Metal-Organic Framework Using $^{69/71}$Ga Solid-State NMR and PXRD

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Metal-organic frameworks (MOFs) are highly ordered materials composed of metals or metal-inorganic clusters joined by organic linkers, forming one-, two-, and three-dimensional networks with desirable properties such as permanent porosity, high surface areas, and exceptional thermal stabilities. Ga-MIL-53 is a highly porous MOF composed of GaO_6 octahedra connected by benzenedicarboxylate (BDC) linkers which exhibits a fascinating "breathing effect;" the pore dimensions and MOF topology are dependent upon the nature of incorporated guest molecules.[1,2] This phenomenon renders Ga-MIL-53 a very promising candidate for adsorption and sensing applications.

Understanding the guest location, binding mechanism, and induced structural changes in Ga-MIL-53 is crucial for the rational design of MOF-based materials for applications in sensing and guest adsorption. We use a blend of $^{69/71}$Ga SSNMR experiments and powder X-ray diffraction techniques to investigate the structural changes associated with the adsorption of CO_2 gas as well as various organic guest molecules in MIL-53(Ga). The $^{69/71}$Ga NMR parameters are highly sensitive to the host-guest binding mechanism (*i.e.*, hydrogen-bonding or π-π stacking interactions) and yield valuable information regarding the adsorbate-induced changes in the local Ga environment. The relationship between the nature of the guest, the phase of MIL-53(Ga), and $^{69/71}$Ga NMR parameters is explored.

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P50

Crystal structure and Mössbauer spectroscopy of 4-ammonium antipyridine trifluorostannate(II) monohydrate $(C_{11}H_{14}N_3O)^+(SnF_3)^-\cdot H_2O$

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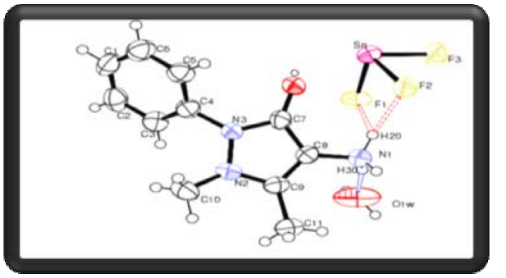

Some amines from the lactam family, that contain in the same molecule two nitrogen atoms and a ketone group, have pharmaceutical applications, mainly as antibiotics. The related compound $(C_{11}H_{14}N_3O)^+$ $(SnF_3)^-.H_2O$ was synthesized by fast evaporation of a HF/H_2O solution at 80 °C of 4-ammonium antipyridine with tin(II) fluoride, in the 1:1 ratio. X-ray diffraction on a yellow plate-like crystal showed that the unit-cell is monoclinic, space group $P2_1/c$, with a = 1.4084 nm, b = 1.0126 nm, c = 1.0533 nm, β = 103.269 °, and Z = 4 unit formulas / unit-cell. The structure refinement resulted in final R = 0.0326, R_W = 0.0699 and S = 1.025. The crystal structure is made of an anionic moiety, $(SnF_3)^-$ trifluorostannate, a monoprotonated cationic moiety, 4-ammonium antipyridine, and a water molecule. The Mössbauer spectrum is a large quadrupole doublet (Δ = 1.134 mm/s) at high isomer shift (δ = 3.615 mm/s) characteristic of divalent tin covalently bonded to fluorine with a highly stereoactive lone pair of electrons on tin. The Mössbauer results are in full agreement with the crystal structure, that shows three short (hence covalent) Sn-F bonds (0.2019 nm, 0.2039 nm and 0.2108 nm) with F-Sn-F bond angles of 88.4 °, 86.8 °. and 82.8 °, in agreement with the Valence Shell Electron Pair Repulsion theory (VSEPR).

P51 Modeling study in reverse combustion mediated by *m*-$BiVO_4$

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The photochemical reduction of carbon dioxide to alcohols using semiconductors presents a promising but challenging approach towards CO_2 neutral fuels. $BiVO_4$ is the most promising photo-semiconductor capable of doing this reduction. To understand how the $BiVO_4$ can catalyze this transformation, and see how it could be improved, it is important to determine what species are involved in the process. The extent of electron transfer from a transition metal in low oxidation state to CO_2 is the factor determining the type of transformation. Metal complexes capable of transferring two electrons normally afford either deoxygenation or disproportionation. These transformations, albeit very attractive and potentially useful, unlikely have the possibility to become catalytic, given the high stability of the M-O bond formed during these processes. However, when the transfer is limited to one electron per CO_2 molecule, radical reactivity may be triggered. During this presentation we will show that, by the judicious choice of the vanadium oxidation state, it is possible to switch from deoxygenation to radical behaviour with an unprecedented insertion into the C-O bond of the aryloxo supporting ligand and formation of organic esters.

P52 Use of Mössbauer spectroscopy to characterize new phases of tin(II)-containing fluorides prepared by leaching of other tin(II)-containing fluorides or chloride fluorides

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Some solid phases leach ions in solutions to give materials with a different stoichiometry. The initial phases, obtained by precipitation, were found to require washing with a very minimal amount of water to avoid a change of overall chemical composition and the formation of a mixture of phases, as shown by X−ray diffraction. Controlled exposure of such leachable phases in water was found to lead to the formation of new phases, pure or mixed with some of the starting phase. The new phases were identified, and some were found to be stoichiometric while others are solid solutions. Stoichiometric crystalline $CaSn_2F_6$ was prepared by the reaction of aqueous solutions of calcium nitrate or calcium chloride with an aqueous solution of stannous fluoride. $CaSn_2F_6$ was found to leach calcium ions in water to give the $Ca_{1-x}Sn_xF_2$ ($x \approx 0.10$) non-stoichiometric nanocrystalline phase. Before the present study, high performance fluoride ion conductor $BaSnF_4$ could be prepared only by high temperature reaction in dry conditions. It was found in this work that it can also be prepared by leaching of chloride ions from two new barium tin(II) chloride fluoride phases newly prepared by us. Leaching of $BaSnClF_3.0.8H_2O$ results in $BaSnF_4$ pure or mixed with another barium tin(II) fluoride, $BaSn_2F_6$ already known (obtained first by precipitation). Pure $BaSn_2F_6$ was never obtained by leaching. Partial leaching of the doubly disordered $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution also gave some $BaSnF_4$ and/or some $BaSn_2F_6$. No full transformation of the $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution was ever obtained. Phase identification and crystallographic studies were carried out by X-ray diffraction. Mössbauer spectroscopy provided the tin oxidation state and bonding type (ionic or covalent), as well as the lattice strength and surface self passivation against oxidation.

P53

High Pressure Studies on the Structural Stabilities of MOFs and Their Performances for CO_2 Storage Probed by Vibrational Spectroscopies and Synchrotron PXRD

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The SDB-based MOF (SDB = 4, 4'-sulfonyldibenzoate) family has attracted much attention because of their permanent porosity and high CO_2 selectivity over other gas molecules.[1] PbSDB was the first reported porous SDB-based MOF.[2] CaSDB has been successfully synthesized recently,[3] and is of great interest since it is nontoxic, inexpensive to make, and has a relatively light metal, which is ideal for practical applications. It is known that pressure can provide an effective driving force to achieve structural modifications. Subsequently, these pressure-induced changes will affect the sorption selectivity, capacity and access to the binding sites of the porous materials.[4] PbSDB and CaSDB have only been studied at a very limited range of elevated pressures. We report the first *in situ* high-pressure investigation of PbSDB and CaSDB by vibrational spectroscopies, including FTIR and Raman, as well as synchrotron PXRD. The PbSDB and CaSDB frameworks were found to be crystalline up to 3 GPa and 5 GPa respectively, and stable across a wide pressure range from 0 to 10 GPa. In addition, the frameworks were investigated when loaded with CO_2 under pressure; additional CO_2 binding sites were discovered in both PbSDB and CaSDB at high pressures. The host-guest interactions between the frameworks and CO_2 have been studied and the CO_2 binding sites have been explored. Our findings demonstrate great potential for PbSDB and CaSDB in gas storage applications that require extreme loading pressures.

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