Chem Con

2017

42nd Annual Science Atlantic/ CSC Student Chemistry Conference

2017

MEMORIAL UNIVERSITY

Science Atlantic Atlantique

Conference Program & Abstract Book

May 4-6, 2017
Memorial University of Newfoundland
St. John's, Newfoundland

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Graduate School Fair

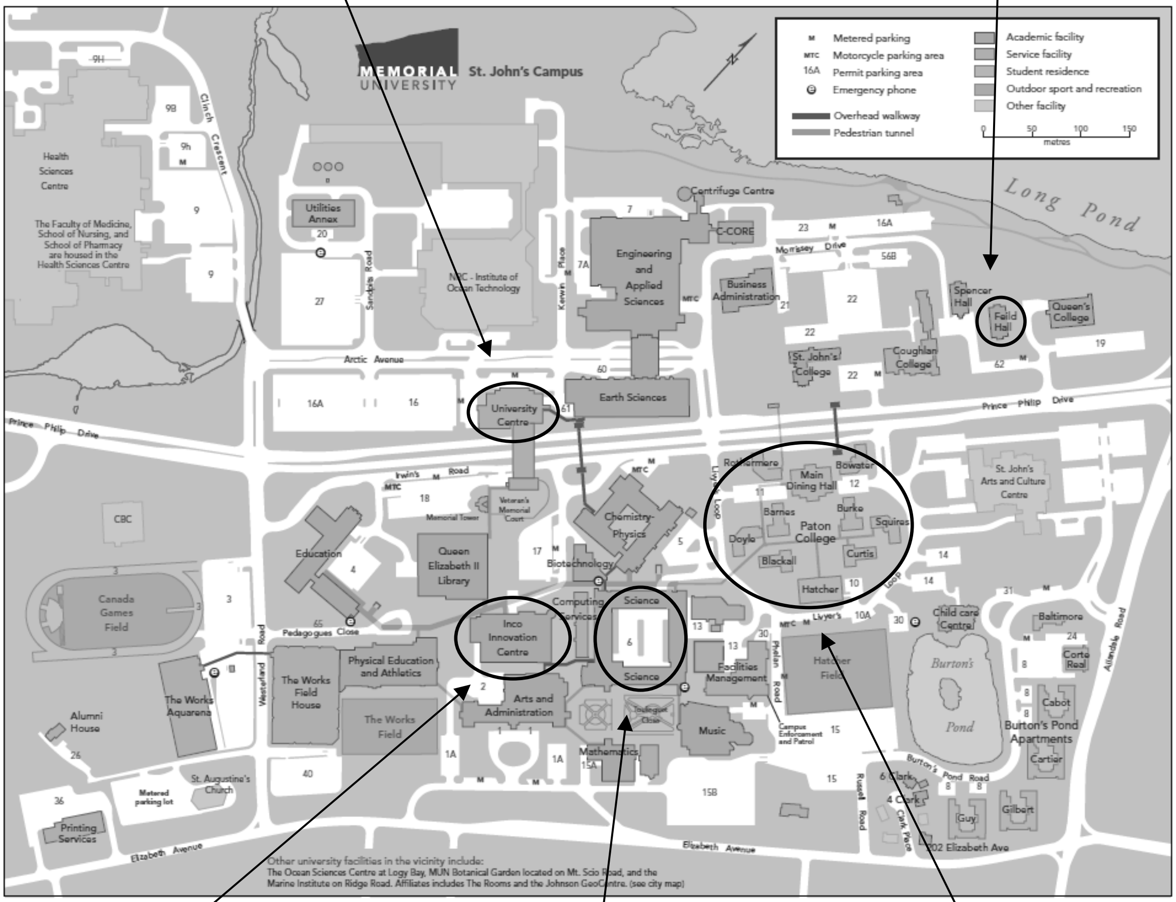
There will be a **graduate school fair exhibition** taking place during the poster session **on May 5th from 4-6 PM.** This event will take place in the Landing, located on the 3rd floor of the MUN University Center. Make sure to drop by and chat with a representative at each table to hear about potential graduate studies opportunities! There will also be a graduate school information session taking place on May 6th from 3:15-4:45 PM in ICC 2001. The following schools will be in attendance:

Brock University
Dalhousie University
McGill University
Memorial University
University of New Brunswick
University of Toronto
University of Victoria
Western University

Campus Map

The University Center
The Breezeway and the Landing
are located here

Bitters Pub
They serve great nachos!!!



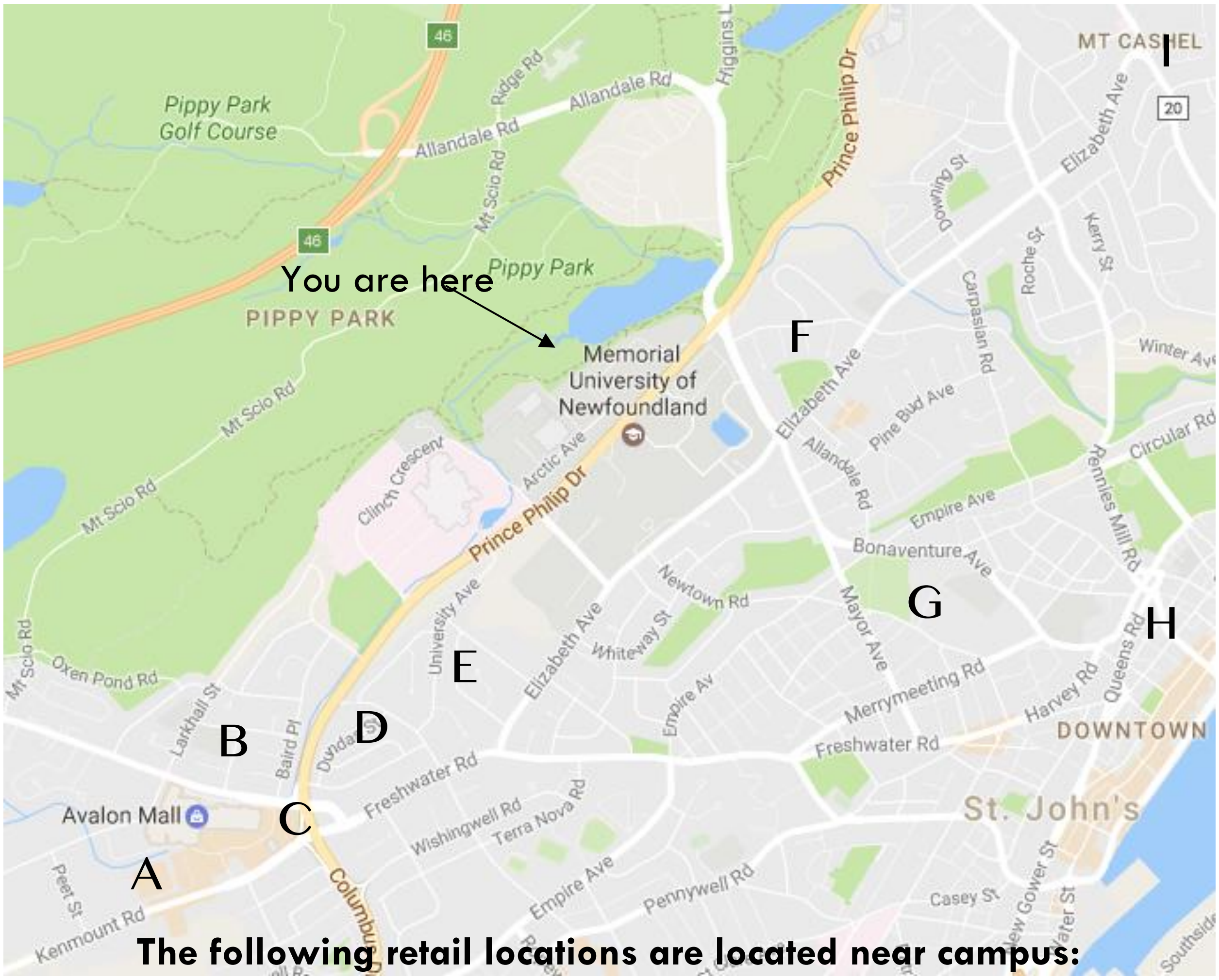
Other university facilities in the vicinity include:
The Ocean Sciences Centre at Logy Bay, MUN Botanical Garden located on Mt. Scio Road, and the Marine Institute on Ridge Road. Affiliates includes The Rooms and the Johnson GeoCentre. (see city map)

The Bruneau Centre
Location of Talks on May 6th
(ICC 2001)

Location of Residence, Dining Hall, and Hatcher House

The Science Building
Location of Talks on May 4th
and 5th (SN 2109)

Partial Map of St John's



The following retail locations are located near campus:

A: McDonalds
B: The Avalon Mall
C: Wendy's
D: Manna Bakery, Mary Browns and Extreme Pita
E: Domino's Pizza
F: Subway, Tim Hortons, Quintana's, Marie's Convenience**
G: Sobeys/ Liquor Store (Merry Meeting Location)
H: Downtown St John's
I: Sobeys/ Liquor Store

****: These establishments are <u>extremely</u> close to campus**

General Information

Presentations

The conference proceedings will be split between two locations on campus. On May 4th and 5th, presentations will take place in the Science building in SN-2109. Poster presentations will take place on May 5th from 4-6 PM in the Landing in the University Centre. On May 6th, presentations will take place in the Bruneau Centre in ICC-2001.

Each oral presentation will be allotted a 12-minute time slot followed by a 3-minute question period. Presentations should be uploaded during the morning of or during a break before your session. Posters can be set up at 3:30 PM directly before the poster session. Material for affixing posters will be provided

Note: Time limits will be strictly enforced

Opening Mixer & Trivia

Join us at the Breezeway, located in the MUN University Centre, for the opening mixer! There will be trivia sign-up sheets available at the door, teams should be of no more than 8 people. Prizes will be awarded for first and second place. **Doors will open at 6:30 PM and trivia will begin at 7:30 PM.** There will be some fantastic drink specials and free pizza will be provided!

Note: IDs required

Screech-In & Pub Crawl

If you're visiting from away come get screeched in and become an honorary Newfoundlander. If you're already from here just come for the good time! The Breezeway will open for 8 PM with a group screech-in taking place from 8:30-9:30 PM. Following this, a bus will pick us up from the Breezeway at 10 PM to head to George Street for a pub crawl. Please see the enclosed sheet which gives detailed pub-crawl information.

Banquet & Awards Ceremony

Banquet – Hatcher House

- Cocktails – 6:45 PM
- Dinner – 7:30 PM
- Awards Ceremony – 8:30 PM
- Bids for ChemCon 2018 and ChemCon 2019 – 9:30 PM

Note: A Banquet ticket must have been purchased in advance for a participant to attend the banquet.

List of Awards

CIC Award for best *Undergraduate* Oral Presentation in Analytical Chemistry

CIC Award for best *Graduate* Oral Presentation in Analytical Chemistry

CIC Award for best *Undergraduate* Poster Presentation in Analytical Chemistry

CIC Award for best *Graduate* Poster Presentation in Analytical Chemistry

CIC Award for best *Overall* Oral Presentation in Biological/ Medicinal Chemistry

CIC Award for 2nd best *Overall* Oral Presentation in Biological/ Medicinal Chemistry

CIC Award for best *Overall* Poster Presentation in Biological/ Medicinal Chemistry

CIC Award for best *Undergraduate* Oral Presentation in Inorganic Chemistry

CIC Award for 2nd best *Undergraduate* Oral Presentation in Inorganic Chemistry

CIC Award for best *Graduate* Oral Presentation in Inorganic Chemistry

CIC Award for 2nd best *Graduate* Oral Presentation in Inorganic Chemistry

CIC Award for best *Undergraduate* Poster Presentation in Inorganic Chemistry

CIC Award for best *Graduate* Poster Presentation in Inorganic Chemistry

CIC Award for best *Undergraduate* Oral Presentation in Organic Chemistry

CIC Award for best *Graduate* Oral Presentation in Organic Chemistry

CIC Award for best *Overall* Poster Presentation in Organic Chemistry

CIC Award for best *Overall* Oral Presentation in Physical, Theoretical or Computational Chemistry

CIC Award for 2nd best *Overall* Oral Presentation in Physical, Theoretical or Computational Chemistry

CIC Award for best *Overall* Poster Presentation in Physical, Theoretical or Computational Chemistry

List of Awards

ACEmat award in Computational Modelling of Material (*Undergraduate*)

CATC award for best *Overall* Theoretical Presentation

CATC award for 2nd best *Overall* Theoretical Presentation

Canadian Journal of Chemistry award for best *Overall Graduate* Presentation

Science Atlantic Science Communication Award

Science Atlantic award for best *Undergraduate* Presentation

Messages of Welcome

Dear Undergraduates, Graduate Students, and Colleagues,

On behalf of the faculty, staff, and students of Memorial's Department of Chemistry, it is my pleasure to welcome you to St. John's for the 2017 Science Atlantic Chemistry Conference, ChemCon. The organizing committee, composed entirely of Memorial chemistry students, has worked tirelessly to bring to you what appears to be an excellent scientific program. No doubt you will be kept occupied with stimulating talks, posters, and plenary presentations. Of course, like any good conference there is plenty of time to network, to talk casually about your science, to talk to potential graduate and postdoctoral supervisors, and to really learn about all the exciting science that is going in the chemistry departments all around Atlantic Canada.

There have been a few changes in the Chemistry Department since the last ChemCon was held at Memorial in 2013; I urge you to reserve some time and ask students and/or faculty to show you around their laboratories. I also hope you have time to take in the gorgeous coastline and get some pictures of the icebergs that have been littering the Avalon's coast.

Good luck at the conference and your presentations. I look forward to hearing about your research.

Travis D. Fridgen

Professor and Head, Department of Chemistry, Memorial University

Messages of Welcome

Welcome to the 42nd annual Science Atlantic-CIC Chemistry Conference!

On behalf of Science Atlantic, it is a pleasure to welcome you to St. John's, NL for ChemCon 2017!

Student conferences such as ChemCon provide important opportunities for bright young scientists like you. Whether it's gaining feedback on your presentation, learning about the exceptional research taking place in our region, or potentially meeting your future supervisor at the Grad Fair, you will be provided with valuable knowledge and the chance to get to know people who share your interests.

I hope you'll also take some time to discover something new about this fantastic region of Canada. Don't hesitate to explore MUN and St. John's. It's the perfect opportunity to go on an adventure with a new friend, or look into a future career or academic option.

Your conference organizers and volunteers have worked hard to make this year's ChemCon a great event. Please take a moment during the conference to show them your appreciation; it wouldn't have happened without them!

Enjoy the conference!

L Whitehead

Sincerely,

Lois Whitehead

Executive Director, Science Atlantic

Organizing Committee

Conference Co-Chairs
Blake Power – Food and Venue Coordinator
Mason Lawrence - Treasurer
Melanie Snow – Chief of Public Relations

Judging and Awards Coordinator
Jeremy Gauthier

Graduate School Fair Coordinator
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Departmental Representatives
Dr. Chris Flinn
Mary Flinn

Presenting Delegates

Acadia University

Anderson Fuller
Lee Brannen
Lucas Coxhead
Melissa O'Brian
Michelle Johnson
Soleil Chahine

Cape Breton University

Amanda Cameron
Amy Clemens
Matthew F Tobin
Shine Xu Zhang
Yaohuan Gao

Dalhousie University

Shayne Gracious

Memorial University

Ahmad Al Shraah
Alexander Newman
Ali Elkurtehi
Amarender Manchoju
Angham Saeed
Archita Adluri
Azam Sayadi
Boyang Gao
Christina Bottaro
Courtney Laprise
Dillon Hanlon
Erika Butler
Ernest Awoonor-Williams
Garrett McDougall
Georgios Margoutidis
Hart Plommer
Heidi Pickard
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Matthew Johnson
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Parisa Ghods
Rakan M Altarawneh
Samuel Atkinson
Stephanie Gallant
Teles Furlani
Tiffany Tozer-MacMillan
Timothy Anderson
Tobias Brueckner
Victoria Downing
Victoria Rose
Yi Liu

Mount Allison University

Samuel Baird

Mount Saint Vincent University

Guilherme Ferreira

Presenting Delegates

Saint Mary's University

Chandika Devi Ramful
Daniel O'Hearn
Ernlie Publicover
Ifenna I. Mbaezue
Jennifer Wright
Julia Killorn
Kaitlyn Blatt-Janmaat
Kyle Awalt
Matthew Laprade
Melanie Davidson
Michael Land
Presley Macmill
Ryan McCoy
Taylor Lynk

University of Toronto

Diya Zhu

University of Victoria

Chris Frazee

Dr. Mark MacLachlan

Mark MacLachlan is a professor in the Department of Chemistry at the University of British Columbia in Vancouver, Canada and is currently the Associate Dean of Research & Graduate Studies for the Faculty of Science. He is also the NanoMat Program Director and was recently appointed as the Tier 1 Canada Research Chair in Supramolecular Materials.

MacLachlan grew up in Quesnel, BC and completed his BSc degree at UBC. He then completed his PhD at the University of Toronto and a post-doc at MIT. His research is in the area of supramolecular materials and he loves the world of materials chemistry - organic, inorganic, porous materials, crystals and polymers. In his research group, they are developing new organic and inorganic materials with interesting properties that may find applications in electronics, photonics, catalysis, and other applications. They make the materials, characterize them, and study their properties, often in collaborations. They develop diverse materials - solid-state structures, polymers, gels, glasses, and others - to address interesting scientific and engineering problems. When not in the department, MacLachlan enjoys drinking coffee, running, mountain biking, and spending time with his family.

May 5th 2017 from 1:15-2:15 PM (SN 2109)

Dr. Jennifer Murphy

Jennifer Murphy is an Associate Professor in the Department of Chemistry at the University of Toronto, where she held a Canada Research Chair from 2007-2016. Her research program focuses on the atmospheric chemistry and biogeochemistry of reactive nitrogen species. Her group participates in atmospheric chemistry field measurement campaigns around the world, including Scotland, California, Utah, Colorado, Ontario, the Alberta Oils Sands Region and the Canadian Arctic.

She serves as an editor at the Geochemical Journal and the open access journal Atmospheric Chemistry and Physics. In 2016, she was nominated to the Scientific Steering Committee of the International Global Atmospheric Chemistry (IGAC) project under Future Earth. She completed her BSc in Chemistry at McGill University in 2000, and her PhD in Chemistry at University of California, Berkeley in 2005.

May 6th 2017 from 1:15-2:15 PM (ICC 2001)

May 5th from 12:00-1:00 PM

From Coast to Coast: A Journey of Accidental Findings

with Dr. Michael Katz
Room SN 2036

Coordination polymers, are a group of materials in which metal centres are linked to one another via a bridging ligand. You can control the structure of these materials by understanding the coordination chemistry of the metal and picking the shape of the bridging ligand. The presentation will focus on the journey from my graduate work on non-porous coordination polymers to my independent work on porous coordination polymers (Metal-Organic Frameworks (MOFs).

During graduate school at Simon Fraser University, I used coordination polymers to sense ammonia gas. I learned that the “easy project” can be full of mystery. When I was a postdoctoral researcher at Northwestern University, I had a “great idea” about making MOFs for CO2 adsorption. Unfortunately, the literature methods for making the MOF I needed didn't work. On accident, I discovered a method of making the MOF; this method is now the prevalent method in the literature. From here, I picked up a project that looked promising, but showed irreproducible data from a previous researcher; the key to success was the irreproducible data. The project was centred on studying how MOFs could be used to convert toxic nerve agents to safe molecules that you could eat. In my independent work at Memorial, we are continuing to study the synthesis and applications of porous material from applications in light sensitive MOFs for separations to applications in environmental monitoring.

May 5th from 12:00-1:00 PM

Half Man, Half Benzene – Light-hearted Reflections on an Incredibly Stable Journey

With Dr. Graham Bodwell

Room SN 2018

With only fear of the unknown and conventional wisdom holding me back, I set forth on a less-travelled path from a comfortable undergraduate existence at a Canadian institution at one end of the country and rode its undulations with abandon until reaching one at the complete opposite end of the country. The end of that journey heralded the beginning of a new and yet unfinished one. The anecdotes, (mis)adventures and common threads of these travels can be spun loosely into lessons, which will be offered in the hope of providing a modicum of amusement, edification and inspiration.

Chalk Talks

May 5th from 12:00-1:00 PM

Environmental Chemistry: What, Why, Where, How?

With Dr. Cora Young

Room SN 2025

Environmental chemistry is a relatively new sub-discipline of chemistry. Over this lunch break, we will informally discuss the nature of environmental chemistry (what is environmental chemistry?), the impact of the work and the marketable skills that can be obtained by working in this discipline (why environmental chemistry?), the type of environments in which environmental chemists work, including labs and the field (where does environmental chemistry happen?), and my path to becoming an environmental chemist (how to become an environmental chemist?).

Schedule of Events

Day 1: Thursday, May 4th 2017

Science Building

1:00-4:30 PM Registration and Check-in — Lobby
4:30-5:00 PM Opening Remarks — SN 2109
5:00-6:15 PM Oral Presentations: Session 1 — SN 2109

The Breezeway

6:30-12:00 AM Opening Mixer (Pizza & Trivia)

Day 2: Friday, May 5th 2017

Science Building

7:30-8:30 AM Continental Breakfast — Lobby
8:30-10:00 AM Oral Presentations: Session 2 — SN 2109
10:00-10:15 AM Break — Lobby
10:15-11:45 AM Oral Presentations: Session 3 — SN 2109
12:00-1:00 PM Chalk Talk Lunch (SN 2018, SN 2025, & SN 2036)
1:15-2:15 PM Keynote Address by Dr. Mark MacLachlan — SN 2109
2:15-3:30 PM Oral Presentations: Session 4 — SN 2109

3rd Floor MUN University Centre (The Landing & The Loft)

3:30-4:00 PM Poster & Exhibition Set-Up
4:00-6:00 PM Poster Presentations and Grad Fair Exhibition

Chemistry Building

6:00-7:00 PM Science Atlantic Meeting — C 4019
7:00-8:00 PM Science Atlantic Maritime Section Meeting — C 4019

The Breezeway

8:00-10:00 PM Screech-In & Social
10:00 PM Depart Breezeway via Bus for Downtown Pub crawl

Downtown

1:00 AM Board Bus back to MUN Campus

Day 3: Saturday, May 6th 2017

Bruneau Centre

7:30-8:30 AM Continental Breakfast — Lobby
8:30-10:00 AM Oral Presentations: Session 5 — ICC 2001
10:00-10:15 AM Break — Lobby
10:15-11:45 AM Oral Presentations: Session 6 — ICC 2001
12:00-1:00 PM Lunch — Main Dining Hall
1:15-2:15 PM Keynote Address by Dr. Jennifer Murphy — ICC 2001
2:15-3:30 PM Oral Presentations: Session 7 — ICC 2001
3:30-3:45 PM Break — Lobby
3:45-5:15 PM Graduate School Information Session — ICC 2001

Chemistry Building

5:15-6:30 PM Judging Meeting — C 4019

Hatcher House

6:45-7:30 PM Cocktails
7:30-8:30 PM Dinner
8:30-9:30 PM Awards Ceremony
9:30-10:00 PM Bids for ChemCon 2018 and ChemCon 2019

Presentation Schedule

May 4th 2017

Session 1

Time	Presenter
5:00-5:15 PM	Soleil Chahine, Acadia University
5:15-5:30 PM	Victoria Downing, MUN
5:30-5:45 PM	Stephanie Gallant, MUN
5:45-6:00 PM	Mason Lawrence, MUN
6:00-6:15 PM	Melissa O'Brian, Acadia University

May 5th 2017

Session 2

Time	Presenter
8:30-8:45 AM	Taylor Lynk, SMU
8:45-9:00 AM	Daniel O'Hearn, SMU
9:00-9:15 AM	Kaijie Ni, MUN
9:15-9:30 AM	Matthew Tobin, CBU
9:30-9:45 AM	Jennifer Murphy, MUN
9:45-10:00 AM	Chris Frazee, UVIC

Session 3

Time	Presenter
10:15-10:30 AM	Heidi Pickard, MUN
10:30-10:45 AM	Melanie Snow, MUN
10:45-11:00 AM	Amy Clemens, CBU
11:00-11:15 AM	Courtney Laprise, MUN
11:15-11:30 AM	Jeremy Gauthier, MUN
11:30-11:45 AM	Matthew Laprade, SMU

Session 4

Time	Presenter
2:15-2:30 PM	Teles Furlani, MUN
2:30-2:45 PM	Victoria Rose, MUN
2:45-3:00 PM	Julia Killorn, SMU
3:00-3:15 PM	Garrett McDougal, MUN
3:15-3:30 PM	Amanda Cameron, CBU

May 6th 2017

Session 5

Time	Presenter
8:30-8:45 AM	Ifenna Mbaezue, SMU
8:45-9:00 AM	Samuel Atkinson, MUN
9:00-9:15 AM	Anderson Fuller, Acadia University
9:15-9:30 AM	Archita Adluri, MUN
9:30-9:45 AM	Melanie Davidson, SMU
9:45-10:00 AM	Ernest Awoonor-Williams, MUN

Session 6

Time	Presenter
10:15-10:30 AM	Dillion Hanlon, MUN
10:30-10:45 AM	Chandika Devi Ramful, SMU
10:45-11:00 AM	Erika Butler, MUN
11:00-11:15 AM	Kenson Ambrose, MUN
11:15-11:30 AM	Kaitlyn Blatt-Janmaat, SMU
11:30-11:45 AM	Marc MacKinnon, MUN

Presentation Schedule

Session 7

Time	Presenter
2:15-2:30 PM	Ernlie Publicover, SMU
2:30-2:45 PM	Matthew Johnson, MUN
2:45-3:00 PM	Joshua Walsh, MUN
3:00-3:15 PM	Michael Land, SMU
3:15-3:30 PM	Parisa Ghods, MUN

The Synthesis of N,C-Bound Phosphenium Cations and Reactivity Studies with Hydrogen, Ammonia and Carbon Dioxide

Soleil Chahine, Acadia University

Division: Undergraduate Inorganic

The scientific community is moving towards eco-friendlier practices. Two areas that pose environmental concern are the emission of greenhouse gases, like carbon dioxide and the storage of gases, like hydrogen and ammonia. N,C-Bound carbenes (R2N–C–R') activate ammonia and hydrogen, so it is hypothesized that N,C-bound phosphenium cations (R2N–P+–R') will also activate these molecules due to similar reactivity to carbenes. If successful, phosphenium cations would be a more cost-effective alternative to carbenes as an industrial method of reducing greenhouse gases and storing gases. The study of N,C-bound phosphenium cations is a very new and promising field in main group chemistry research, as only two synthesized examples of these compounds have been reported in literature. A series of phosphenium cations were synthesized using combinations of the following carbon-bound groups: 2,4,6-trimethylphenyl, 2,4,6-triisoproylphenyl, 2,6-diisoproylphenyl and 2,6-dimesitylphenyl, and the following nitrogen-bound groups: diisopropylamine and dicyclohexylamine. The synthesis of different salts of the phosphenium cation was attempted, using the following anions: tetrachloroaluminate, tetrafluoroborate and trifluoromethanesulfonate triflate. Solutions of the salts were treated with excess amounts of small molecule reagents (carbon dioxide, hydrogen and ammonia). The resulting products were characterized by 31P, 13C and 1H NMR spectroscopy

Notes:

The Role of NO^+ Formation on Nitrous Acid Sequestration

Victoria Downing, Cora Young and Michael J. Katz, Memorial University

Division: Undergraduate Inorganic

The metal-organic frameworks (MOFs) UiO-67-NH_2 and UiO-68-NH_2 were synthesized to investigate the role of distance on the mechanism for which HONO sequestration occurs. Based on previous research, UiO-66-NH_2 has been shown to selectivity react with gas-phase HONO to form a diazonium intermediate which further decomposes in the environment to form the hydroxyl containing MOF. To get a better understanding of how this mechanism occurs with regards to the formation of the nitrosonium ion on the zirconium cluster and where the NO^+ reacts on the MOF, MOFs with different sized linkers were synthesized. UiO-67-NH_2 showed no selective reaction with gaseous HONO. This can either be attributed to the increase in distance between the two reactive sites or to insufficient purification of the MOF before exposure to HONO resulting in formylation of the amine group. The ion chromatography results showed an increase in HONO production after exposure to UiO-67-NH_2, likely due to the self-reaction of HONO and heterogeneous reaction of NO_2.

Notes:

Preparation of Gold Thin Film-Iron Oxide Nanoparticle Composites for SERS Detection of Environmental PAH's

Stephanie M. Gallant and Erika F. Merschrod, Memorial University
Division: Graduate Inorganic

Polycyclic aromatic hydrocarbons (PAHs) are persistent pollutants in the environment, and are a common product of oil and fuel-related processes. Though oceans and natural waters may contain low concentrations of these pollutants, their bioaccumulation in organisms over time is a major concern. PAHs are well-established carcinogens, and can also lead to things like decreased immune function, birth defects, and organ damage. We are working on developing new substrates for surface-enhanced Raman spectroscopy (SERS) detection of these low-level concentrations of PAHs. Specifically, we are looking at composites of iron oxide nanoparticles (NPs) and gold thin films for our substrates. Iron oxide NPs are cheap and methodically simple to synthesize, and when surface-functionalized with silanes, have shown to be stable and reliable. Our research goals include simple substrate fabrication and assembly, ppb-level LODs for multiple PAHs, and reusable substrates.

Notes:

Mo' Humidity Mo' Problems: A UiO-67 Stability Study with Respect to Relative Humidity

Mason C. Lawrence and Michael J. Katz, Memorial University

Division: Undergraduate Inorganic

Metal-organic frameworks (MOFs) have been gaining a lot of attention over the last decade for their versatile applications ranging from gas storage and separations to light harvesting. MOFs are comprised of two components: inorganic cations or clusters known as nodes, and organic bridging ligands known as linkers. The linkers and nodes connect to one another to form an infinite 3D porous network. Zirconium-cluster-containing MOFs such as MOF-841, NU-1000, PCN-222 and UiO's have been of great interest due to the applications previously mentioned. The UiO family of MOFs, Especially UiO-66 has been studied for many applications. With applications in mind, it has also even studied for its stability with respect to pH, pressure, temperature, and solvent response. UiO-66 is made up of a $Zr_6O_4(OH)_4^{12+}$ cluster (Figure left) that is joined by terephthalate linkers (Figure middle). Switching the terephthalic acid linker for biphenyldicarboxylate forms UiO-67 (Figure right). Like UiO-66, this MOF has also been featured in a wide range of applications. The stability of UiO-67, however, has had a precarious history. Unlike UiO-66, there are mixed reports on the long-term stability of this MOF. The literature data is incomplete and does not offer a definitive answer to the stability of UiO-67. To probe the stability of this MOF, in order to better understand which applications this MOF can be used for, this presentation will discuss the stability of UiO-67 with respect to humidity (23%, 54% and 75%) over the course of 100 days. This presentation will illustrate our findings when UiO-67 is exposed to 23%, 54% and 75% relative humidity conditions for up to 99 days.

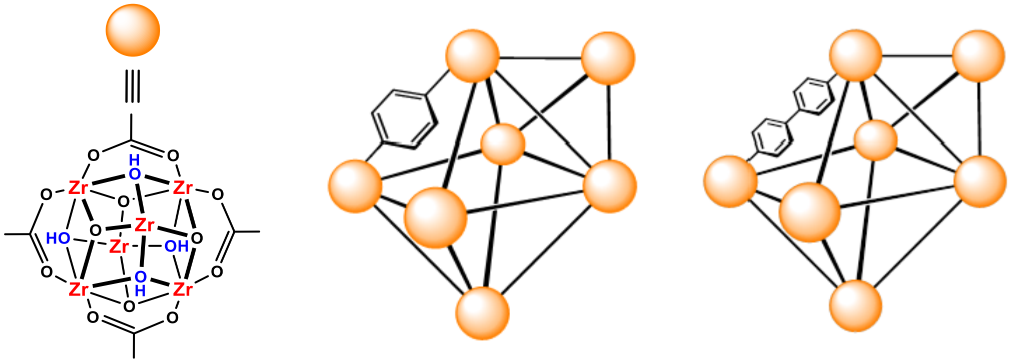


Figure: (left) The Zr-Cluster of the UiO-family of MOFs. The structure of UiO-66 (middle), and UiO-67 (right) showing one octahedral pore and one face-sharing tetrahedral pore; this connectivity continues in all three dimensions to form the full MOF structure.

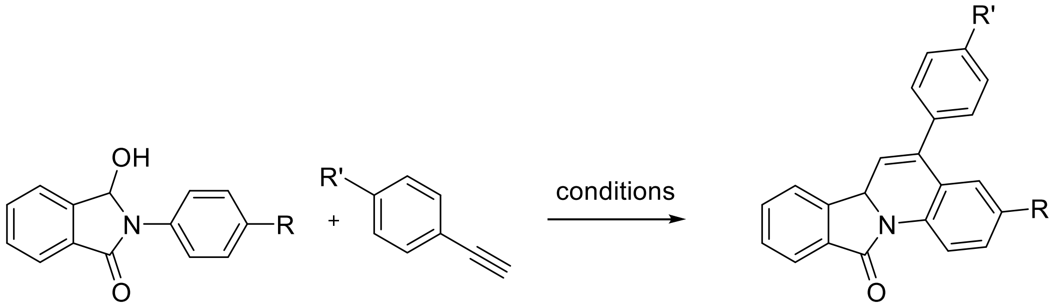
Notes:

5-Arylisoindolo[2,1-a]quinolin-11(6aH)-ones from N-Acyliminium Ions and Aryl Acetylenes through Cycloaddition Reaction

Melissa O'Brien, Minati Kuanar, Rachael Weagle, Prabhu P. Mohapatra and
Amitabh Jha, Acadia University

Division: Undergraduate Organic

Fused heterocycles, such as isoindoloquinolines are found in many natural products and biologically active molecules. 5-Arylisoindolo[2,1a]quinolin-11(6a*H*)-ones were synthesized from phthalimide derivatives and substituted aryl acetylenes in one pot under Lewis acid-catalyzed conditions in good yields. The results obtained thus far will be presented.



Notes:

Green Synthetic Approaches for the Production of High Performance Plasmonic Sensors

Taylor P. Lynk, Osai J.R. Clarke, and Dr. Christa L. Brosseau, Saint Mary's University,
Division: Undergraduate Analytical

With the increasing popularity of nanotechnology, it is undoubtedly necessary to render the synthesis of nanomaterials more environmentally benign to allow for continued growth in the field. Natural extracts have become a green alternative to harsh chemical reducing and capping agents in noble metal nanoparticle synthesis. In this work, silver nanoparticles (AgNPs) are synthesized using a variety of natural extracts, and are then used to fashion substrates for surface enhanced Raman spectroscopy (SERS). The advantage of employing a chloride displacement treatment to reduce the effects of the biogenic corona associated with green extracts is demonstrated. Avocado pit extract proved to be superior to other plant and fruit extracts in terms of efficacy and applicability, as well as being superior to traditional methods. The size and shape uniformity of these AgNPs was assessed using scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM). SERS performance is demonstrated using both para-aminothiophenol (p-ATP) and 4,4'-bipyridine (4,4'-BiPy) as probe molecules. The effect of electrochemical SERS (EC-SERS) on the performance of AgNPs made using avocado pit extract was also investigated using adenine as a probe molecule. The green nanoparticles presented in this work, especially those synthesized using avocado pit extract, have shown their ability to be incorporated into specific, high performance plasmonic sensors, with the potential to be used for quantitative detection of a variety of molecules.

Notes:

The Design of an Imidazolium Functionalized SIFSIX Pillared Metal-Organic Framework

Daniel O'Hearn, Saint Mary's University
Division: Graduate Inorganic

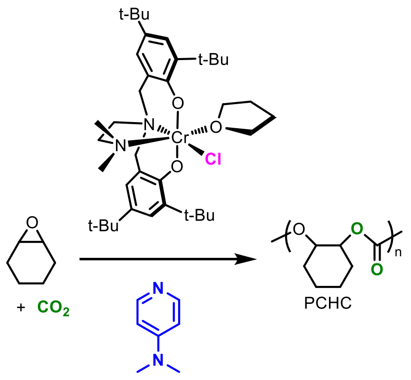
The use of pyridyl functionalized imidazolium salts as ligands for a metal-organic framework is attractive in the context of CO2 adsorption. The imidazolium functionality can provide enhanced CO2 capture via chemisorption, as well as the potential for the catalytic conversion of CO2. The target framework is a 2-dimensional coordination polymer consisting of 1,3-bis(pyridylmethyl) imidazolium salt linkers and copper(II) cations that are pillared with hexafluorosilicate (SIFSIX) anions. The outcomes and obstacles of this work will be discussed, as well as some context from preceding work.

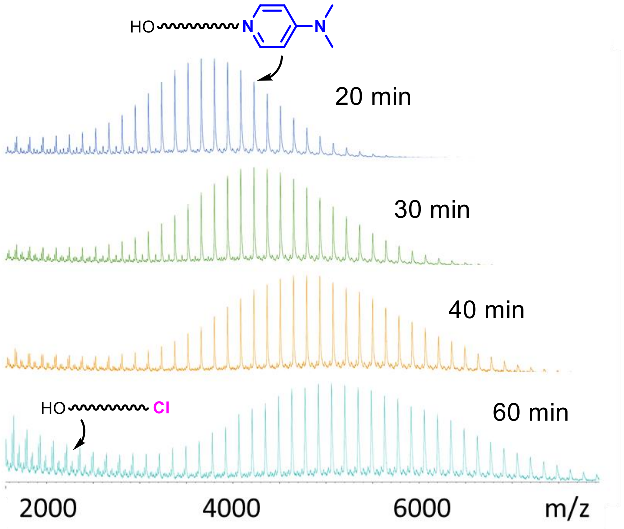
Notes:

Cr(III) Amine-bis(phenolate) Complexes as Catalysts for Copolymerization of CO_2 and Epoxide

Kaijie Ni and Christopher Kozak, Memorial University
Division: Graduate Inorganic

The utilization of carbon dioxide (CO_2) as a carbon feedstock is attractive as CO_2 is widely available, non-toxic, non-flammable and inexpensive. One of the promising processes for CO_2 utilization is the copolymerization of CO_2 and epoxides to afford polycarbonates. In the past decades, various homogeneous catalysts have been developed for CO_2/epoxide copolymerization, wherein salen ligands coordinated to Cr or Co are one of the most studied catalyst systems and have achieved impressive success in terms of high catalytic activities, molecular weight control and narrow dispersities. Cr(III) complexes of amine-bis(phenolate) ligands are structurally and electronically different from salen complexes. Their steric and electronic properties can also be easily tuned by changing the substituents on the phenolate groups or pendant arms. MALDI-TOF mass spectrometry studies indicated both DMAP and chloride can initiate the reaction. In this talk, the Cr(III) amine-bis(phenolate) complexes as a new family of catalysts for the copolymerization of CO_2 and cyclohexene oxide will be presented.





Notes:

Synthesis and Characterization of Chiral Biocarbon for use as Chiral Stationary Phases in Enantioselective Chromatography

Matthew F. Tobin and Stephanie L. MacQuarrie, Cape Breton University
Division: Undergraduate Inorganic

Living organisms are made up of macromolecules abundant in chiral centres of defined configuration e.g., D-sugars, L-amino acids, and often exhibit different biological responses to drug enantiomers when administered separately. It is not uncommon for one enantiomer to be active while the other exhibits toxicity. As a result, the FDA requires evaluation of each enantiomer during the development of stereoisomeric drugs. Subsequently, the pharmaceutical industry has increased its emphasis on the generation of enantiopure compounds before undertaking pharmacokinetic, metabolic, physiological and toxicological evaluation in the search for drugs with greater therapeutic benefits and low toxicity. An area that deserves investigation is the development of cheaper chiral columns, which are used to separate different drug enantiomers, as many currently used columns are incredibly expensive and synthetically taxing to derive costing upwards of thousands of dollars. For example, as of October 2016, a protein-based chiral column with a length and inner diameter of 10 cm and 2 mm respectively costs $2500.00. The proposed project will investigate the modification of the surface of biocarbons generated from forestry waste, specifically birch, with chiral molecules, such as the amino acids L-Valine, L-Isoleucine, and L- Proline which have been shown to bond to aminopropylated silica gel. The cyclic oligosaccharide β-cyclodextrin immobilized on biocarbon will also be investigated and the potential of these chiral biocarbons as a cheap and effective chiral stationary phase for the purpose of enantiomeric separations will be studied.

Notes:

Making Waste Mussels Work: A Story of Road Salt, AMD Remediation and Manicures

Jennifer N. Murphy, Kelly Hawboldt and Francesca Kerton, Memorial University

Division: Graduate Inorganic

Green chemistry has played a key role in the field of renewable feedstocks, an area of research that has been increasing rapidly over the last decade. Memorial University has been leading the way in the search for ocean-based renewable feedstocks.[1] Since 2011 mussel farming has grown by 47 % in NL and continued growth is limited by waste disposal problems. Mussel shells are >95 % $CaCO_3$ and the residual protein is a rich source of amino acids. With an enzymatic shell-cleaning protocol in place to separate the protein from the shell, this presentation will focus on the development of shell based applications. Making a biodegradable and non-corrosive road salt using waste mussel shells as a starting material, using mussel shells to remove Zn, Cd, Fe, and Cu from tailing ponds, as well as how mussel shells can enhance a manicure will be discussed.

1. Kerton, F. M., Liu, Y., Omari, K. W. and Hawboldt, K. Green Chem., 2013, 50, 860.

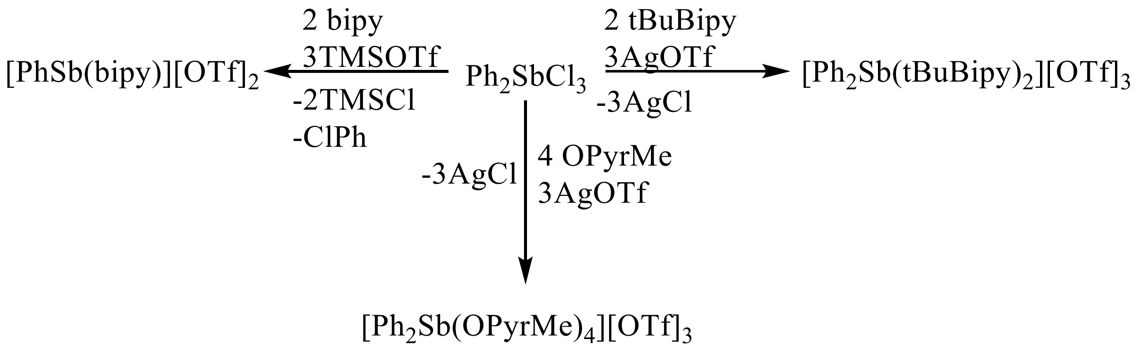
Notes:

New Developments in the Coordination Chemistry of Antimony(V) Cations

Chris Frazee, Neil Burford, University of Victoria

Division: Graduate Inorganic

Antimony(V) acceptors have been shown to form coordination complexes with a wide range of ligands.[1] Recently, the reactivity of mono and di-cationic antimony (V) acceptors, Ph4Sb(OTf) and $Ph3Sb(OTf)_2$, has been studied and shown to form coordination complexes with a variety of redox resistant donors offering a wide array of structural diversity.[2] However, structural characterization of tri- and tetra- cationic complexes of Pn(V) are, as of yet, unreported. The synthesis and characterization of the first Sb(V) tri-cations as well as their reactivity will be discussed.



1. Robertson, A. P. M., Gray, P. A. and Burford, N., Angew. Chem. Int. Ed., 2014, 53, 6050–6069.
2. Robertson, A. P. M., Burford, N., McDonald, R. and Ferguson, M. J., Angew. Chem. Int. Ed., 2014, 53, 3480–3483.

Notes:

A 38-Year Temporal Record of Perfluoroalkyl Acids in the Canadian Arctic

Heidi M. Pickard, Cora J. Young, Amila O. De Silva, Christine Spencer, Derek C.G. Muir, Martin Sharp, and Alison Criscitiello, Memorial University

Division: Graduate Analytical

Perfluoroalkyl acids (PFAAs) are persistent, bioaccumulative compounds found ubiquitously within the environment. They can be formed from the atmospheric oxidation of volatile precursor compounds and undergo long-range transport (LRT) through the atmosphere and/or the ocean to remote locations. Ice caps preserve a temporal record of PFAA deposition making them useful in studying the atmospheric trends in LRT of PFAAs as well as understanding major pollutant sources and production changes over time. A 15 m ice core representing 38 years of deposition (1977-2015) was collected from the Devon Ice Cap in Nunavut and analyzed for PFAAs. The C2-C13 perfluorocarboxylic acids (PFCAs), C4, C7 and C8 perfluorosulfonic acids (PFSAs), and FOSA were all detected in the samples, with fluxes ranging from <LOD to 4.44×10^4 ng m^{-2} yr^{-1}. Devon Ice Cap receives pollutants via atmospheric LRT from both North American and Eurasian sources. Air mass back trajectory analyses allow us to determine the fractions of air masses that originate from source regions to the Devon Ice Cap from across the globe. Ion chromatography analyses of marine aerosol tracers further allow us to determine if Devon Ice Cap receives PFAA contamination from marine aerosols or solely from atmospheric oxidation. Assessments of deposition, homologue profiles, and air mass back trajectories will improve current understandings of LRT of PFAAs to the Devon Ice Cap. This presentation will examine temporal and homologue trends in atmospheric PFAA deposition and compare to known changes in production as well as previous and current ice cap, lake and ocean water measurements.

Notes:

Environmental Sampling to Understand Long-Range Transport of Flame Retardants: A Temporal and Spatial Analysis of Precipitation Samples from Across the NL-BELT

Melanie A. Snow and Cora J. Young, Memorial University

Division: Undergraduate Analytical

Persistent organic pollutants (POPs) are compounds which break down very slowly over time and therefore have a tendency towards environmental ubiquity. The use of POPs in the production of consumer goods can result in both local and global dissemination. POPs can undergo various forms of long-range transport (LRT), and are often found long distances from their source of origin. A better understanding of how these compounds travel in the environment is essential to reducing and regulating their use. Polybrominated diphenyl ethers (PBDEs), a class of compounds commonly used as flame retardants, have recently been recognized as POPs. PBDEs have been found in pristine environments, including the Arctic, where no known anthropogenic sources are present. This is indicative of LRT of the compounds, the mechanism for which is still widely disputed and not well understood.

To further understand the transport properties of BDEs precipitation samples collected from four regions along the NL-BELT were analyzed. Targeted analysis completed using both GC-ECNI-MS and GC-APCI-QTOF-MS found no detectable BDEs in spatially or temporally resolved samples. This implies that the concentrations in precipitation from these regions are likely lower than those seen in the arctic. Non-targeted analysis allowed for the discovery of an unknown halogenated compound. Structural elucidation experiments highly suggest the unknown compound is a commonly used fungicide, chlorothalonil. This compound is present in each sample and at each location. Temporally resolved samples show that the signal from the unknown compound potentially matches usage due to agricultural activity.

Notes:

LC Analysis of Cyanidin-3-O-glucoside in Haskap Berries

Amy Clemens and Dr. Bierenstiel, Cape Breton University

Division: Undergraduate Analytical

Haskap berries (Lonicera caerulea) were introduced to Canada in 2006 through the University of Saskatchewan's Fruit Breeding Program. These berries contain a trove of nutrients such as vitamins A and C, but have primarily attracted interest for their anti-inflammatory, anti-proliferative, and antioxidant effects with the anthocyanin pigment cyanidin-3-O-glucoside as the active compound. However, this component degrades thermally into protocatechuic acid, phloroglucinaldehyde, and other less significant products which is problematic when processing haskap berries into various food products. The goal of this research project was to characterize and quantify the composition of the degradation of cyanidin-3-O-glucoside in haskap berries samples that have been exposed to 2 h and 8 h of heating at 90 °C versus a non-heat-treated sample. A method for separation of haskap berries extracts was developed for UPLC-QToF-MS/MS instrumentation in positive and negative ESI modes. The chromatograms of the extracts were compared and major components of cyandin-3-O-glucoside decomposition identified. Extended heat treatment of the berries' extract has significant effect on cyandin-3-O-glucoside so it is recommended that haskap berries products should be limited to heat treatment in order to ensure high contents of the nutraceutical compounds. This project was a collaboration project with Dr. Rupasinghe at Dalhousie University.

Notes:

Quantitation and speciation of total phosphorous inputs from precipitation and dust deposited along a latitudinal transect in Newfoundland and Labrador

Courtney M. Laprise, Memorial University

Division: Undergraduate Analytical

Long range transport of mineral dust in the atmosphere from arid regions is thought to be the primary source of external phosphorous (P) to terrestrial and marine ecosystems. In this work, dry deposition of dust and precipitation were collected in bulk and precipitation-only samplers over three years. Total P (TP) was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES), while phosphate (PO_4^{3-}) was quantified by colourometric derivatization, and organic-P (orgP) by difference. Due to the small quantities of orgP present, rigorous assessment of accuracy and precision of the methods was required for quantitation. Measurement errors of TP by ICP-OES, assessed via check standards, were 23 % for accuracy and 29 % for precision, for TP below 5 µg P L^{-1} while they were 3 % and 5 % for TP above. Similarly, the accuracy in the PO_4^{3-} was determined to be 2 % below 0.4 mg P L^{-1}, and 3 % above. The average limit of detection for PO_4^{3-} was 0.006 mg P L^{-1}. Fluxes of TP, PO_4^{3-} and orgP to four boreal ecosystems, spanning 5 degrees latitude, were analyzed for seasonal and interannual trends. Fluxes from individual collections in the TP inputs range from below detection limits, to over 3.5 kg P ha^{-1} a^{-1}. Identification of potential atmospheric P sources to each location were determined using modeling with NOAA HYSPLIT back trajectories.

Notes:

Save the Bees using MIPs:

A Method for High Throughput Detection and Analysis of Neonicotinoids

J. Gauthier and C. Bottaro, Memorial University

Division: Graduate Analytical

Neonicotinoids are a class of recently developed insecticides, originally used as a replacement for widely used organophosphate and carbamates pesticides. The continued widespread use of neonicotinoids is believed to be a contributing factor towards a global decline in populations of pollinating species, particularly bees. In this presentation, work will be presented on novel methods of analysis for the detection and analysis of environmental levels of neonicotinoids using molecularly imprinted polymers coupled to UHPLC-MS/MS. MIPs are template recognition devices, which are capable of selectively up-taking target molecules from complex environmental matrices such as river water, surface water, or honey. They replace the requirement to perform separate extraction, separation, and pre-concentration of analytes from their matrices, minimizing sample workup, and increasing analytical throughput. The use of MIPs developed specifically for the uptake and analysis of neonicotinoids will be examined, as well as the development of a new UHPLC method using superficially porous column technology, which has demonstrated significant advancement in speed and efficiency of analytical separations.

Notes:

Magnesium and Zinc Complexes of Naphthenic Acid Model Compounds

Matthew Laprade, Saint Mary's University

Division: Undergraduate Analytical

Bitumen is a key Canadian petroleum resource making up 33% of the world's demand. Bitumen contains naphthenic acids, an undesired component, both environmentally and industrially, due to their toxicity and acidity. Many methods have been proposed for lowering the toxic effects of these acids, to reduce their harmful environmental impacts and to increase the value of the bitumen. In this work, esterification and metal coordination, to zinc and magnesium, were chosen to derivatize several model naphthenic acid compounds, in an attempt to reduce toxicity, bitumen viscosity and corrosion to metal infrastructure. The RP-HPLC partition coefficient determination showed that esterification is a better method for reducing the polarity of naphthenic acids compared to metal coordination complexes. This is due to the metal complexes also coordinating to water, which is confirmed by the crystal structure data. This water coordination raises the water affinity and polarity of the metal complexes to a higher level than expected. Both the esterification method and the metal coordination method demonstrate the ability to reduce the polarity of model naphthenic acids.

Notes:

Do the Twist! New Materials from Cellulose Nanocrystals

Dr. Mark MacLachlan, University of British Columbia

Nature is a remarkable source of inspiration for the self-assembly of complex structures. Bone and silk, for example, are two materials that have hierarchical properties that give them excellent mechanical properties. Inspired by their diverse structures and properties, chemists are using these natural materials to construct new synthetic materials with fascinating properties.

Cellulose nanocrystals (CNCs) are obtained from wood and food. These crystals self-assemble into a helicoidal arrangement that mimics the organization of chitin in crab shells and chiral nematic (cholesteric) liquid crystals. This organization can be used as a template to construct composite films of CNCs and other materials, such as silica and polymers. Thus, new responsive materials with photonic properties can be constructed.

In this talk, Mark MacLachlan will discuss his group's efforts to construct new nanostructured materials with photonic properties.

Notes:

Gas Phase and Particulate Hydrogen Chloride (HCl) in the Polluted Marine Boundary Layer Using Cavity Ring-Down Spectroscopy (CRDS) and Medium Volume Particulate Sampling

Teles Furlani, Kathryn Dawe, Trevor VandenBoer, and Cora Young, Memorial University
Division: Graduate Analytical

Chlorine atoms in the atmosphere have complex reaction pathways that can cause both the formation and destruction of ozone. Oxidation of organics initiated with Cl· atoms yields more ozone than oxidation initiated with hydroxyl radicals (OH·). Although reasons for this are not fully understood, implications for mechanisms of oxidation chemistry are significant.[1,2] Cl· has not been directly measured to date in the atmosphere and its abundance is usually inferred through steady-state approximations from all known formation and loss processes. A major reservoir of Cl· in the troposphere is by proton abstraction of organics to form HCl.[3] HCl can also be formed heterogeneously via acid displacement reactions between ubiquitously found solid sodium chloride (NaCl) and nitric acid (HNO_3). HCl is not a perfect sink and can be photolyzed or react with OH to form Cl·. Measuring HCl in the gas and aerosol phase is important to the understanding of chlorine chemistry in the polluted marine boundary layer. HCl levels in the polluted marine boundary layer are typically between 100pptv–1ppbv,[3] requiring sensitive and selective detection capabilities.[4] Here we report the first use of a cavity ring-down spectroscopy method to detect ambient gaseous HCl in the polluted marine boundary layer of St. John's, NL. Co-located annular denuder and particulate measurements were made using a medium-volume sampler. Implications for reactive chlorine chemistry will be discussed.

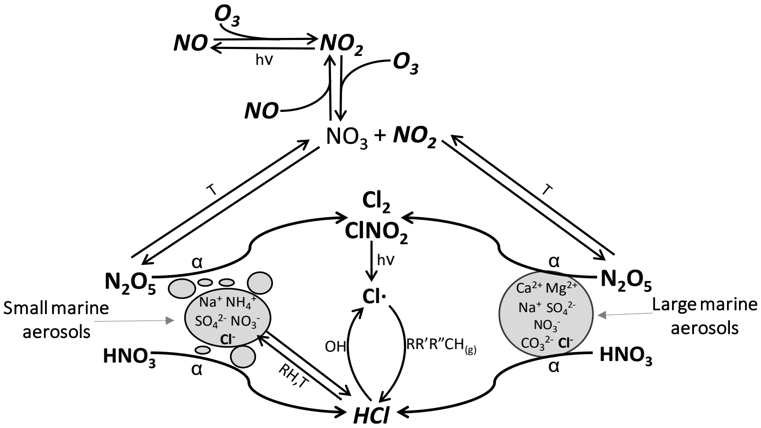


Figure 1. Hypothesized chlorine activation processes, sources, and sinks.

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2. Young, C. J. *et al*. *Atmos. Chem. Phys.* **14,** 3427–3440 (2014)
3. Crisp, T. a *et al. J. Geophys. Res. Atmos.* 6897–6915 (2014)
4. Hagen, C. L. *et al*. *Atmos. Meas. Tech.* **7,** 345–357 (2014)

Synthesis of Substituted Carbazole Derivatives as Cannabinoid Receptor Type 2 PET Tracers

Victoria Rose[1], Dominik Heimannb[2], and Dr. Bernhard Wünschb[2], [1]Memorial University; [2]Westfälishe Wilhelms-Universität Münster Institute of Pharmaceutical and Medicinal Chemistry

Division: Undergraduate Biological/ Medicinal

The cannabinoid receptor type 2 (CB2) is part of the endocannabinoid system. While it was first considered to be the ‘peripheral cannabinoid receptor’, we know today that it also occurs in the central nervous system. There, this G protein-coupled receptor is involved in many physiological and pathological processes like Alzheimer's disease, depression and schizophrenia. However, the level of expression of the CB_2 receptor in healthy and diseased brain has not been fully elucidated. To achieve a better understanding of the regulation of the endocannabinoid system in the normal and diseased human brain and of the potential therapeutic effects of cannabinoid ligands, non-invasive quantitative visualization of the CB2 receptor subtype is highly desirable. Therefore, highly potent and selective compounds for the central CB2 receptor are required, which can be radiolabeled by ^{18}F for positron emission tomography (PET) imaging purposes. In addition to the previously mentioned high affinity for the CB2 receptor and good selectivity over the CB1 receptor and other targets, synthesized test compounds should have appropriate pharmacokinetic and physicochemical properties. This presentation will outline the synthesis and subsequent biological testing of molecules with a 3,6,9-trisubstituted carbazole scaffold.

Notes:

Modified Polonovski Reactions in Ionic Liquid Solvents

Julia Killorn and Robert D. Singer, Saint Mary's University

Division: Undergraduate Biological/ Medicinal

A modified Polonovski reaction using an iron (0) catalyst has been shown to be an effective means of *N*-demethylating opiate and pseudo-opiate compounds.[1] It has also been demonstrated that the choice of solvent in this reaction is of major significance as solvent effects play a large role in yields of *N*-demethylated product; isolated yields ranged from 59% (methanol) to 97% (chloroform). The current work aims to utilize the highly polar yet non-coordinating properties of ionic liquids as a reaction solvent. Ionic liquid solvents possess the added benefit of maximizing the solubility of the *N*-oxide hydrochloride starting material necessary for the modified Polonovski reaction. Use of commercial iron dust or nanoscale zero-valent iron catalysts in ionic liquids for the modified Polonovski reaction will be discussed.

1 Gaik B. Kok et al. *J. Org. Chem.* **2010**, 75, 4806–4811

Notes:

AFM Characterization of Hypertension-Induced Nanomechanical Dysfunction in Cardiovascular Tissues

Garrett McDougall, Shaykat Saha, Reza Tabrizchi, Erika Merschrod, Memorial University

Division: Graduate Biological/ Medicinal

Arterial stiffness is an indicator of the pathogenesis and progression of hypertension. Here an Atomic Force Microscopy (AFM)-based minimal nanoindentation technique has been used to compare the nanoscale elastic and viscoelastic properties of the tunicas intima and adventitia of both healthy and hypertensive rats. Minimal nanoindentation indicates both elastic and viscoelastic distinctions between the tunicas intima and adventitia, between tissues resected from the thoracic and abdominal aorta, and between healthy and pathological tissues. Specifically, our findings indicate a degeneration of both tissue elasticity and viscous dissipation in the pathological case. The consequences of these effects on energy dissipation and blood flow are discussed. This work has been recently extended to investigate the effects of increased cardiac afterload on cardiac tissues.

Notes:

Investigation into the Effects of Salmon (Salmo Salar) Hydrolysate Enhanced Biochar (from Birch Bark) on the Growth of Barley (Hordeum Vulgare L.)

Amanda Cameron and Stephanie MacQuarrie, Cape Breton University

Division: Undergraduate Biological/ Medicinal

As population increases, the gap between productivity and consumption grows larger. Implementing soil management and efficient use of waste to improve food production is a crucial step towards avoiding a major food crisis.[1] Biochar has often been used as a soil amendment; however, the mechanism in which it interacts with the soil is not largely understood. To gain insight on the role and the mechanism of biochar in soil, the growth and the impact of enhancing biochar with a fish hydrolysate derived from off-cut salmon (*salmo salar*) was investigated. The fish hydrolysate, high in nutrients, was adsorbed onto both native and amine functionalized biochars to examine the influence on the growth of barley (*Hordeum vulgare L*.). The biochar was nitrated by electrophilic substitution to a nitroarene then was the reducted to an aniline. The adsorption of a fish hydrolysate onto the biochars was studied by Bradford assay. The biochars were characterized using FT-IR, physisorpotion, elemental analysis, XRD and SEM. Six treatments were applied as soil amendments at a rate of 5%. Fourteen days after planting, the plants were analyzed by root:shoot ratios, fresh and dry weight analysis, chlorophyll and sugar determination as well as average root volume, surface area and length.

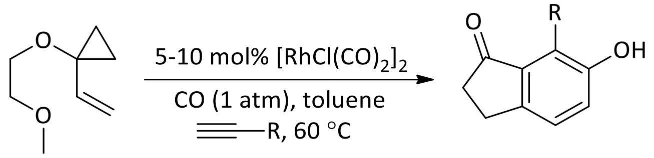
Notes:

A Spectroscopic and Computational Investigation of the Rh-catalyzed [5 + 1 + 2 + 1] Cycloaddition Reaction

Ifenna I. Mbaezue and Kai E. O. Ylijoki, Saint Mary's University

Division: Undergraduate Physical, Theoretical and Computational

The Rh-catalysed [5 + 1 + 2 + 1] cycloaddition is a four-component reaction that affords hydroxydihydroindanone products.[1] In the absence of CO, the [5 + 2] cycloaddition occurs instead, yielding 7-membered carbocycles.[2] Our spectroscopic investigations of the [5 + 1 + 2 + 1] cycloaddition suggest the existence of catalyst resting states at high Rh loading. Our DFT calculations at the ωB97XD/SDD-6-31G* level of theory show that the reaction proceeds via coordination of vinylcyclopropane to the active Rh-catalyst, followed by C-C bond activation.[3] Subsequently, two competing pathways complete the cycloaddition phase via coordination and insertion steps which incorporate 2 CO and an alkyne unit into the ring. Reductive elimination yields a Rh-coordinated 9-membered intermediate. Subsequently, off-metal tautomerization, electrocyclization and acid-catalysed aromatization afford the hydroxydihydroindanone. In addition, our calculations support the experimentally determined regioselectivity of alkyne insertion, as well as probe the effect of electron-withdrawing groups on C-C bond activation.



1. Wender, P. A.; Gamber, G. G.; Hubbard, R. D.; Pham, S. M.; Zhang, L. *J. Am. Chem. Soc.* **2005**, 127, 2836.
2. Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, 117, 4720.
3. Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, 126, 9154.

Notes:

Exploring [M(Gly)(Ura)-H]$^+$ Complexes Through CID, IRMPD Spectroscopy and Computational Chemistry

Samuel C. Atkinson and Travis D. Fridgen, Memorial University

Division: Graduate Physical, Theoretical and Computational

Chemists have put a great deal of focus on the interaction of metal ions with nucleotides, particularly on their resulting complexes and their conformations. Recent studies of uracil have turned to ternary complexes of uracil, metals and other biological molecules, including amino acids, due to the data it may offer on π-π stacking and enzyme-nucleic acid recognition.[1] In collecting characteristic data regarding how these complexes fragment and absorb infrared radiation, the stability and structure of such complexes can be explored, creating a greater understanding of DNA/RNA/protein/metal cation interactions. Previous work on uracil-based complexes has been performed in the Fridgen group, and this research serves to expand upon the findings of that work.[2,3] This presentation will explain the features seen in [M(Gly)(Ura)-H]$^+$ complexes, where M is a doubly-charged metal cation. Fragments observed through sustained off-resonance irradiation collision-induced dissociation (SORI-CID) will be explored, including secondary/tertiary fragments observed through tandem mass spectrometry. Lowest-energy conformer calculations using the M06-2XD3 hybrid functional with 6-31+g(d,p) basis set for [M(Gly)(Ura)-H]$^+$ complexes will be compared against the collected infrared multiphoton dissociation (IRMPD) data within the 2700-3900 cm^{-1} region, accomplished with a tunable infrared laser, to determine the structures most resembling that of experimental data. These results will paint a detailed picture for each complex and help chemists better understand how nucleotide complexes may form with metals.

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2. Power B. et. al. J. Mass. Spectrom. 2016. DOI: 10.1002/jms.3739
3. Ali O.Y., Randell N.M., Fridgen T.D. ChemPhysChem 2012. DOI: 10.1002/cphc.201200015

Notes:

Photophysical Investigation of Ru(II) Dyads as Photosensitizers for Photodynamic Therapy

Anderson Fuller[1], Mitch Pinto[1], Huimin Yin[1], Marc Hetu[1], and Sherri A. McFarland[2], [1]Acadia University; [2]The University of North Carolina at Greensboro

Division: Undergraduate Physical, Theoretical and Computational

Photodynamic therapy (PDT) is a form of cancer therapy that employs a light-activatable photosensitizer (PS) to target and destroy tumours and tumour vasculature with temporal and spatial selectivity. Traditionally, porphyrin-based compounds have been used as PSs, and these prodrugs work by forming cytotoxic singlet oxygen ($^1O_2$) from triplet ππ* excited states. There is much interest in developing coordination complexes as alternatives to such organic systems in order to access additional excited states that may employ oxygen-independent mechanisms for photocytotoxicity (among other advantages). We are currently developing Ru polypyridyl complexes (RPCs) of the type $[Ru(bpy)2(LL)]^{2+}$ that incorporate α-oligothiophene-appended imidazo[4,5-*f*][1,10]phenanthroline ligands (LL) for this purpose. These RPCs possess several excited state configurations that can be accessed using visible and near-infrared light, which gives rise to both oxygen-dependent and oxygen-independent mechanistic pathways for destroying cancer tissue. This talk will highlight the influence of the number of thiophene units on the photophysical and photobiological properties of this family of RPCs.

Notes:

DFT-Calculated Molecular Polarizability as a Single Parameter Descriptor for the Partitioning and Phase Behaviour of Chlorinated and Brominated Compounds

Archita Adluri, Christopher Rowley and Cora Young Memorial University

Division: Undergraduate Physical, Theoretical and Computational

Organochlorine and organobromine compounds like polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent environmental pollutants with significant toxicity. The partitioning and volatility of these compounds are important factors in predicting their toxicity and environmental fate. A general but simple Quantitative Structure Predictive Relationship (QSPR) was developed for the the vapor pressure (Pvap) and water/octanol partition coefficient (Kow) of organochlorine and organobromine species. Simple linear regression was used to determine the relationships between these properties and the calculated molecular polarizability of a test set of 167 molecules. The polarizability was calculated using density functional theory (B3LYP/aug-cc-pVTZ). The coefficients of determination were R2=0.96 for both log Kow and log Pvap. Even the relative properties of structural isomers within this set were predicted with generally good accuracy. This relationship is used to predict pVap and KOW for 26 organochlorine and organobromine species where there are no experimental values available. This QSPR provides a straightforward means to estimate the partitioning of these compounds using only a single descriptor that can be calculated routinely using standard quantum chemistry programs

Notes:

Exploration of Surface Plasmon-Assisted Catalysis (SPAC) as a New Route for Heterogeneous Catalysis

Melanie D. Davidson, and Dr. Christa L. Brosseau, Saint Mary's University

Division: Undergraduate Physical, Theoretical and Computational

Plasmonics is the study of the interactions between the free electrons of a metal, and the electric field component of light. In the presence of the oscillating electronic field, the free electrons in the metal oscillate collectively, resulting in a localized surface plasmon resonance (LSPR). This LSPR is the reason for the enhanced spectra of surface enhanced Raman spectroscopy (SERS) compared to Raman spectroscopy. A commonly used Raman reporter is 4-aminothiophenol (4-ATP), which has been well studied. 4-ATP is known to undergo a surface catalytic coupling reaction to produce an aromatic azo species: 4,4'-dimercaptoazobenzene (4,4'-DMAB). This work explores the generality of the surface plasmon-assisted catalysis (SPAC) by studying the constitutional isomers, the 2- and 3- constituents of 4-ATP. The reusability of the catalyst (electrode set-up) is also tested to suggest a new route for heterogeneous catalysis, and further tested if the oxidative product, 4,4'-DMAB, could be obtained once removed.

Notes:

Advancing Kinase Inhibitor Drug Discovery through Computational Modelling

Ernest Awoonor-Williams and Christopher N. Rowley, Memorial University

Division: Graduate Physical, Theoretical and Computational

The protein kinase family of signalling enzymes has over the years become a prolific target of inhibition for therapeutics, particularly cancer treatments.[1] In effect, most modern anticancer drugs act by inhibiting sites in protein kinases that are involved in cancer cell proliferation. Traditionally, most drugs bind to their targets through non-covalent interactions like hydrogen bonding. Recently, there has been renewed interest among drug developers and medicinal chemists to design drugs that bind covalently to their targets, since these drugs tend to be more therapeutically potent than conventional non-covalent binding drugs. However, the vast number and structural similarity of protein kinases in the human kinome makes it difficult to design covalent-binding drugs that can selectively target particular kinases. Kinase inhibitors typically target reactive cysteine in the active site of proteins because these cysteines are more susceptible to binding. Identifying which cysteines that are most reactive in a given kinase is a major challenge for drug developers, and most computational methods lack the desired accuracy in predicting cysteine reactivity in proteins.[2] I will present an overview of current efforts that we are undertaking to predict the reactivity of targetable cysteines in the active sites of protein kinases and how such methods can potentially enhance the discovery of more selective targets for covalent modification.

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Notes:

Brillouin Light Scattering Studies of Ceramic $PbSc_{0.5}Ta_{0.5}O_3$

Dillon F. Hanlon, Stephen J. Spencer, and G. Todd Andrews, Memorial University

Division: Undergraduate Physical, Theoretical and Computational

Brillouin light scattering spectroscopy was used to probe acoustic phonons in ceramic lead scandium tantalate ($PbSc_{0.5}Ta_{0.5}O_3$), a relaxor ferroelectric exhibiting chemical disorder. Spectral peaks observed at frequency shifts of ~ 25 GHz and ~ 44 GHz were attributed to longitudinal and transverse bulk acoustic modes with velocities of $v_L = 2670$ m/s and $v_T = 4610$ m/s, respectively. The corresponding elastic constants were found to be $c_{11} = 192$ GPa and $c_{44} = 64$ GPa. Attempts to observe surface acoustic phonons in an Al-coated sample of ceramic $PbSc_{0.5}Ta_{0.5}O_3$ were unsuccessful.

Notes:

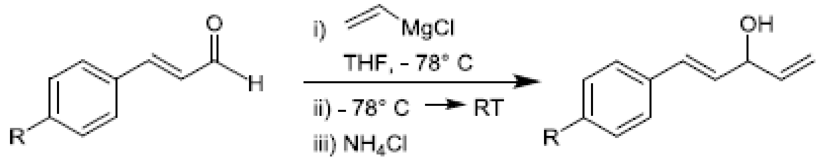
Synthesis of Cobalt-Pentadienyl Complexes for intercalation between layers of Molybdenum Disulfide

Chandika D. Ramful and Kai E.O. Ylijoki, Saint Mary's University

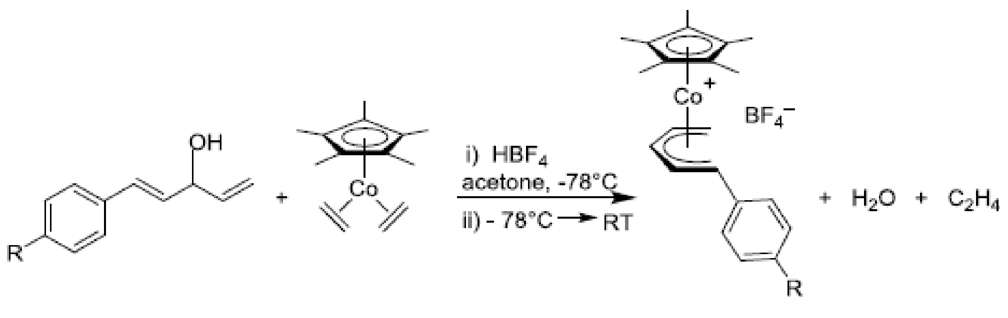
Division: Undergraduate Inorganic

It is known that molecules can be incorporated into layers of molybdenum disulfide.[1] It has been conceived that aryl-substituted cobalt-pentadienyl complexes can be intercalated between layers of molybdenum disulfide to create novel layered mixed-metal materials. We have therefore decided to synthesise a range of these aryl substituted cyclopentadienyl complexes and have so far prepared methoxy, dimethylamino, fluoro and methylenedioxy substituted analogues. Our approach involves the reduction of the substituted cinnamaldehyde with vinyl magnesium chloride, to a dienol via a Grignard reaction. The subsequent reaction of the dienol with cyclopentadienylbis(ethylene)cobalt(I) yields the cobalt-cyclopentadienyl complex (Scheme 1). The latter step being air and moisture sensitive, requires rigorously dried solvent, as well as an inert atmosphere. Successful intercalation of the cobalt-pentadienyl clusters between layers of molybdenum sulfide has been determined through diffractograms. The properties of the mixed-metal materials obtained will be investigated.

Vinylation of unsaturated aldehyde to form 1,4-dienyl alcohol



Reaction of 1,4-dienyl alcohol with cyclopentadienylbis(ethylene)cobalt(I)



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Notes:

Iron Amine-phenolate Complexes as Catalysts for CO_2 Activation

ED Butler and CM Kozak, Memorial University

Division: Graduate Inorganic

The increase of CO_2 emissions in the atmosphere from the burning fossil fuels, is of great concern as it is the most important gas for controlling climate change. A better understanding in how to reduce this phenomenon, or finding ways to utilize CO_2 as an alternate carbon source has become a rewarding area of science. This can be attributed to the fact that CO_2 is an inexpensive, abundant feedstock with low toxicity, and it can react with epoxides to produce polycarbonates or cyclic carbonates. Both products have value as cyclic carbonates can act as polar aprotic green solvents as well as chemical intermediates for the synthesis of other small molecules and polymers, whereas polycarbonates can be used to synthesize several biodegradable plastics. The Kozak group has had success in this area using inexpensive, earth abundant metals with amine-phenolate ligands, and these complexes can be readily modified to control steric and electronic properties. Iron is just one of the metals used, and is of value as it not only abundant, but non-toxic/biocompatible. The synthesis and characterization of iron(III) amine-phenolate complexes will be discussed, along with the screening of these complexes with various co-catalysts for the reaction of CO_2 with epoxides.

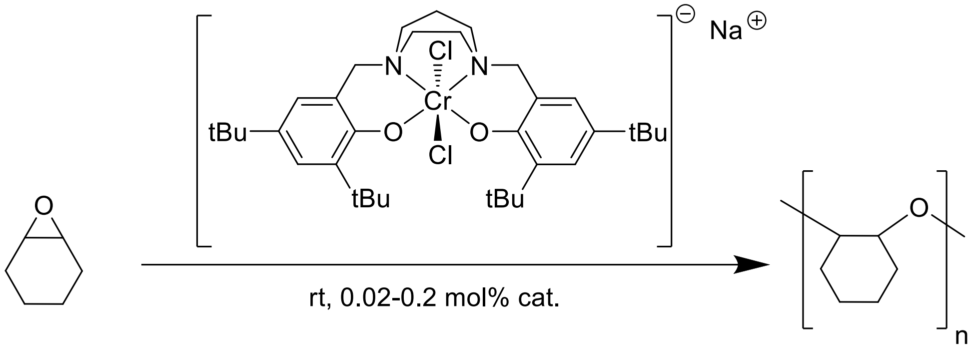
Notes:

Chromium(III) Amino-bis(phenolate) Complexes for Ring-Opening Polymerization (ROP) of Cyclohexene Oxide

Kenson Ambrose and Christopher M. Kozak, Memorial University

Division: Graduate Inorganic

Carbon dioxide is currently known to be the most abundant greenhouse gas therefore researchers have been attracted to its use as a C1 feedstock for chemical transformations into useful materials.[1] One process termed 'organic incorporation' affords the formation of polycarbonates or cyclic carbonates when it is reacted with epoxides.[2] Both types of products possess useful potential such as less volatile polar aprotic solvents (cyclic carbonates) and materials with good electrical insulation or good elasticity (polycarbonates).[3] Numerous catalysts containing metals such as Co, Cr, Zn, Fe and Al have been reported showing high activity towards these types of reactions.[1] More specifically, Cr(III) bis(phenolate) based complexes have been primarily known to produce polycarbonates.[1] Based on this premise, a new Cr(III) amino-bis(phenolate) complex containing a homopipirazine backbone was synthesized and investigated; recent results involving its synthesis and characterization, as well as its unexpected high catalytic activity towards ROP reactions will be discussed.



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Notes:

Adventures in Ionic Thiourea Organocatalysis in Ionic Liquid Solvents

Kaitlyn L. Blatt-Janmaat and Robert D. Singer, Saint Mary's University

Division: Undergraduate Organic

Green chemistry practices that utilize organocatalysts and ionic liquid solvents have been investigated in recent years. Organocatalysts offer a greener alternative to transition metal catalysts while ionic liquids are polar, non-coordinating solvent systems with lower vapour pressures than traditional volatile organic solvents. Thiourea catalysts have been implemented in many reactions to significantly enhance the rate with loadings as low as 1 mole %. Immobilizing these catalysts in an ionic liquid solvent for recycling purposes has been achieved by functionalizing the catalyst with an ionic moiety. The synthesis and utilization of several ionic thiourea derivatives will be discussed in terms of rate enhancement, scope, and recyclability.

Notes:

[*n*](2,9)Peropyrenophanes: Expanding A Cyclophane Family

M. R. MacKinnon[1], G. J. Bodwell[1], and T. Kubo[2], [1]Memorial University; [2]Osaka University

Division: Graduate Organic

The [*n*](2,7)pyrenophanes [1] and [*n*](2,11)teropyrenophanes [2] are molecules of interest because they have enabled study into how the properties of the aromatic system change as the degree of bend is altered. The parent aromatic systems, pyrene and teropyrene, are both members of a homologous series of PAHs. However, they are not immediately adjacent to each other in the series with peropyrene occupying that space. In addition to being a member of this series, peropyrene has gained increased attention due to its potential use in luminescent devices. Only a single peropyrenophane example has appeared in the literature, and it was formed as a byproduct and was not the intended target [4]. This work aims to develop a synthetic route to [*n*](2,9)peropyrenophanes by exploiting the oxidative coupling of tethered phenalene systems [4].

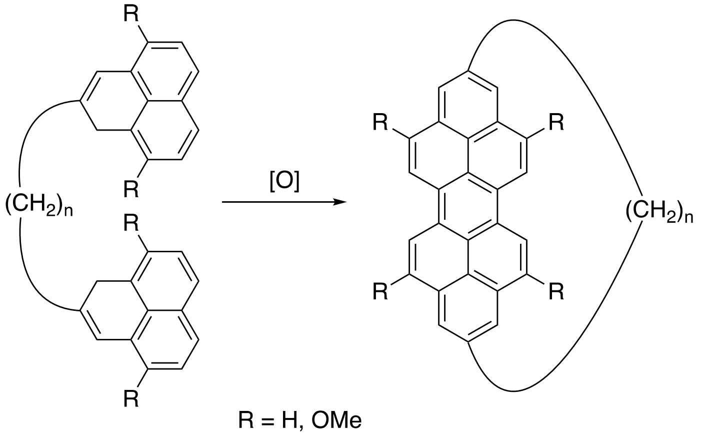

Figure 1: Oxidative coupling of tethered phenalenes

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Notes:

Quantifying Reduced Nitrogen Compounds in the Atmosphere's Gas and Particle Phases

Dr. Jennifer Murphy, University of Toronto

Our atmosphere contains a range of reduced nitrogen compounds, including ammonia, amines, amides, and isocyanates, typically present at mixing ratios in the parts per trillion to parts per billion range. Some of these compounds impact air quality and the Earth’s radiative balance by promoting the formation and growth of particulate matter, while others are of concern due to toxicity. In this talk, I will describe various analytical techniques we use to measure ammonia and amines in the gas and particle phases in the ambient atmosphere. Measurements have been made in a variety of rural and urban environments to identify and quantify important sources and sinks. Recent measurements made from an icebreaker in the Canadian Arctic suggest that migratory seabird colonies represent a significant summer source of ammonia, contributing to a significant climate cooling through the promotion of new particle formation. Laboratory studies of the oxidation of ethanolamine, a benchmark solvent for carbon capture, indicate that formamide and isocyanic acid are produced in significant yield. A subsequent study combining lab experiments and computational work indicates that most gas phase oxidation pathways result in the complete oxidation of the carbon in organic nitrogen compounds, while reaction at the N is not favoured. This implies that isocyanic acid (HNCO) actually represents the most oxidized form of organic reduced nitrogen compounds formed in the gas phase. We performed measurements of its Henry’s Law constant and hydrolysis rates to inform predictions of it

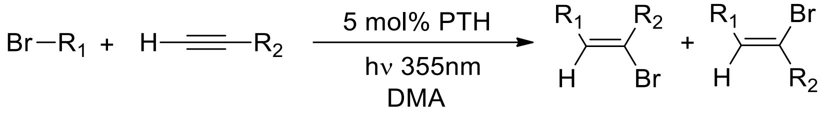
Notes:

Photocatalyzed Radical Addition to Alkynes using an Organic Catalyst

Ernlie A. Publicover and Kai E. O. Ylijoki, Saint Mary's University

Division: Undergraduate Organic

The reaction of an alkyl halide and an alkyne to yield an alkenyl halide is commonly performed with a metal catalyst[1-4]. Some of these metal catalysts which incorporate the heavy metals rhodium and iridium, are expensive. The development of an organic catalyst will provide a cost effective and environmentally friendly alternative to the heavy metal catalysts. The organic photocatalyst 10-phenylphenothiazine (PTH) has been selected for this reaction because it is reported that PTH can dehalogenate alkyl and aromatic halides[5]. The mechanism of this process is believed to begin via alkyl radical formation. We have captured this radical using a terminal alkyne and in the process, elicited the synthesis of alkenyl halides via C-C bond formation. Catalyst loading and light wavelength are being optimized to ensure reaction efficiency and higher yields. In addition, the issue of competing cis and trans products is being resolved via thermodynamic control.



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Notes:

Mechanistic Studies of Intramolecular Allene-Dithiolium Cycloaddition

Matthew Johnson, Chris Flinn, and Yuming Zhao, Memorial University

Division: Undergraduate Organic

Recently, a unique intramolecular alkyne-dithiolium cycloaddition was discovered for *ortho*-alkynyl subsituted phenyldithiafulvene systems. This reaction occurs under acidic and oxidative conditions and can be used to make fused tricyclic indenothiophene structures. To further expand the understanding on this cycloaddition reaction, this thesis work carried out investigations on the intramolecular cycloaddtion of dithiolium with a different counterpart — allene. Theoretically, the allenyl group is more reactive than the alkyne and can lead to more sophisticated reaction outcomes. To better understand the reactivity, density functional theory (DFT) calculations were conducted on a model compound with a structure of *ortho*- allenyl substituted phenyldithiafulvene. The detailed cycloaddition mechanism was mapped out by modeling the key stationary points (transition states and intermediates) involved, while intrinsic reaction coordinate (IRC) analysis was conducted to confirm the connection among them. Besides the theoretical analysis, a multi-step synthesis toward a dithiafulvalene-allene molecule was undertaken. The synthetic work successfully led to the key intermediates, while efforts to make the target compound have been tried

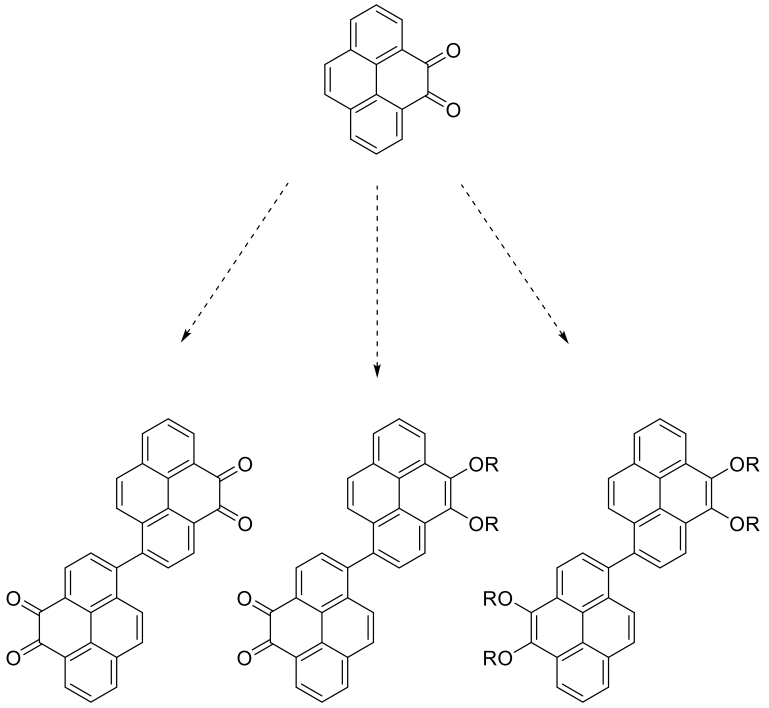
Notes:

Synthesis of Pyrene Dimers Utilizing an Intramolecular Scholl Reaction

J. C. Walsh and G. J. Bodwell, Memorial University

Division: Graduate Organic

Pyrene with its long fluorescence lifetime, large Stoke's shift and proclivity towards excimer formation has become the gold standard in the sensing of microenvironments using fluorescence spectroscopy. [1] A SciFinder search yields nearly one hundred thousand publications involving pyrene since 1880, with more than a quarter of these being published since 2010.[2] Pyrenes interesting properties coupled with its relatively low price in comparison to similar PAHs make selective functionalization methods highly desirable. Building complex derivatives and oligomers of pyrene still poses a serious synthetic problem, efforts to address this problem and the synthesis of three interesting dimers will be outlined.



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Notes:

Structure and Reactivity of Halogen-Substituted, Small Unsaturated Organic Molecules

Michael A. Land, Katherine N. Robertson, Jason A.C. Clyburne, Saint Mary's University

Division: Graduate Organic

We have prepared the unsaturated compound 1,3-*bis*(dimethylamino)-3-iodopropargyl iodide, which had previously been reported as a reactive intermediate stabilized by triphenylphosphine.[1] Investigations into its reactivity have also been started and these reactions will be discussed. A series of vinamidinium salts (X = H, F, Cl, Br, I, or CN) have been prepared and comprehensively characterized, including the use of X-ray crystallography. Comparisons between their solid state structures and *ab initio* (ω-B97XD/6-31G*) calculations suggest that the anions have significant stabilization effects, either through sigma-hole interactions or by filling a π^* orbital of the unsaturated carbon chain. Structural elucidation of other small molecules will also be discussed.

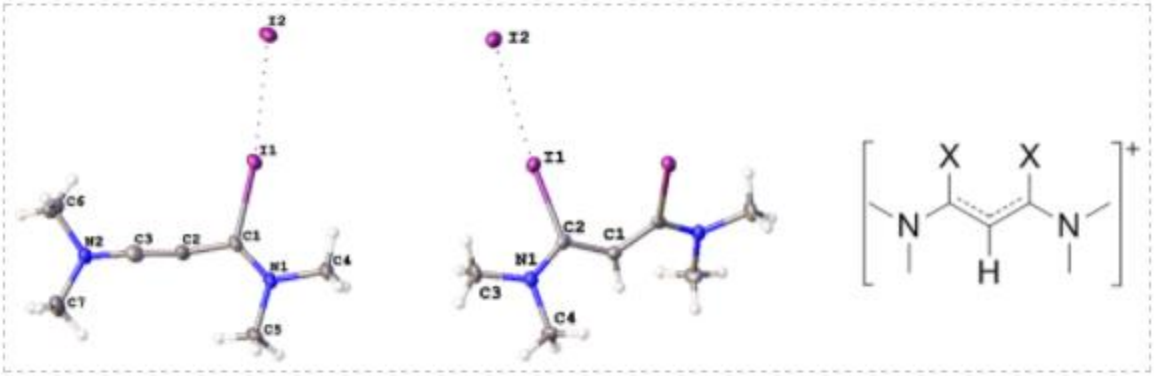

Figure 1: Structures of 1,3-*bis*(dimethylamino)-3-iodopropargyl iodide (left) and *N,N,N',N'*-tetramethyl-1,3-diiodovinamidinium iodide (center). Sigma-hole interactions are explicitly shown in each structure. The general structure of the vinamidinium cations is shown on the right.

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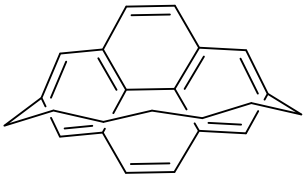
Notes:

Tied Together: The Marriage of Pyridine and Nonplanar

Parisa Ghods G. and Graham J. Bodwell, Memorial University

Division: Graduate Organic

Single-walled carbon nanotubes (SWCNT)s have attracted considerable attention recently. To date, no synthetic method to produce a carbon nanotube in the laboratory has been reported. These compounds may be applicable in the fields of nanotechnology, molecular electronics, optics and other areas of material sciences due to their extraordinary mechanical and electrical properties.[1,2] The Bodwell group has a particular interest in the synthesis and study of cyclophanes containing pyrene and teropyrene as aromatic systems. These compounds might serve as sidewall segments of (SWCNTs). A series of aromatic half-belts called [*n*](2,11)teropyrenophanes (n = 7-10) **(1)** and [*n*](2,7)pyrenophane **(3)** have been made. [3,4,5] Meanwhile, some of the aliphatic bridge carbon atoms were replaced with small aromatic systems to make progress towards the synthesis of full aromatic belts, these new type of compounds contain a small aromatic ring at the carbon chain **(2,4)** which offer opportunities to investigate host-guest complexes. However, there is not yet any clear evidence for the incorporation of any guests into the cavity. Results will be discussed.



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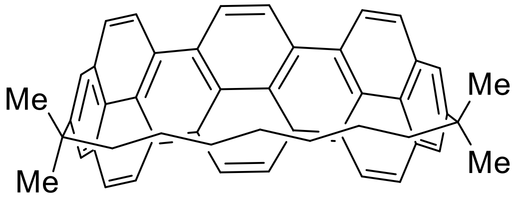

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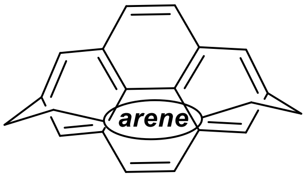
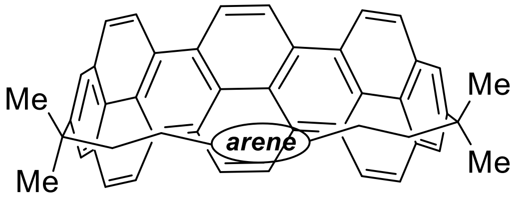


3

arene = pyridine



4

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Notes:

Improvements in Fuel Cell Technology

Azam Sayadi, Memorial University

Division: Graduate Analytical

The world is facing serious problems with the energy crisis in recent years. Fossil fuels are non-renewable and limited natural resources of energy, and their consequent pollution has become a very serious concern. The desire to improve urban air quality has lead to the considerable development of fuel cell (a device which converts chemical reaction energy into electricity [1]) technology over the last 25 years. However, there are some imperfections in this technology, which decreases the energy efficiency, such as incomplete electrocatalytic oxidation of fuels. A better understanding of the electrocatalytic oxidation mechanisms and interaction of catalysts and fuels, and determination of the average number of exchanged electrons in terms of fuel cell efficiency will be effective approaches to deal with these sorts of problems and enhance the energy efficiency of them. In our research, rotating disc voltammetry (RDV) and steady-state measurements have been applied to study the electrocatalytic oxidation of formic acid, methanol and ethanol as fuel cell fuels. Since RDV emulates the hydrodynamic conditions of a fuel cell anode, it provides less expensive, reliable, and controllable situation for study purposes. Our results showed that this technique could be applied to provide accurate stoichiometric and kinetic parameters, which are crucial for fuel cell applications [2-4]. Also, for the first time, we showed that this method could be a convenient and effective technique for estimation of the average number of the electrons involved in organic fuels oxidation.

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Notes:

Towards a Method for the Partial Extraction of Metals in Soils

Lee A. L. Brannen, John Murimboh, and Clifford R. Stanley, Acadia University

Division: Undergraduate Analytical

Partial extraction geochemical methods have become increasingly popular in the last 40 years as alternative techniques for determining buried mineral deposits, given their relative convenience and inexpensiveness with respect to drilling methods. Metals from buried mineral deposits diffuse upwards as a result of i) a concentration gradient in the soil solution, ii) the process of evapotranspiration. The metals eventually accumulate in the lower B-horizon and adsorb to the negatively charged surfaces of weathered secondary clays and oxyhydroxides, such as amorphous $Fe(OH)_3$. Partial extractions selectively leach metals adsorbed at the soil surface using weak extracting reagents such as deionized water, dilute acid, and dilute base solutions. Our lab conducted a batch matrix partial extraction on a representative dystric brunisol soil sample using nine different extracting reagents at four different water-to-soil ratios, in order to i) determine optimum extraction conditions, ii) predict the speciation of metals during partial extraction. Total dissolved metal concentrations in the soil extracts were measured using inductively-coupled plasma mass spectrometry (ICP-MS). A standard phenanthroline method was also used to determine the amount of dissolved Fe^{2+} in conjunction with the total dissolved concentration of Fe determined by ICP-MS. The presentation highlights the optimum extraction conditions and demonstrates the importance of $Fe(OH)_3$ as both a redox and acid-base buffer in the soil solution, i.e. how iron influences metal speciation.

Notes:

Degradation Studies of Coal tar PAHs using Mg/EtOH System and Fenton Oxidation

Ahmad Al-Shra'ah [a], Bob Helleur [a], Stephanie MacQuarrie[b], Martin Mkandawire[b], Yuming Zhao[a], and Paris Georghiou[a], [a]Memorial University; [b]Cape Breton University

Division: Graduate Analytical

Polycyclic aromatic hydrocarbons (PAHs) are toxic chemicals; therefore, their degradation has become an environmental concern. As a pilot study designed with the aim of being able to effect an efficient and convenient reductive and oxidative degradation of PAHs in coal tar, anthracene was chosen for the initial studies as a model compound. Anthracene reduction using activated magnesium with anhydrous ethanol (Mg/EtOH) at room temperature and anthracene oxidation using Fenton's reagent (Fe^{+2} + H_2O_2) were successfully achieved. The effect of magnesium dosage, glacial acetic acid volume, and time on the anthracene reduction and the effect of H_2O_2 dosage, Fe^{+2} dosage, temperature, and time on Fenton oxidation of anthracene were studied. An experimental design approach was used to minimize the number of experiments and to determine the optimum conditions for anthracene reduction and oxidation. The results indicated that the main product from anthracene reduction is 9,10-dihyrdoanthracene and from anthracene oxidation is 9,10-anthraquinone. A double dosage of reagents (Mg/EtOH for reduction and Fenton's reagent for oxidation) was necessary to obtain a high removal (90%) of some of the PAHs. The reduction of PAHs in coal tar using Mg/EtOH is selective, where anthracene and fluoranthene were efficiently removed, while Fenton oxidation is not selective. The sample analyses were achieved using GC-MS and GC-FID.

Notes:

Fabrication of Molecularly Imprinted Polymers using Hansen Solubility Parameters

Maryam Jafari and Christina S. Bottaro, Memorial University

Division: Graduate Analytical

Molecularly imprinted polymers (MIPs) are smart polymers for selective recognition of target solutes. MIPs can be used for detection organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), and can be deployed in harsh environments. Generally, these polymers are prepared with a monomer, cross linker, template or pseudo-template and solvent (porogen) [1]. MIPs should exhibit certain properties such as high surface area and porosity, controlled pore size and mechanical stability. It is recognized that the porogen plays a key role in a pore generation, influencing shape, size and volume of pores in MIPs. A true porogen is thermodynamically compatible with the functional monomer, crosslinker and template. The Hansen solubility parameter is a practical criterion for predicting the thermodynamic compatibility of a porogen with the prepolymerization components, as well as the propensity to form a polymeric network with the required characteristics [2]. Rather than take a trial-and-error approach, we used Hanson solubility parameters to develop a method to predict the suitability of porogen for formation of a MIP film with specified porosity. To best of our knowledge this work is the first report of predictive model for porogen selection in preparation of porous MIP monoliths.

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Notes:

Product Distributions and Efficiencies for Ethanol Oxidation in Proton Exchange Membrane Electrolysis and Fuel Cells

Rakan Altarawneh, Memorial University

Division: Graduate Analytical

The direct ethanol fuel cell (DEFC) is an efficient electrochemical device for conversion of the chemical energy of ethanol into electricity without production of pollution or noise.It is considered as an attractive power source with much potential for electronic devices and vehicles.Ethanol has a high energy density, low toxicity, simple handling and storage,and is produced in large quantities from agriculture waste and biomass. However, the high theoretical efficiency (97%) of the DEFC is based on complete oxidation of ethanol to CO_2, while the main products from DEFCs are acetic acid and acetaldehyde. Therefore, new catalysts must be developed to facilitate the complete oxidation of ethanol, and these need to be evaluated comprehensively by simple and fast methodologies. The methodologies reported here can provide information on the efficiency and product distribution for ethanol oxidation in a direct DEFC or ethanol electrolysis cell.The efficiencies of these cells are dependent on the cell voltage, crossover of ethanol, and stoichiometry of the ethanol oxidation reaction (i.e. the average number of electrons transferred per ethanol molecule). The stoichiometry, efficiency, and product distribution for ethanol electrolysis in fuel cell hardware has been determined at 80 °C for commercial Pt/C, PtRu/C and PtSn/C anode catalysts. The amounts of ethanol consumed and acetic acid and acetaldehyde produced were determined by proton NMR spectroscopy while CO_2 was measured with a non-dispersive infrared CO_2 monitor.

Notes:

Fast Analysis of Sulfide and Sulfur-oxyanions in Saline Waters by Capillary Zone Electrophoresis using Direct and Indirect UV-vis Spectrophotometry

Angham Saeed, Ali Modir-Rousta, Christina S. Bottaro, Memorial University

Division: Graduate Analytical

Sulfides and sulfur oxyanions (e.g., thiosulfate, sulfate, polythionates, etc.) can impact environmental quality and have negative economic consequences for industrial processes, e.g., anaerobic reduction reactions can produce toxic and corrosive hydrogen sulfide and oxidation can lead to acidification of the environment and mobilization of toxic metals. Understanding the chemistry of various systems so that the reductive or oxidative processes can be curtailed requires methods to quantify key sulfur species. Accurate quantitation requires baseline separation and accommodation for co-migrating interferents, e.g., thiosulfate co-migrates with chloride, which is found in abundance in briny waters. A strategy that used two capillary zone electrophoresis (CZE) methods, one with direct detection and the other with indirect detection, has been developed for the speciation analysis of charged sulfur species (sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), sulfite (SO_3^{2-}), and sulfide (S^{2-})) in saline water. Both CZE methods were developed with reverse-polarity in which the anions migrate toward the detector and the electroosmotic flow (EOF) is away from the detector. Hexamethonium hydroxide (HMOH) was added to modify the capillary surface chemistry and reduce EOF, affording methods with shorter time of analysis and better peak resolution. The components of the background electrolyte (e.g. pH (buffers), flow modifiers, chromophoric probes, etc.) were considered for each method. For indirect detection, selection of the chromophoric probe needed for detection of non-absorbing or weakly absorbing anions is important. Pyromellitic acid (PMA) was selected from a range of options because it is non-oxidizing, has high molar absorptivity (high sensitivity), and is a good mobility match for thiosalts. Other factor taken into consideration include: the capillary length, separation temperature, potential applied, and used of a stabilizing agent to limit spontaneous oxidation of some of sulfur-containing compounds. Optimization efforts and results will be presented.

Notes:

Analysis of the Adsorption of Metal Ions From Water Onto Charcoal

Shayne Gracious, Dalhousie University

Division: Undergraduate Analytical

As drinkable water becomes an increasingly scarce resource, more convenient filtration techniques will become of rising interests. In particular, a simple portable water filter could serve as a more accessible alternative in many circumstances. Charcoal could be a viable candidate for such a system, however, the majority of the studies have revolved around the use of commercial charcoal. In practice, many individuals may find it more convenient to use materials that are readily available. Such a filter would be responsible for removing various contaminants, such as metal ions. As such, this research project aimed to determine if charcoal from household settings could serve as an effective medium for such a system and, if so, how the source of charcoal would affect the adsorption capacity.

Notes:

Langmuir-Blodgett Deposition of Functionalized AuNRs Towards Multidimensional LSPR Sensing

Presley MacMillan, Najwan Al Barghouthi and Christa L. Brosseau, Saint Mary's University

Division: Undergraduate Analytical

Understanding the surface plasmon resonance properties of gold nanorods (AuNRs) and exploring their sensitivity has attracted much attention due to their potential applications in the biomedical field. This includes detection of various disease biomarkers through an optimal localized surface plasmon resonance (LSPR). A variety of different techniques are currently available for the synthesis of AuNRs, one of which is the bottom-up approach known as seed-mediated growth[1]. This method introduces a gold seed into a growth solution to obtain gold nanorods of a desired aspect ratio. The goal is to assemble these nanorods at the air-water interface of a Langmuir-Blodgett trough and then compress the nanorods so that a uniform monolayer of well orientated nanorods can be obtained. The goal is to use this monolayer for the synthesis of an LSPR sensor, which will be used for the detection of biomarkers.

1. Jana, N. R.; Gearheart, L.; Murphy, C. J. Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio. *Chemical Communications* **2001**, 617-618.

Notes:

Progress Toward Just-in-Time Environmental Monitoring using Smart Polymers

Christina S. Bottaro, Stefana N. Egli, Jeremy R. Gauthier, Hassan Y Hijazi, and Geert van Biesen, Memorial University

Division: Analytical

Real-time and near real-time analytical systems can be used in spatial and temporal environmental quality assessments. The resulting just-in-time dat are used in mitigation and treatment protocols. Such systems need to be fast, sensitive, and inexpensive. We are working towards that goal by developing selective molecular recognition materials, molecularly imprinted polymers (MIPs), for use with desorption electrospray ionization mass spectrometry (DESI-MS). These smart materials can be employed for in situ uptake, then directly interrogated by DESI-MS or other detection systems, thereby largely circumventing the need for collection and transport of water samples. This approach has been applied to a range of aquatic contaminants including polycyclic aromatic hydrocarbons, thiophenes, pesticides and pharmaceuticals. Efforts to reliably employ MIPs for environmental analysis be presented.

Notes:

Formation and Emission of Reactive Chlorine Species in Indoor Air

Kathryn E.R. Dawe, Teles C. Furlani, Trevor C. VandenBoer and Cora J. Young,
Memorial University

Division: Graduate Analytical

It is well known that presence of reactive chlorine species in urban air, originating from both marine and anthropogenic sources, has been known to play a large role in regional air quality [1]. To date, there has been little focus on the chemistry and health consequences of reactive chlorine species in indoor air. According to the US Environment Protection Agency (EPA), humans, on average, spend ~90% of their lives indoors thus extensive indoor air quality research is required [2]. Emission sources of household reactive chlorine include washing machines, dishwashers, showers and faucets, all of which require the use of tap water [3-6]. Furthermore, when tap water is combined with chlorinated detergents, soaps and other cleaners, exposure to these compounds is increased significantly. An additional formation mechanism of reactive chlorine species such as HCl is via photolysis, thus the amount of light present in a household will affect human exposure. Using a combination of instruments and techniques suitable for trace constituents in the atmosphere, the first measurement of HCl in indoor air was recorded.

1. Young, C.J., Washenfelder, R.A., Edwards, P.M., Parrish, D.D., Gilman, J.B., Kuster, W.C., Mielke, L.H., Osthoff, H.D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P.R., Roberts, J.M., Griffith, S., Dusanter, S., Stevens, P.S., Flynn, J., Grossberg, N., Lefer, B., Holloway, J.S., Peischl, J., Ryerson, T.B., Atlas, E.L., Blake, D.R., and Brown, S.S. Chlorine as a primary radical: Evaluation of methods to understand its role in initiation of oxidative cycles. Atmospheric Chemistry and Physics 14:3427-3440 (2014).

2. U.S. Envionmental Protection Agency. 1989. Report to Congress on indoor air quality: Volume 2. EPA/400/1-89/001C. Washington, DC.

3. Olson, D.A., and Corsi, R.L., "In-Home Formation and Emissions of Chloroform: The Role of Residential Dishwashers," Journal of Exposure Analysis and Environmental Epidemiology, 14:109-119 (2004).

4. Moya, J., Howard-Reed, C.L., and Corsi, R.L., "Volatilization of Chemicals from Tap Water to Indoor Air from Contaminated Water used for Showering," Environmental Science & Technology, 33(14): 2321-2327 (1999).

5. Howard, C., and Corsi, R.L. "Volatilization of Chemicals from Drinking Water to Indoor Air: The Role of Residential Washing Machines," Journal of the Air and Waste Management Association, 48(10): 907-914 (1998).

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Notes:

The synthesis of *N*-methylpiperidine-4-thiol and *N*-methylpyrrolidine-3-thiol, compounds required to make potential SPECT imaging agents for Alzheimer's disease

Guilherme L. Ferreira[1], Sultan Darvesh[1,2], Earl Martin[1] and Ian R. Pottie[1,3], [1]Mount Saint Vincent University; [2]Dalhousie University; [3]Saint Mary's University

Division: Undergraduate Biological/ Medicinal

Background: Alzheimer's disease (AD) is a neurodegenerative disorder that causes dementia. Symptoms progress over time, becoming severe enough to interfere with daily activities. At present, definitive diagnosis of AD occurs at post mortem via pathology examination of the brain. An accurate, early diagnosis of AD during life is required and could help with disease management and the facilitate development of possible new therapeutics. *N*-Methylpiperidin-4-yl 4-[^{123}I]iodobenzoate, a radioligand that targets butyrylcholinesterase, has shown promise in a mouse model experiments as a radioligand SPECT imaging agent that could aid in an early diagnosis of AD.[1,2]. It has been demonstrated that thioesters are acceptable surrogates of ester compounds to validate biochemical targets histochemically. To aid in validating the biochemical target of *N*-methylpiperidin-4-yl 4-[^{123}I]iodobenzoate in an animal model, thioester analogues (*N*-methylpiperidin-4-yl) 4-iodobenzenecarbothioate and (*N*-methylpyrrolidin-3-yl) 4-iodobenzenecarbothioate are targeted for synthesis.

Methods: Following known methods,[1] the synthesis of the targeted *N*-methyl-4-piperidinethiol and *N*-methyl-2-pyrrolidinethioliperidinethiol can be synthesized by mixing the appropriate ketone with H_2S. Isolation of the 1,1-dithiol followed by reduction with $NaBH_4$ produces the desired thiol. Each thiol is mixed with 4-iodobenzoyl chloride to produce the desired thioester.

Results: *N*-methyl-4-piperidinethiol has been generated in low yields. This thiol has been used to synthesize the surrogate (*N*-methylpiperidin-4-yl) 4-iodobenzenecarbothioate in high yield. The synthetic investigations to prepare *N*-methylpyrrolidin-3-one using *N*-methylpyrrolidine-3-thiol will also be presented.

Conclusions: A radioligand surrogate has been synthesized and the synthesis of another is now being investigated.

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2. DeBay, D.R.; Reid, G.A.; Pottie, I.R.; Martin, E.; Bowen, C.V.; Darvesh, S. *Alz. Dem.: Trans. Res. Clin. Interven.* **2017**, *3*, 166-176.

Notes:

Chemotherapeutic Agents and Potential Off-Target Interactions Involved in the Induction of Adverse Effects

Maria Flynn, Kali Heale, Laleh Alisaraie, Memorial University

Division: Undergraduate Biological/ Medicinal

Cancer patients face many challenges, the most predominant being chemotherapy and its many serious and undesirable side-effects. Chemotherapeutic medications are highly potent, and their toxicity is associated with side-effects ranging from mild nausea to fatal suppression. This presentation will discuss the potential unwanted targets of chemotherapeutic agents and study their interactions by means of molecular modeling and computational calculations. In this project, a library of chemotherapeutic agents and their possible metabolites were created and screened against a number of potential off-target proteins to determine probable interactions. The protein-ligand interactions were predicted by the use of an incremental construction strategy based algorithm. The interactions between the various ligands and the possible off-target proteins were determined, allowing identifications of the amino acids involved in the bindings. Chemotherapeutic medications and their metabolites have the potential to interact with a number of off target proteins within the body. In conclusion, the interactions between chemotherapeutic agents, and their metabolites, with off-target protein networks provides a probable mechanism of the mediation of medication related adverse effects, such as nausea, constipation, diarrhea, and mucositis. This will provide information for the modification or development of more tolerable anti-neoplastic agents in the future.

Notes:

Human Thymidine Phosphorylase Complexed with 5-Fluorouracil

Tiffany Tozer, Kali Heale, and Laleh Alisaraie, Memorial University

Division: Undergraduate Biological/ Medicinal

5-Fluorouracil (5-FU) is a medication often given intravenously to treat both colorectal cancer and cancers of the aerodigestive tract. Human thymidine phosphorylase (hTP) is involved in pyrimidine nucleoside metabolism, affecting tumour growth and angiogenesis. The present investigation aimed to determine the molecular dynamic structure of hTP in complex with 5-FU. Four systems of hTP were investigated: unlinganded monomer, unlinganded dimer, monomer liganded with neutral 5-FU, and monomer liganded with protonated 5-FU. An important segment of hTP contributing to the stabilization of 5-FU-bound hTP and its dimer structure was identified. In the drug-bound monomeric systems, the protein segment interacted with residues across the 5-FU binding site. Intra- and inter-chain interactions were observed in the unliganded dimeric system. MD simulations of a drug-protein system can be used to identify key protein regions involved in drug binding, such as the stabilizing segment identified in hTP. This information will be further utilized in drug discovery.

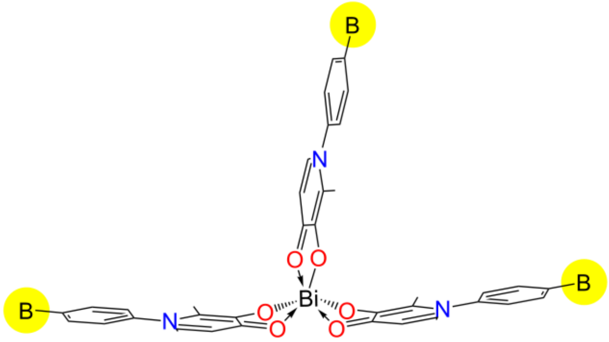
Notes:

Hydroboration and Phosphinoboration of 3-Hydroxy-4-pyridinone Bismuth(III) Compounds

Samuel R. Baird,[1] Hannah R. Caron,[1] Haley A. Dupont,[1] Christopher M. Vogels,[1]
Stephen J. Geier,[1] Jason D. Masuda,[2] Glen G. Briand,[1] and Stephen A. Westcott[1],
[1]Mount Allison University; Sackville, [2]St. Mary's University

Division: Undergraduate Inorganic

There has been recent considerable interest in the synthesis and design of new small-molecule boron compounds for their potential pharmaceutical activities.[1] A boropeptide compound was recently approved by the FDA as the first boron-containing small molecule. Velcade, or bortezomib, is used for the treatment of multiple myeloma (a cancer of the plasma cells) and mantle cell lymphoma (a cancer of the lymph nodes). Since this remarkable discovery, compounds containing boronic acid [$RB(OH)_2$] or boronate ester [$RB(OR')_2$] groups are now being examined as potential pharamaceuticals. In this study, we have prepared 3-hydroxy-4-pyridinone bismuth(III) complexes containing boronate ester appendages utilizing hydroboration and phosphinoboration strategies. 3-Hydroxy-4-pyridinones are a privileged class of ligands frequently used in medicinal bioinorganic chemistry for their strong chelating abilities.[2] We have begun to examine the antimicrobial activities of these species to see what role the boron group plays in the associated bioactivites.



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2. Scott, L. E.; Orvig, C. *Chem. Rev.* **2009**, *109*, 4885-4910.

Notes:

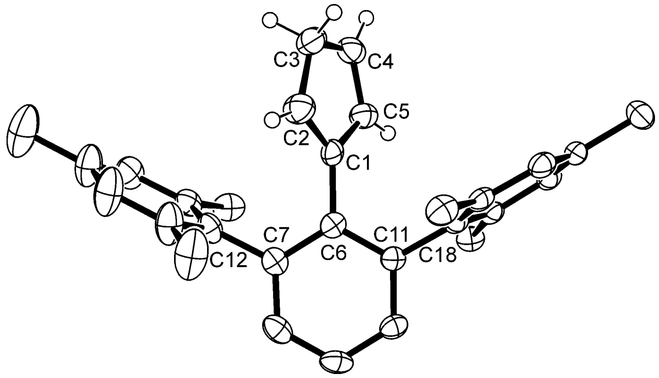
m-Terphenyl Substituted Cyclopentadienyl Ligands

Alex J. Veinot, Jennifer S. Wright, and Jason D Masuda, Saint Mary's University

Division: Undergraduate Inorganic

Sterically hindered cyclopentadienyl (Cp) ligands are valued for their ability to stabilize highly reactive metal centres, which allows 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 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.



Notes:

The Use of the Waste Cellulose-Made Solvent Cyrene as a Green Alternative to DMF in MOF Synthesis

Jinfeng Zhang and Michael J. Katz University

Division: Graduate Inorganic

Due to the multitude of applications observed for MOFs, MOFs are, and will continue to be, an integral of the future of green/sustainable chemistry. With the introduction of the Registration, Evaluation and Authorisation of Chemicals (REACH) legislation in the EU there is a growing trend towards safer production and use of chemicals by industry. Traditional dipolar aprotic solvents including *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methylpyrrolidinone (NMP) are now on a list of 'substances of very high concern' (SVHC) and are therefore likely to face future legislative restrictions under REACH. With the increased implementation of MOFs, it is of vital importance to find safer and preferably bio-derived solvents that can substitute these traditional dipolar aprotic solvents, DMF or *N*,*N*-diethylformamdie (DEF), used in their manufacturing. With this in mind, the presentation will demonstrate our efforts to use an environmental friendly dipolar aprotic solvent, Cyrene, which can be derived from waste cellulose in two simple steps, to synthesize MOFs. The presentation will demonstrate the design principles necessary to implement Cyrene as an alternative solvent for five archetypal MOFs (HKUST-1,UiO-66, MOF-74, Zn2(BDC)2(Dabco), and ZIF-8).

Notes:

Aluminum Complexes for the Copolymerization of Cyclohexene Oxide and Carbon Dioxide

Hart Plommer and Francesca M. Kerton, Memorial University

Division: Graduate Inorganic

Earth abundant metals are becoming increasingly popular in catalysis due to their low cost, prevalence, and generally low toxicity. Of these metals, aluminum is the most abundant and its complexes have been extensively studied in polymerizations of polar monomers such as lactones, epoxides, and carbon dioxide/epoxides [1]. In our research of aluminum amino-phenolate complexes, we have found that different heteroatoms within the outer-sphere of the complex, unbound to the metal atom, affect reactivity towards epoxides [2]. The use of a sterically bulky designer Lewis acid to activate cyclohexene oxide in copolymerizations catalyzed by a chromium(III) amino-bis(phenolate) complex can control the number of ether linkages in the obtained poly(ether-carbonate). Our results obtained in polymerization reactions and carbon dioxide activation using these complexes will be presented.

1. N. Ikpo, J. C. Flogeras and F. M. Kerton, *Dalton Trans.*, 2013, 42, 8998-9006
2. H. Plommer, I. Reim and F. M. Kerton, *Dalton Trans.*, 2015, 44, 12098-12102

Notes:

Surface Chemistry of Doxorubicin Interacting with Gold and TiO_2 Nanoparticles

Shine Xu Zhang, Cape Breton University

Division: Inorganic

Materials with structure features at the nanoscale often demonstrate unique optical, electronic, or mechanical properties, thus gaining wide interest in various industries such as additive manufacturing, chemical engineering, environmental remediation, and biomedical industry. However, the efficacy of their applications is often determined by their surface interaction with various adsorbed molecules. It is critically important to establish an in-depth understanding of such interactions. Herein, I will talk about how doxorubicin, an effective anthracycline anti-cancer agent and a representative pharmaceutical molecule, interacts with two important nanomaterials gold and TiO2 nanoparticles, and how such surface chemistry implicates in drug delivery and photo-degradation of environmental pharmaceuticals

Notes:

Hydrogen Peroxide Sensing in an Ion-Exchange Membrane Separated Electrochemical Cell

Yaohuan Gao, Xu (Shine) Zhang, Cape Breton University

Division: Graduate Inorganic

Quantitative detection of hydrogen peroxide (H_2O_2) is of great interest due to the wide application of H_2O_2 in biological and environmental systems, as well as in many industries including the pulp and paper industry and health care industry. The electrochemical methods are usually preferable for instantaneous signal generation and their ability of automatically monitoring of H_2O_2 levels over time. In addition, the electrochemical sensors can be mass-produced, thus being cost-effective for widely adoption in practice. This study examined the benefits of incorporating an ion-exchange membrane in a traditional H_2O_2 sensing system. The results indicate that commonly observed problems, such as narrow linear ranges, using expensive platinum electrode, and accumulation of gas bubbles on a counter electrode, can be overcome, which is critical to construct more cost-effective and efficient electrochemical sensors.

Notes:

Water Liquid Repellent Surfaces on Engineering Metals

Boyang Gao and Kristin M. Poduska, Memorial University

Division: Graduate Inorganic

Super-hydrophobic surfaces are usually fabricated by the combination of roughening the surface and coating it with a low surface energy material. The present work describes our attempts to make a super-hydrophobic carbon steel by the combination of an electrodeposited zinc-coating layer, followed by the application of an organic coating. We used different electrolytes to produce amino-complex zinc layers ($Zn(NH_3)_4^{2+}$) at alkaline pH, whereas chloro- ($ZnCl_4^{2-}$) formed at low pH values. We investigated stearic acid and dodecanethiol as hydrophobic coatings for the zinc-coated carbon steel. Electrochemical impedance spectroscopy measurements demonstrate that, both hydrophobic coating can effectively protect the metal substrate from corrosion while immersed in a 3.5% NaCl solution. Contact angle measurements show that the most water repellent surfaces are produced by using a combination of both the electrodeposited material and an organic coating.

Notes:

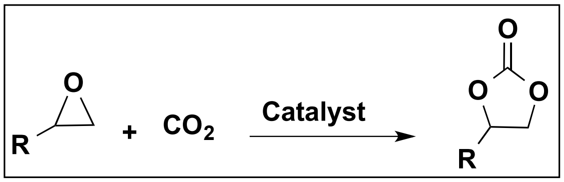
Cycloaddition of Epoxide and CO_2 to Cyclic Carbonate Catalyzed by Vanadium Complexes of Amine-Bis(Phenolate) Ligands

Ali Elkurtehi and Francesca M. Kerton, Memorial University

Division: Graduate Inorganic

The addition of carbon dioxide to epoxides to produce either cyclic carbonates or polycarbonates is an important reaction allowing the conversion of a renewable, inexpensive and non-toxic feedstock such as CO_2 into useful products with many potential applications. Vanadium compounds have been shown by others to be very active for the catalysis of cyclic carbonate synthesis from epoxides and CO_2.[1, 2, 3]

A series of easily prepared oxovanadium complexes with amine-bis(phenolate) ligands possessing different steric, geometric and electronic parameters were prepared and used effectively for cyclic carbonate synthesis from epoxides and carbon dioxide without utilization of any solvents. All reactions displayed excellent selectivity to cyclic carbonate without polycarbonate or other by-products. However, as with many other catalysts, polymer can be form when cyclohexene oxide is used. The synthesis and structural characterization of the complexes as well as the effects of reaction time, CO_2 pressure, co-catalyst, reaction temperature, and the catalytic results will be presented.



1. T. Bok, E. K. Noh, B. Y. Lee, Bull. Korean Chem. Soc. 2006, 27, 1171.
2. A. Coletti, C. J. Whiteoak, V. Conte, A. W. Kleij, Chem. Cat. Chem. 2012, 4, 1190.
3. D. Bai, Z. Zhang, G. Wang, and F. Ma, Appl. Organometal. Chem. 2015, 29, 240.

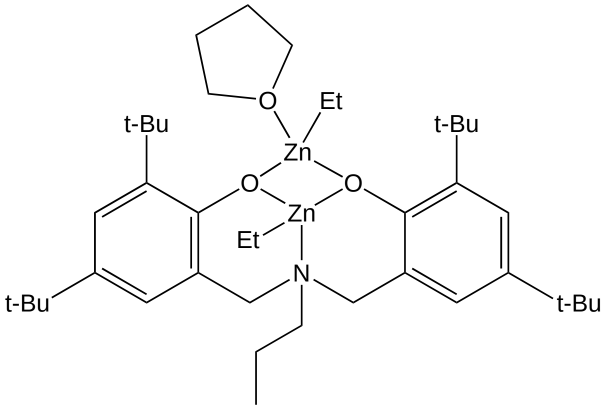
Notes:

Zinc Catalysts for the Ring-Opening Polymerization of Epoxides

Timothy S. Anderson and Christopher M. Kozak, Memorial University

Division: Graduate Inorganic

The Kozak group is interested in first row transition metal complexes of aminephenolate ligands for CO_2 and epoxide copolymerization.[1,2] Zinc complexes have demonstrated significant ability to catalyze these reactions under mild conditions[3] yet zinc-based homogeneous catalysts for copolymerization reactions are lesser explored than other transition metal complexes. Previous work by our group has shown that the zinc complex pictured demonstrates good activity toward lactide ring-openeing polymerization. We are now exploring the use of this compound for the catalytic ring-opening polymerization of epoxides to give polyethers, and the copolymerization of epoxides with CO_2 to give polycarbonates. Our advances in these areas of polymer synthesis will be presented.



1. K. Devaine-Pressing and C. M. Kozak. *ChemSusChem* **2017,** *10*, 1266-1273.

2. K. Devaine-Pressing, L. N. Dawe, and C. M. Kozak. *Polym. Chem.*, **2015**, *6*, 6305-6315.

3. M.R. Kember, P.D. Knight, P.T.R. Reung & C.K. Williams, *Angew. Chem. Int. Ed.* **2009**, *5*, 931-933.

Notes:

Glucose conversion to 5-hydroxymethylfurfural (5-HMF) using metal-organic framework (MOF) catalysts

Jue Gong and Francesca Kerton, Memorial Univerity

Division: Graduate Inorganic

5-HMF is a heterocyclic organic compound, containing both aldehyde and alcohol functional groups in the 2,5 positions of a furan ring. 5-HMF can be used as a building block to synthesize other compounds, such as furandiol and furandicarboxylic acid. These compounds can be used to make a broad range of valuable products including fuel additives and the bio-derived polymer PEF, which has properties like the widely-used petroleum-derived polymer PET. 5-HMF can be prepared via dehydration reactions from glucose and fructose using different homogeneous or heterogeneous catalysts. In this poster, the conversion of glucose to 5-HMF using metal-organic framework (MOF) catalysts will be described. MOFs are porous materials consisting of metallic components or clusters linked together with organic units. Reactions have been performed using three different Zr-cluster MOFs (UiO-66, UiO-66-NH_2 and MOF-808). In our studies to date, UiO-66 has provided the highest yields of 5-HMF. Research is ongoing to optimize the reaction conditions (e.g. temperature, time) and to recycle the catalyst.

Notes:

Formation of a Renewable Amine and an Alcohol via Transformations of 3-acetamido-5-acetylfuran

Yi Liu and Francesca M. Kerton, Memorial University

Division: Graduate Organic

Chitin can be obtained from the shells of crustaceans (i.e. shellfish waste), and is the most abundant biopolymer in the ocean. *N*-acetyl-D-glucosamine (NAG), a sugar, is the monomer of chitin. Controlled dehydration of NAG can generate a new compound, 3-acetamido-5-acetylfuran (3A5AF).[1] The reactivity of 3A5AF as a platform chemical was explored. Hydrolysis of the amido group to yield the amino-substituted furan, 2-acetyl-4-aminofuran (**1**), was achieved via NaOH-catalysis. Reduction of the acetyl group could be achieved stoichiometrically using $NaBH_4$ or catalytically via transfer-hydrogenation using an Ir catalyst. The product alcohol, 3-acetamido-5-(1-hydroxylethyl)furan (**2**) underwent dehydration during analysis via GC-MS to yield an alkene (**3**). The potential reactivity of 3A5AF and **1** towards carbon dioxide was studied but no reaction was observed due to the inherent acidity of 3A5AF and **1** despite the latter being an amine. The computationally determined pK_a values for 3A5AF and **1** are reported. Interestingly, in this work, tautomerism of 3A5AF was observed in CD_3OD as evidenced by H-D exchange within the acetyl group.

1. X. Chen, Y. Liu, F. M. Kerton and N. Yan, *RSC Adv.*, 2015, **5**, 20073-20080.

Notes:

The Reactions of DETA-CO_2 with Organic Acids (DETA = Diethylenetriamine)

Ryan N. McCoy, Katherine N. Robertson, Michael A. Land, and Jason A. C. Clyburne, Saint Mary's University

Division: Undergraduate Organic

CO_2 is a molecule of great importance, as it plays a powerful role in contributing to global warming. A number of amines have been used to reduce the rate of global warming by capturing CO_2. Previous work has shown that CO_2 reacts with monoethanolamine to create an ionic carbamate salt but reacts with diethylenetriamine (DETA) to create a neutral zwitterionic species where the CO_2 is bound at the terminal position of the adduct formed. Organic and inorganic acids can be used to protonate up to 3 sites of DETA ($H_2N^+CH_2CH_2N^+(H)CH_2CH_2N^+H_2$). Previously, using inorganic acids such as HBr, HCl, and HNO_3, monoprotonated salts of DETA have been prepared. Like DETA, these DETA salts also absorb CO_2, the difference being that the CO_2 now binds to the central nitrogen atom of $DETAH^+$ instead of binding terminally. In this work the relationship between the following two sets of results has been investigated. The questions we wanted to answer were i) DETA-CO_2 + HX → Would this give a monoprotonated CO_2 salt? If so, where does the CO_2 bind? ii) DETA·HX + CO_2 → Where does the CO_2 initially bind? Does the CO_2 subsequently migrate to another position? Can a salt with a terminally bound CO_2 be isolated. To begin our investigation, *p*-Toluenesulfonic acid (PTSA) was reacted with DETA-CO_2. The formation of a salt with CO_2 bound terminally to $DETAH^+$ is suggested by the spectroscopic evidence. PTSA was also used to form a 1:1 salt with $DETAH^+$ in solution (the 2:1 salt being preferred in the solid state). Spectroscopic evidence suggests that adding CO_2 to this solution yields a salt where the CO_2 again binds terminally to $DETAH^+$.

Notes:

Mechanochemical Amorphization of Chitin and Conversion into Oligomers of N-acetyl-D-glucosamine

Georgios Margoutidis and Francesca Kerton, Memorial University

Division: Graduate Inorganic

Our group has highlighted processes for a wide range of useful products from inedible parts of seafood such as the biopolymer of chitin and its subsequent units.[1] In this poster, we investigate the potential that mechanochemical conditions[2] offer towards chitin amorphization and depolymerization. Using powder X-ray diffraction (XRD) we show that crystallinity can be reduced in a controlled way up to more than 50% in 2 h using a steel ball mill system with a packing degree of 3%. We correlate this observation with a decrease in the interchain hydrogen bonding network which we realize when we monitor the behaviour of the amide I split with infrared spectroscopy (FT-IR). Furthermore, our quantitative readings of the spectra reveal a decrease in the glycosidic linkage content and a retention of the *N*-acetyl group. A corresponding increase in chitin solubility is being demonstrated which offers the chance to disclose that a packing degree of 18% can give a solubility of 35.0% when milling for 6 h. The addition of the natural clay kaolinite functions catalytically in the ball mill achieving a maximum of 75.8% of water soluble products in 6 h. Acetylated oligomers with degrees of polymerization between 1 and 5 were detected in these water soluble products using matrix-assisted laser desorption-ionization mass spectrometry (MALDI MS) and data were complemented by a colorimetric approximation of reducing ends and a size-exclusion chromatography (SEC) analysis. The monomer and dimer were quantified at levels comparable to cellulose ball milling with their yields reaching 5.1 wt.% and 3.9 wt.% respectively within 6 h.

1. F. M. Kerton, Y. Liu, K. W. Omari and K. Hawboldt, *Green Chem.*, 2013, **15**, 860-871.
2. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friscic, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413-447.

Notes:

Exploring New Directions in Frustrated Lewis Pair (FLP) Chemistry

Diya Zhu and Doug Stephan, University of Toronto

Division: Graduate Inorganic

The Stephan group focuses on a wide range of inorganic main group chemistry, with a particular focus on fundamental aspects of this chemistry. New reactivity and chemical transformations are targeted to develop novel catalysts, entirely new catalytic processes, or new materials. The last decade of research has shown that Frustrated Lewis Pairs (FLPs) offer a rich landscape of reactivity. Currently, we are exploring new directions in FLP chemistry. This poster will illustrate three recent areas of investigation: 1) the synthesis and application of stable boron-containing radicals; 2) a single electron transfer mechanism for FLP reactivity; and 3) the study of proazaphosphatrane-containing FLPs.

Notes:

The Synthesis of Novel Stannylenes and Testing their Reactivity towards Forming Heavy Element Multiple Bonds

Michelle L. Johnson, Acadia University

Division: Undergraduate Inorganic

The syntheses of several *N*,*N*-bound stannylenes ($Sn(NR_2)_2$, NR_2 = Mes_2Mal and $Dipp_2Nacnac$) and *N*,*C*-bound stannylenes ($ArSnN^iPr_2$, Ar = Mes, Tripp, TerMes, and Mes^*) were attempted, but the stannylenes were unable to be isolated. The syntheses of several compounds featuring heavy element multiple bonds were also attempted using a bis(amido)stannylene ($Sn(N(TMS)_2)_2$ and nitrogen ($TMSN_3$) and phosphorus reagents ($(TrippP)_3$, $(MesP)_4$, and $(PhP)_5$). Only the reaction with $TMSN_3$ resulted in a product consistent with having a tin-nitrogen double bond. The redox chemistry of bis(amindo)stannylene was also further investigated through a cycloaddition reaction with 2,3-dimethyl-1,3-butadiene which yielded a tin heterocyclic product. Reaction products were characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ nuclear magnetic resonance spectroscopy. Further work is necessary to confirm the tin-nitrogen double bond geometry and determine its reactivity, as well as to optimize the synthesis conditions.

Notes:

Iron Amino-bis(phenolate) Complexes for CO_2 Activation

Kori A. Andrea and Francesca M. Kerton, Memorial University of Newfoundland

Division: Graduate Inorganic

The production of cyclic carbonates derived from the renewable C-1 feedstock CO_2, and epoxide substrates is a growing area of research due to their wide applications as aprotic solvents and as starting materials for polycarbonates.[1] Several measures have been taken to design catalysts allowing the transformation of CO_2 and epoxides to cyclic carbonates under mild conditions. However, many of these involve the use of costly, toxic metals such as cobalt and chromium. Iron is one of the most promising metals to catalyze these reactions due to its low toxicity, high earth abundancy and cost-effectiveness. Recently the Kerton group has discovered an exciting family of iron amino-bis(phenolate) catalysts for these transformations.[2] To provide further insight into the active form of these catalysts we have prepared the bimetallic species (LFe(μ-O)FeL) for comparison. Results involving the comparison of these two catalytic systems in the coupling of CO_2 and various epoxide monomers for cyclic carbonate formation will be discussed.

1. North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12* (9), 1514–1539.
2. Alhashmialameer, D.; Collins, J.; Hattenhauer, K.; Kerton, F. M. *Catal. Sci. Technol.* **2016**, *6* (14), 5364–5373.

Notes:

Testing Solid Phase Extraction Techniques for Preparing Dissolved Organic Matter Samples from the Terrestrial-to-Aquatic Interface for Liquid-State NMR Analysis

Alexander Newman, Jamie Warren, and Susan Ziegler, Memorial University

Division: Graduate Organic

Solid phase extraction (SPE) using a styrene−divinylbenzene copolymer (PPL) sorbent has become a common method in studies that seek to isolate dissolved organic matter (DOM) from natural waters. However, parameters of SPE methodology using PPL, such as flowrate which could introduce chemical selectivity or a reduction in recovery due to differences in the rate at which analytes are introduced to the solid-phase, remain understudied. Additionally, differences in the composition of DOM and matrix components from natural water sources, particularly those spanning the terrestrial-to-aquatic interface, could introduce chemical selectivity that makes comparisons among these sources impossible. These comparisons of DOM from different natural environments are what many researchers seek to accomplish in recent studies of DOM, investigating any selectivity that may be introduced through the PPL-SPE methodology is vital. Flowrate was investigated and regulated manually over a range of 10ml-50 ml min^{-1}. Loading volume experiments were performed over a range of 0.5 to 10 liters, a range representative of the sample volumes required to obtain a viable sample for liquid NMR analysis across the full range of natural sources of DOM across the terrestrial-to-aquatic interface. The mass balance of the applied sample DOM was also assessed to determine the possible avenue for sample loss through this technique. Both recovery and mass were assessed by measuring dissolved organic carbon (DOC) using high-temperature catalytic oxidation. Findings of this study will be further informed by two-dimensional liquid state nuclear magnetic resonance spectroscopy which will help to provide context on the mechanisms of any chemical selectivity.

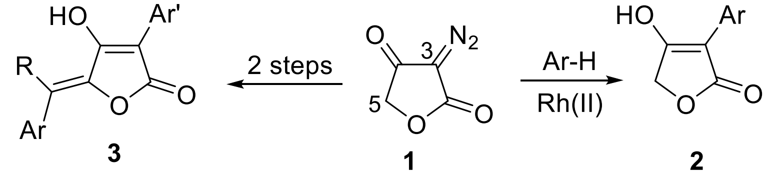
Notes:

Catalytic Undirected Intermolecular C-H Functionalization of Arenes with 3-Diazofuran-2,4-Dione: Synthesis of 3-Aryl Tetronic Acids, Pulvinic Acids and Pulvinones

Amarender Manchoju and Sunil V. Pansare**,** Memorial University

Division: Graduate Organic

A variety of 3-aryl tetronic acids (**2**) have been synthesized by an undirected, intermolecular C-H functionalization of arenes with 3-diazofuran-2,4-dione (**1**). This methodology featured as a key step in the synthesis of a series of naturally-occurring 3-aryl-5-arylidene tetronic acid derivatives (pulvinic acids and pulvinones, **3**) from commercially available tetronic acid. Salient features of the pulvinic acid synthesis include a one-step, stereoselective synthesis of the C5 arylidene group and a single step introduction of the C3 aryl substituent. Details of these studies will be presented.



3

1

2

R = H pulvinones
R = CO_2Me pulvinic acids

19 examples
(32-96%)

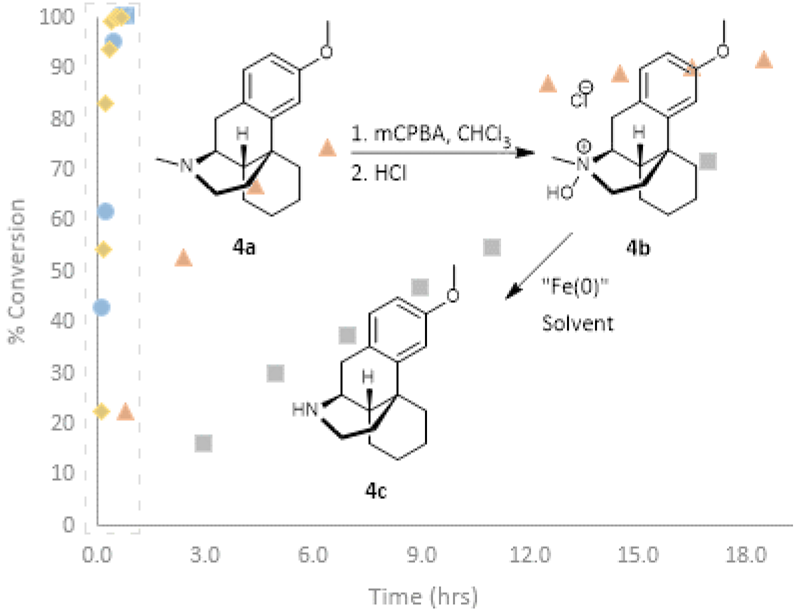
Notes:

Utility of Iron Nanoparticles and a Solution-Phase Iron Species for the *N*-demethylation of Alkaloids

Jon Kyle Awalt, Raymond Lam, Barrie Kellam, Bim Graham, Peter J. Scammells, and Robert D. Singer, Saint Mary's University,

Division: Undergraduate Organic

The *N*-demethylation of selected *N*-methylalkaloids using a modified Polonovski reaction can be accomplished using a novel green methodology employing nanoscale zero-valent iron, nZVI, in isopropanol. Use of nZVI promotes a much faster conversion to *N*-demethylated products due to much higher surface area on the metal surface as shown by SEM analysis. Rates of conversion can be further enhanced using catalytic quantities of the solubilised iron(0) species triiron dodecacarbonyl, $Fe_3(CO)_{12}$.



Notes:

Screening of Catalysts for Electrochemical Oxidation of Bio-Fuels

Tobias Brueckner, Peter Pickup and Kelly Hawboldt, Memorial

Division: Graduate Physical, Theoretical & Computational

Fuel cells are a promising technology to meet the increasing global energy demand. This work focuses on liquid fuels for polymer electrolyte membrane fuel cells, which overcome the storage and transport issues of gas fed direct hydrogen fuel cells. Furthermore, use of renewable liquid fuels such as bioethanol and biomethanol in fuel cells can help to reduce global greenhouse gas emissions, since the net carbon dioxide exhaust of a liquid feed fuel cell is zero if the fuel is generated from a renewable feedstock. In this work fractions of pyrolysis liquids produced by thermochemical decomposition of forestry residuals were used as a liquid fuel feed source. The light fraction of the oil contains a number of short C1 to C3 molecules such as methanol, ethanol, hydroxyacetone, and acetic acid. Ethanol and methanol can be used to power fuel cells in electric vehicles, consumer electronics, and remote power systems. However, impurities such as acrolein poison the fuel cell catalyst. Therefore, separation and purification of the chemicals must be improved or new anode catalyst are needed to solve these problems. The activities of various Pt based anode catalysts for the oxidation of methanol and ethanol have been evaluated in a multi-anode fuel cell and the effects of impurities from the pyrolysis oil have been investigated.

Notes:

A Synthetic and Computational Investigation into the Reactivity of Silylenes towards Small Molecule Activation and Heavy Element Multiple Bonds

Lucas Coxhead, Acadia University

Division: Undergraduate Physical, Theoretical & Computational

The synthesis of the silylenes (*tert*-butyl)$_2$(1,4-diaza-1,3-butadiene)Si, (2,6-di-*iso*-propylphenyl)$_2$(1,4-diaza-1,3-butadiene)Si, (2,4,6-trimethylphenyl)$_2$(1,4-diaza-1,3-butadiene)Si and (2,4,6-trimethylphenyl)$_2$(1,4-diaza-1,3-butadiene)Si was attempted and their air sensitive silyl chloride precursors were synthesized. The silyl chlorides were also used as precursors for the attempted synthesis of an asymmetric heavy element multiple bond between silicon and carbon. The synthesized compounds were characterized by $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ nuclear magnetic resonance (NMR) spectroscopy. Three new silyl chlorides were synthesized and characterized using ^{29}Si NMR spectroscopy; (2,6-di-*iso*-propylphenyl)$_2$(1,4-diaza-1,3-butadiene)SiCl$_2$ (δ: -40.7 ppm), (2,4,6-trimethylphenyl)$_2$(1,4-diaza-1,3-butadiene)SiCl$_2$ (δ: -41.2 ppm) and (2,4,6-trimethylphenyl)(N-*iso*-propyl$_2$)SiCl$_2$ (δ: -18.3 ppm). The formation of Si-C adducts was observed using this technique, with these silyl chlorides as precursors, although no double bonds were isolated based on NMR data. A computational investigation into five series of silylenes and adducts between silicon and carbon, nitrogen, phosphorus and germanium was performed. Adducts appeared to be favourable with nitrogen and phosphorus, but not with carbon and germanium.

Notes: