

Lycoming College Chemistry Newsletter

Issue No. 1(!)

November 2008



Contents

Hello!	p. 2
2008 Graduates and Their Placement	p. 3
2008 Award Winners	p. 3
2008 Gamma Sigma Epsilon Inductees	p. 3
Chemistry Faculty Members' Updates	p. 4
New Instrumentation	p. 14
Endowment Funds	p. 15
Invitation to Email Us	p. 15

Hello!

We've been toying with the idea of writing a newsletter for the past several years. This project finally got off the ground because of Dave Franz's interest in making it a reality. Many of you received a postcard from Dave asking for current email addresses updated information. We are attempting to send this newsletter to everyone for which we have a current email address. If you find someone who might be interested in this newsletter and you find they didn't receive it, please feel free to forward it to them. Many of you



made it back for Homecoming and it was good to see you again. Our speaker at the Homecoming colloquium (formally known as The William and Barbara Haller Endowed Lectureship in Biology and Chemistry) was Jason Stamm, class of 1994. After graduating from Lycoming, Jason obtained a M.S. from the University of Michigan in Medicinal Chemistry. Thereafter he pursued a M.D. from the Pennsylvania State College of Medicine at Hershey. Jason was stationed at Lackland Air

Force base in Texas and from there had two tours of duty at Balad Air Base with the Air Force Expeditionary Hospital, Intensive Care Unit in Iraq (within the infamous Sunni Triangle). Jason has recently left the military and has accepted a Fellowship in Pulmonary/Critical Care at the University of Pittsburgh Medical Center. Jason's talk at Homecoming was based on how his time at Lycoming prepared him for his subsequent adventures with a focus on his time in Iraq. His parents and brother were also in the audience. We thanked Jason for his service to our country.

We've had several students conduct research within the department over the past year or so. Lauren Raby worked with Dr. Bendorf on synthesizing substrates for hydroacylation promoted by chelating amines. Brandon Zarzycny and Alex Hunter, under the direction of Dr. Mahler, investigated the synthesis and spectroscopic correlations of various phosphine complexes of ruthenium. James Grant and Kyle Totaro worked with Dr. McDonald on different aspects of synthesis/characterization of HMPA analogs for complexation to samarium diiodide. James spoke at the Intercollegiate Student Chemists Convention at Elizabethtown College on his work. Christie Groller examined the modification carbon electrodes by attaching organic monolayers for Dr. Ramsey. Chris Heist labored under the tutelage of Dr. Ramsey on new techniques for preparing arrays of carbon electrodes. John Stutzman also is working for Dr. Ramsey on detection of outgassing of cell phones and other electronic devices.

Several of our students pursued summer research opportunities off campus through NSF sponsored REU (Research Experience for Undergraduates) programs. Trisha Lindenmuth traveled to Auburn University to work with Dr. Curtis Shannon and examined the modification of electrodes by polyoxometallates. John Stutzman headed to the University of Southern California to work for Dr. Travis Williams on ^{13}C kinetic isotope effects associated with hydride abstraction from 1-phenylethanol. Oscar Wheeler

did his summer research at the University of Southern Mississippi with Dr. Karl Wallace on the synthesis and characterization of an anion specific sensor. All of our student researchers gave presentations on their work at our traditional Friday afternoon chemistry colloquium.

In sports news, Chemistry beat Biology once again in the annual Fall softball game (21-9). They were closer than last year but they still have a ways to go to match our athletic prowess. There were unfounded accusations of steroid use.....

2008 Graduates and Their Placement

(Our information is incomplete at the time of sending out the newsletter)

Nancy Berger	Ph.D. program in chemistry, Georgia Tech University
Scott Bower	Chemist, J.W. Aluminum Company, Mt. Holly, SC
James Grant	Colgate-Palmolive, NJ
Christie Groller	LaFarge Company
Chris Heist	M.S. program in chemistry, Bucknell University
Nick Johnson	High School Chemistry Teacher, Johnathon Dayton HS, Springfield, NJ
Lauren Raby	Characterization/Process Technician, IQE Inc.
Brandon Zarzyczny	

2007-2008 Department of Chemistry Award Winners

Kaitlin Horn	CRC Freshman Chemistry Award
Damian Mariano	PolyEd Organic Chemistry Award
John Stutzman	Analytical Award
James Grant	Trask Award
Sarah Readler	Brunstetter Award

2008 Gamma Sigma Epsilon Inductees

Brittany Bryan	Eric Dingler-Brown	James Dolak
Tess Duffin	Kristin Fahey	Carrie Harsomchuck
Trisha Lindenmuth	Damian Mariano	John McDonough
Cole Pizzingrilli	Casey Walls	Stephanie Woodhouse
Debbie Smith		

Biographical Sketch, Dr. Holly D. Bendorf

Dr. Holly Bendorf joined the Department of Chemistry in 1995, returning to her native Pennsylvania after completing graduate work at UCLA and a one-year teaching position at Bowdoin College in Maine. Dr. Bendorf teaches Organic Chemistry, Spectroscopy and Molecular Structure, and Organometallic Chemistry. She also teaches a chemistry course for non-science majors, Chemistry in Context, and shares in the teaching responsibilities for both Chemistry Research Methods and General Chemistry.



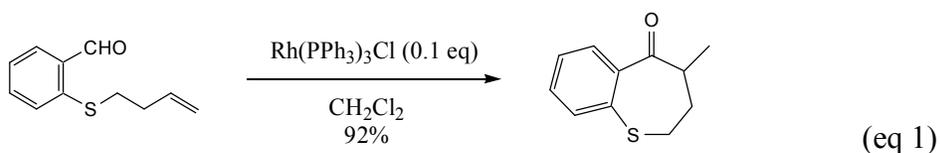
In addition to teaching classes, Dr. Bendorf mentors undergraduate student researchers in her lab. Her research focuses on exploiting organotransition metal chemistry for the synthesis of medium-ring heterocycles and carbocycles. Student researchers in Dr. Bendorf's lab have had their work published in *Tetrahedron Letters*, an internationally recognized journal of organic chemistry, and have presented their work at conferences. Research in Dr. Bendorf's lab has been supported by grants from the Petroleum Research Fund, the Merck Foundation and the Council on Undergraduate Research.

Last summer, Dr. Bendorf married Dr. Chriss McDonald, and she has been trying to keep up with him on her mountain bike ever since. Dr. Bendorf also enjoys playing tennis, kayaking and skiing. She is a volunteer ski patroller at Ski Sawmill.

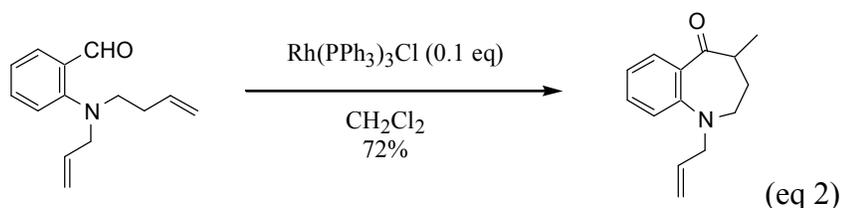
Research Synopsis, Bendorf Lab

The goal of our research is to develop new chemical methods for the synthesis of biologically active compounds. In particular, we are designing new routes to medium-ring heterocycles via rhodium-catalyzed intramolecular hydroacylation. While the synthesis of 5-membered rings via hydroacylation is well-documented, the synthesis of larger ring sizes via this chemistry remains a challenge.¹

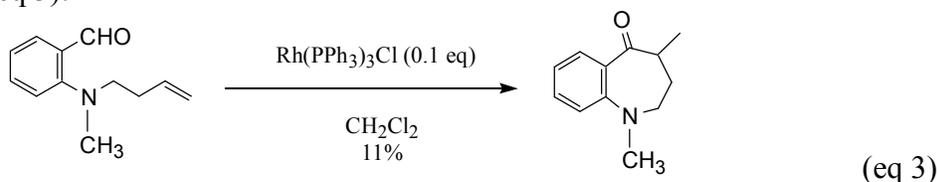
We make use of a chelation-assisted strategy to overcome the entropic issues associated with medium-ring formation and have used this chemistry to prepare a variety of sulfur-containing heterocycles (eq 1).² This sulfur heterocycle work represents one of only three published examples of the application of hydroacylation chemistry to medium ring synthesis.^{3,4}



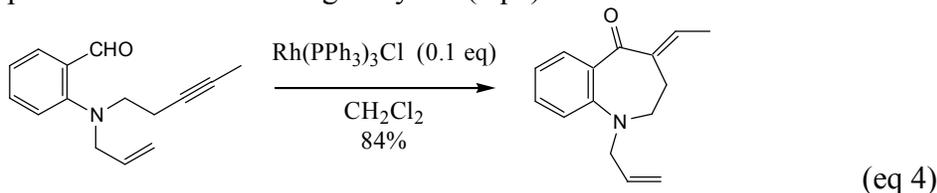
Current work is directed at expanding the intramolecular hydroacylation to the synthesis of medium-ring nitrogen heterocycles. We have found that Wilkinson's catalyst smoothly converts allyl-substituted amines into benzazepinones (eq 2).



The presence of the allyl substituent on the amine is critical for the success of the reaction and we believe that initial coordination of the amine and the allyl pi-bond are necessary to promote hydroacylation. Experiments with the benzyl- and methyl-substituted analogs, which react sluggishly and provide only low yields of cyclized product, support this assertion (eq 3).



Alkyne-containing substrates also undergo hydroacylation. The densely-functionalized benzazepinone products are obtained in good yield (eq 4).



On-going work in our lab includes optimizing the reaction conditions, identifying alternatives to the allyl substituent, and exploring the range of ring sizes accessible by this methodology.

References:

1. For a recent review, see: Fu, G. C. in *Modern Rhodium-Catalyzed Organic Reactions*, P. A. Evans, Ed. Wiley-VCH: Weinheim, Germany, **2005**, 79-91
2. Bendorf, H. D.; Colella, C. M.; Dixon, E. C., Marchetti, M.; Matukonis, A. M.; Musselman, J. D.; Tiley, T. A. *Tetrahedron Lett.* **2002**, *43*, 7031-7034.
3. Synthesis of cyclooctenones via hydroacylation: Aloise, A. D.; Layton, M. E.; Shair, M. D. *J. Am. Chem. Soc.* **2000**, *122*, 12610-12611.
4. Synthesis of cycloheptenones via hydroacylation: (a) Sato, Y.; Oonishi, Y.; Mori, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 1218-1221. (b) Oonishi, Y.; Mori, M.; Sato, Y. *Synthesis* **2007**, 2323-2336.

Biographical Sketch, Dr. Charles Mahler

Dr. Charles H. Mahler joined the Department of Chemistry in 1994 after teaching in a one-year visiting position at Mercer University in Macon, Georgia. He received his Ph.D. from Northwestern University, where he did synthetic inorganic work on soluble transition-metal selenides, characterizing them with single-crystal X-ray diffraction studies and ^{77}Se NMR spectroscopy. He then spent a little over two years as a postdoctoral fellow at the Universität Karlsruhe (TH) in Germany, with fellowships from NATO and the Alexander von Humboldt Foundation. At Lycoming he teaches General Chemistry, Physical Chemistry, Advanced Inorganic Chemistry, and Chemistry Research Methods (and taught Analytical Chemistry once, his first year here, as a sabbatical replacement).

Like all members of the Department of Chemistry, Dr. Mahler directs undergraduate research. He has several research projects with student collaborators at Lycoming. Currently he and a series of students are synthesizing a series on known organometallic ruthenium phosphine complexes to investigate their ^{31}P NMR spectra and their correlation with the Ru-P bond lengths and enthalpies of these complexes. Other research



projects with students include synthesis and characterization of transition metal phosphine selenides, and computational chemistry.

Dr. Mahler and his wife Melissa live in Williamsport and have two sons: Samuel, 6, and Ross, 2. Samuel is a first grader who enjoys reading about dinosaurs and

doing science experiments with his dad (dry ice in soapy water is a lot of fun). Ross is talking up a storm (even if he sometimes requires a translator) and wants to do everything his big brother does too. The Mahler family and their dog Gibbs enjoy hiking in the woods of northcentral Pennsylvania.

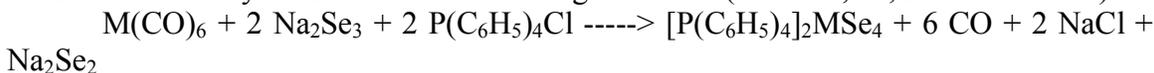
Research in the Mahler lab currently consists of two projects, both involving air-sensitive synthetic techniques and characterization by NMR spectroscopy.

Research Synopsis, Mahler Lab

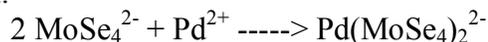
1. Synthesis and Structural Determination of Early Transition-Metal Compounds

Although the chalcogenides (O, S, Se, Te) have well known chemistry, most of their compounds with transition-metals are insoluble; indeed many metals are found as chalcogenide ores. Recently, though, a growing number of soluble transition-metal chalcogenides have been synthesized and studied.¹ This project involves the synthesis of new, soluble compounds of the early transition-metal chalcogenides, their characterization, growth of single-crystals of the compounds, and the determination of their structures by single-crystal X-ray diffraction studies.

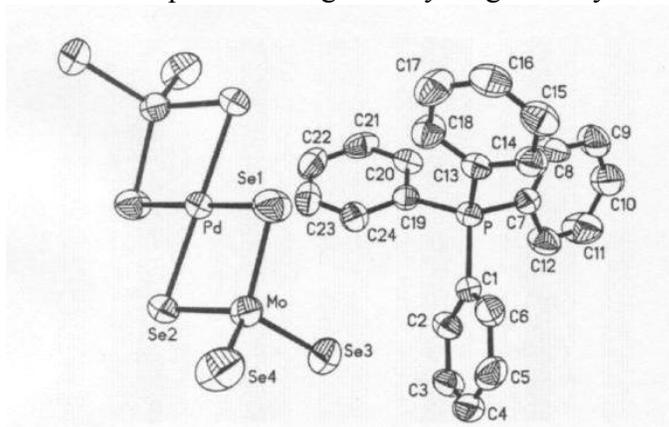
The building blocks used to synthesize the new compounds are the soluble tetraselenometalate ions, MSe_4^{2-} , where the metal is either tungsten or molybdenum. These anions are synthesized in the following reaction: (M = Mo, W; solvent = DMF)



These MSe_4^{2-} anions can then be reacted with organic compounds, selenium and sulfur containing compounds, and a variety of divalent transition-metal salts. Mixed-metal selenides form on reaction of MSe_4^{2-} and divalent metal salts.² The following reaction is typical:



The compounds can be characterized using infrared, ultraviolet-visible, and nuclear magnetic resonance spectroscopies, as well as by X-ray structure determination. Crystals of these compounds can generally be grown by solvent layering or slow cooling methods.



We have used these crystals to determine the structures of our compounds with single-crystal X-ray diffraction techniques. $[PPh_4]_2[Pd(MoSe_4)_2]$ has the structure shown at left³ (determined in collaboration with Dr. Marj Kastner at Bucknell University).

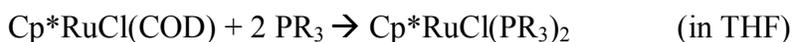
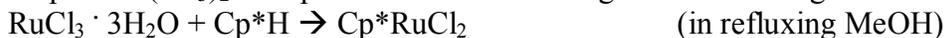
All of these compounds are air-sensitive, decomposing on exposure to moisture and/or oxygen. They are therefore synthesized and isolated under a non-reactive, inert-gas atmosphere using Schlenk line techniques. This also eliminates any odors associated with selenium.

Student Researchers: Brian Belz, Josemar Castillo, Olivia English, Stacy Howerter, Joe Keane, Matt Barr, Ed Slavin, Zach Shiffler, and Matt Zarzeczny

2. Synthesis and Nuclear Magnetic Resonance Studies of Ruthenium Phosphines

A series of organometallic ruthenium phosphine complexes of general formula $\text{Cp}^*\text{RuCl}(\text{PR}_3)_2$ have been synthesized, where Cp^* is the pentamethylcyclopentadienyl ligand, and PR_3 can be PMe_3 , PPhMe_2 , PMePh_2 , PPh_3 , PEt_3 , and $\text{P}(\text{n-Bu})_3$. A strong linear correlation between the enthalpy of bond formation for the Ru-P bond and the crystallographically determined Ru-P bond length has been determined.⁴

Synthesis of the $\text{Cp}^*\text{RuCl}(\text{PR}_3)_2$ complexes is done according to the following scheme:⁵

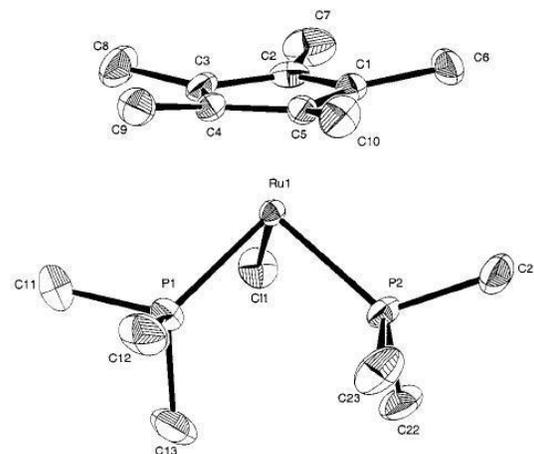


We have been able to synthesize these compounds using air-sensitive techniques and have then determined their ^{31}P -NMR spectra. These also correlate with both the bond distance and bond enthalpy and provide another means of investigating the reactivity of these complexes (single crystal X-ray structure of $\text{Cp}^*\text{RuCl}(\text{PMe}_3)_2$ pictured).

Student Researchers: Sara Bartlett, Hans Bottesch, Alex Hunter, Kim McDowell, and Brandon Zarzyczny

References:

1. Ansari, M.A.; Ibers, J.A. *Coord. Chem. Rev.*, **1990**, *100*, 223 - 266.
2. Ansari, M.A.; Chau, C.-N.; Mahler, C.H.; Ibers, J.A. *Inorg. Chem.*, **1989**, *28*, 650- 654.
3. Shiffler, Z.J.; Baldwin, S.M.; Keane, J.M.; Belz, B.L.; Barr, M.L.; Slavin III, E.R.; Kastner, M.E.; Mahler, C.H. *Acta Cryst.*, **2004**, *E60*, 1-3.
4. Smith, D.; Haar, C.; Luo, L.; Li, C.; Cucullu, M.; Mahler, C.; Nolan, S. *Organometallics* **1999**, *18*, 2357-2361.
5. Luo, L.; Nolan, S.; Fagan, P. *Organometallics*, **1993**, *12*, 4305-4311.



Biographical Sketch, Dr. Chriss McDonald

Dr. Chriss McDonald joined the Department of Chemistry in 1988 after a one-year teaching position at Berea College in Kentucky. He received his doctorate in organic chemistry from Miami University where he focused on the synthesis of highly oxygenated natural products. His undergraduate degree is from Manchester College in Indiana where he majored in medical technology. At Lycoming he teaches General Chemistry, Organic Chemistry, Advanced Organic Chemistry, Spectroscopy, Chemistry Research Methods, and team teaches Biochemistry (with Jeff Newman). He is particularly interested in the development of new inquiry-based laboratory experiments for his various organic courses.



Like all members of the Department of Chemistry, Dr. McDonald directs undergraduate research. The main thrust of his research at Lycoming involves the development of new ligands for the reductant samarium diiodide. The goals are to find ligands which are better at facilitating reductions by samarium diiodide and safer to use than the standard ligand (HMPA). Over the years his research has been funded by the Petroleum Research Fund, Research Corporation, the Merck Foundation, and the Council on Undergraduate Research.

Dr. McDonald has two sons, Matt (age 26, a mechanical engineer for Lutron Corporation), and Jim (age 18, a freshman at Penn State Erie majoring in mechanical engineering). Dr. McDonald has recently married Dr. Holly Bendorf. They live in the middle of the woods outside of Trout Run, PA with their somewhat overweight cat Porcupine. In his free time, Dr. McDonald enjoys playing basketball (where he just received a broken nose), tennis and biking. When he's not too exhausted from all of that running around, he does some gardening.

Research Synopsis, McDonald Lab

Samarium (II) iodide (SmI_2) is a versatile reductant used by organic chemists. Its uses include direct reductions of alkyl halides¹, aldehydes/ketones², and α,β unsaturated carbonyl compounds.² It's most important synthetic application is in the area of carbon-carbon bond formation. It can be used to couple a pair of aldehydes (or ketones) as well as a carbonyl to a C-C pi bond.³ This research laboratory has previously uncovered a route to cyclize unsaturated amides with SmI_2 after electrophilic activation of the amide by triflic anhydride.⁴ Several research groups have explored the use of various ligands to "tune" the reductive power of the SmI_2 .^{5,6} Hexamethylphosphoric triamide (HMPA, **1**) is the most important ligand used to increase the reducing power of SmI_2 , unfortunately this ligand has been associated with nasopharyngeal cancer.⁷ Much effort has gone into

References:

1. Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chemistry Lett.* **1987**, 1485.
2. Girard, P.; Namy, J.; Kagan, H. *J. Am. Chem. Soc.* **1980**, *102*, 2693.
3. Kagan, H. *Tetrahedron* **2003**, *59*, 10351.
4. McDonald, C.; Galka, A.; Green, A.; Keane, J.; Kowalchick, J.; Micklitsch, C. *Tetrahedron Lett.* **2001**, *42*, 163.
5. Kagan, H.; Namy, J. *Topics in Organometallic Chem.* **1999**, *2*, 155.
6. Shabangi, M.; Sealy, J.; Fuchs, J.; Flowers, R. *Tetrahedron Lett.* **1998**, *39*, 4429.
7. Vogel, E.; Von Zeeland, A.; Raaymakers-Jonsen, E.; Verplanke, C.; Zijlstra, J. *Mutation Res.* **1985**, *150*, 155-198.
8. Enemaerke, R.; Hertz, T.; Skydstrup, T.; Daasbjerg, K. *Chem. Eur. J.* **2000**, *6*, 3747.
9. Dahlen, A. Hilersson, G. *Tetrahedron Lett.* **2001**, *42*, 5565.



Biographical Sketch, Dr. Jeremy Ramsey

Born and raised in western Pennsylvania, Dr. Ramsey started his career in chemistry by earning a B.S. in chemistry at Clarion University of Pennsylvania. His education continued at The Ohio State University in Columbus, Ohio, where five years later, he completed a Ph.D. program in analytical chemistry through study of electrochemical systems using spectroscopic methods. In an effort to expand his area of expertise, Jeremy moved to Tennessee to work at Oak Ridge National Laboratory. There he acquired skills related to biological analysis and microfabrication. This experience led directly to a position with a defense contractor at the Naval Research Laboratory in Washington, DC. His work there was related to the development of methods for sensing explosives and other warfare agents. He joined the Lycoming faculty in 2005.



Dr. Ramsey's research focuses on the electrochemical kinetics of neurotransmitters at carbon electrodes surfaces. The goals of the research are to develop methods of altering the surface structure via covalent modification to provide specific detection of neurotransmitters such as dopamine in the complex brain environment and to prevent fouling of carbon electrode surfaces during *in vivo* neurotransmitter detection. His research is also focused on developing microfabrication techniques that can be utilized in an undergraduate research laboratory.

At home with his wife, Heather, and two children, Madison and Simon, there is also a lot of excitement. This year brought a new stage as Madison began kindergarten. Although Mommy and Daddy struggle with the adjustment at times, Madison has been having a blast at school, while Simon keeps himself busy playing Star Wars. With any luck, they will be heading to Disney World for vacation next summer.

Research Synopsis, Ramsey Lab

Electrochemistry is a branch of chemistry that deals with the chemical action of electricity and the production of electricity by chemical reactions. The contribution of electrochemical processes to our economy is staggering. It is estimated that the current market for electrochemical methods is well over \$20 billion. The major areas where electrochemistry contributes to the economy is in the detection of chemical species (glucose meters, acidity), the treatment of corrosion (infrastructure, machinery, computers), the storage of energy (batteries, fuel cells), and the production of materials (aluminum, chlorine).

Carbon electrodes are widely used as working electrodes due to their high electrochemical reactivity as well as their rich surface chemistry. More importantly, techniques to electrochemically deposit self-assembled, pinhole-free organic monolayers have been developed¹ and used in the study of molecular electronics.² The monolayers are deposited through the reduction of a diazonium reagent to form a covalent bond directly with the carbon surface (Figure 1).

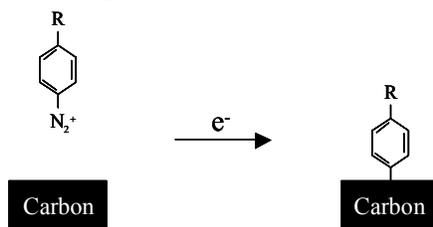


Figure 1. Attachment of organic monolayers through diazonium reduction

The goal of research in our laboratory is to utilize the rich surface chemistry of carbon electrodes to alter their reactivity and, in particular, to aid in the detection of analytes in complex chemical environments. Recently, we have begun to develop methods for preparing electrodes with diameters on the order of 10 to 100 microns. Small sensing platforms have a wide range of applications including the monitoring of chemical species inside the human body, the instantaneous diagnosis of medical conditions by the physician, and the detection of chemical pollutants in the field.

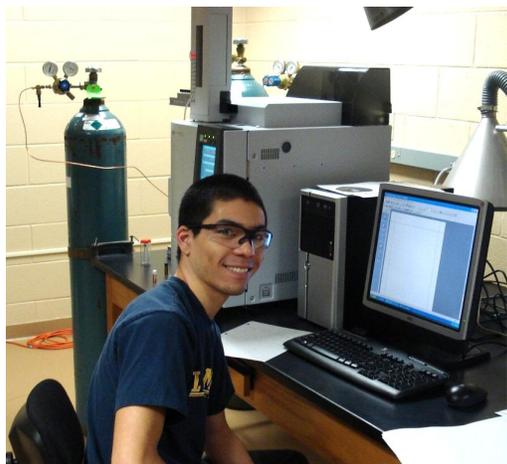
References:

1. Allongue, P.; Delmar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1997**, 119, 201.
2. Ranganathan, S.; Steidel, I.; Anariba, F.; McCreery, R. L. *Nano Lett.* **2001**, 1, 491-494.

Student Researchers: Stephanie Falcioni, Katherine Kressler, Jamie Tribo, Melissa Pownall, John Stutzman, Christi Groller, Christopher Heist

New Instrumentation 2007 – 2008

The department is always looking to modernize our instrument and equipment holdings. Funding for this endeavor takes three forms. Small items (chromatography columns, rotary evaporators, computers...) can be obtained through the normal Lycoming



budgetary process. Very expensive instruments such as the NMR and GC-MS require external funding from organizations such as the National Science Foundation. The acquisition of moderately priced instruments can be facilitated by using funds generated from the David A. Franz Instrument Endowment Fund. In late 2007, the department acquired a Shimadzu 2014 gas chromatograph. Prior to this we did not possess a GC which had either an autosampler or a computer with software for data manipulation. This instrument has been used in Organic Chemistry 1 and 2. It has also played a key role in our research program. Here 2008

graduate James Grant uses the new GC to monitor reaction kinetics as part of his independent studies in the spring of 2008.

We have also obtained an updated computer hardware and software for our NMR in September 2008. Below is a picture of senior chemistry major Kyle Totaro taking a proton spectrum as part of his Chem 449 (Chemistry Research Methods) project with a new ligand for samarium diiodide.

We have also modified the old Labconco glove box so that cyclic voltammetry measurements can be taken in an inert atmosphere. The total cost of this project was about \$100. The first measurements were taken in November 2008 by Drs. McDonald and Ramsey on various samarium II species.



Endowment Funds Benefitting the Department of Chemistry and Its Students

The Department of Chemistry is pleased to offer a wide variety of investment opportunities to donors. If you are interested in “giving back” or “paying forward”, please consider one of these endowment funds. Each is very useful to the department and its students and all are in need of additional funding. Your gift will be very much appreciated.

The John A. Radspinner Endowed Scholarship Fund was started by a group of local area alumni. It was named in honor of Dr. Radspinner who taught general chemistry and physical chemistry at Lycoming from 1957 to 1987, and who made such an impact on the lives of so many Lycoming students. This scholarship benefits talented chemistry majors. The James K. Hummer Endowed Scholarship Fund was started in 2007 by one of Dr. Hummer’s colleagues in the department. It recognizes his contributions to students and the department from 1962 to 1988. This endowment fund provides a scholarship for a chemistry major who is also a participant in one of the college’s musical groups (choir, band, orchestra). The Brian Belz ’96 Endowed Scholarship Fund was started by Lycoming alumnus Brian Belz himself and benefits chemistry majors demonstrating financial need.

The David A. Franz Chemistry Instrumentation Endowed Fund was started by an anonymous donor, and renamed in 2005 for Dr. Franz upon his retirement. This fund has grown over the years and now provides annual revenues that can be used to help acquire small instruments or matching funds for grants procured from outside agencies. The Chemistry Research Endowed Fund was also started by an anonymous donor. The goal of this fund is to assist with the stipends given to students who participate in the longstanding summer research program that the department has had since 1987.

Invitation to Contact Us!

We would love to hear from you. Send us an update or and let us know if you want us to include it in the next issue of the newsletter. Any comments or ideas for the newsletter will be much appreciated. We’d love a current picture of you too. You can send your updates to the following address, mcdonald@lycoming.edu. We hope you enjoyed reading this. We promise to write more in the future.