

# Lycoming College Chemistry Newsletter

Issue No. 4/5

November 2012



2011 Summer research folks



Summer 2012 version

## Greetings from Lyco

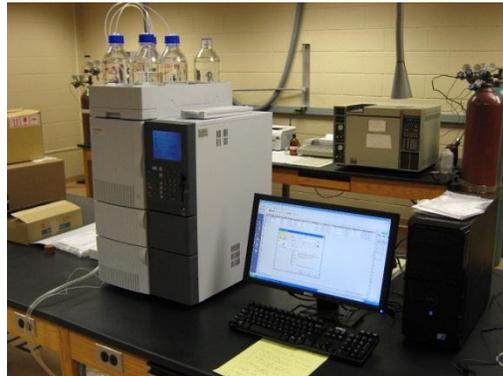
Hi, I'm Chriss McDonald, Professor of Chemistry at Lycoming College. I hope this newsletter finds you well. It's been a while since I've been able to put one of these together. Other writing projects (grant proposals, papers, lab manuals, class supplements....) have taken precedence over the last 24 months, but I've got a window, so I've cranked this out. As I've mentioned before, the goal for this newsletter is to keep people updated on what is going on around here, show off some faces and events, and just basically keep in touch. As I heard recently, when you go to college, you may only be there four years (hopefully) but you start a relationship for life.

Since I last wrote we've acquired two new instruments. Just recently we've gotten an Ocean Optics UV-vis probe instrument. Jeremy and I are using it to characterize complexes of  $\text{SmI}_2$  and a new anionic phosphoramidate ligand that the CEM research group has developed. The funds for this came from a PRF grant and the college is kicking in some. We've used the David Franz Instrument Endowed Fund to purchase a Shimadzu HPLC and a new/better autosampler for the GCMS.

We've also introduced one new course. It's a distribution course that Holly teaches called "Chemistry of Food and Cooking". It went over pretty well.



New Ocean Optics UV-vis (2012) in action –  
 $\text{SmI}_2/4\text{DPMPA}^-$



New Shimadzu HPLC (2011)

Over the past two year we've had several students conduct research within the department. Holly Bendorf had three different students work for her over the past two summers. Katie (KT) Wellmon worked both summers while Caitlin DeAngelo worked there Summer 2011 and Laura Anderson in Summer 2012. Kyle Ruhl (Kruhl) worked with them in May 2011 before heading off to Colorado State and grad school. They were funded by Holly's PRF grant. They've made significant progress on the cyclization of allyl amines onto aldehydes via coordinatively unsaturated rhodium complexes. Holly and coworkers published a paper last year on their progress, very nice.

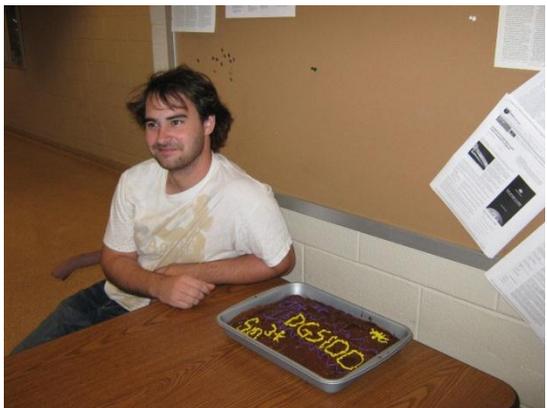
Jeremy Ramsey had Elisabeth (Lis) Feld and then Allyson (Ally, everyone has a shortened version of their name it seems) Marianelli work for him, mainly in the area of modifying glassy carbon electrodes with diazonium cation-derived layers.

Charles Mahler had Rory McAtee work for him during the Summer of 2012. They focused on the  $^{31}\text{P}$  NMR studies of iron phosphine complexes, looking for correlations with previously determined physical and spectroscopic properties of these species. Charles has been a member of the \$4.5 million dollar "Pennsylvania Three (PA 3) Region Math and Science Partnership" since December 2010. This B federal grant from the U.S. Department of Education, involves faculty from Lycoming College, Immaculata University, The University of Pittsburgh at Greensburg, and Bucknell University and aims to improve teaching of science and math at public schools. Participants spend three days each summer at NASA's Goddard Space Flight Center in Greenbelt, Maryland, and attend a week-long Summer Institute at Immaculata University taught by six science faculty (including Mahler) and six math faculty from the participating college and universities. There are also monthly sessions where the science and math faculty meet with local teachers.

Charles was also part of the PA 3 Partnership which received one of eight "NASA Summer of Innovation" grants awarded nationwide. The \$750,000 grant funds four years of summer programs in Science, Technology, Engineering, and Math for students in Pennsylvania, and began in 2011. In conjunction with these two grants Mahler attended a

NASA GLOBE (Global Learning and Observation to Benefit the Environment) program at the NASA IV and V center in West Virginia, and is now a certified GLOBE instructor. GLOBE is a worldwide hands-on, primary and secondary school-based science and education program.

I had Dave Sampsell work with me the last two summers and Laura (Double Duty) Anderson lent a hand as well. We are progressing nicely on our work involving



Young Dave Sampsell ran his 100<sup>th</sup> rxn so he gets a cake!



Old Dave Sampsell, One of the few to run 200, more cake!

the activation of  $\text{SmI}_2$  with anionic phosphoramides. As a matter of fact, a paper regarding this work is being written this semester. Four Lycochem alums (Ahren Green, Joe Keane, Dan Dirocco, and Kyle Ruhl) are actually looking it over for us before we submit. A really nice thing, they continue to make a contribution to Lycoming chemistry after they have graduated. I was also fortunate enough to receive a PRF grant that will fund students over the next three summers. This continues an excellent trend by the department of acquiring outside funding to support our summer research efforts.

Students present their work at the Intercollegiate Student Chemists (ISC) and Undergraduate Research Symposium in the Chemical and Biological Sciences at UMBC most years.



The ugliest rxn I've ever seen  
(I blame Sampsell)



KRuhl at 100+ and lusting for cake



A semi-willing participant in Dr. Bendorf's food chemistry course, Spring 2012



The colored utensils of Advanced Organic Chemistry, Fall 2012

One of the things I really appreciate about teaching at Lycoming is how well we get to know our students. I teach stuff from the 100 to 400 levels. By the time students are Juniors and Seniors we know each other pretty well. In 400 level courses such as Spectroscopy and Advanced Organic, I feel like we are just “hanging out” in a very structured way. The atmosphere is both loosey-goosey (where about anything might be said) but also we are very serious about gaining knowledge about chemistry (count me in on that too). I know the other chem faculty feel the same way.

We've begun to be more intentional about having “events” for our current students. We now schedule four each year. We have advising/informational events for both Freshman (the Freshman Confabulation) and Sophomores (the Sophomore Sitdown) as well as a sporty event each semester. The last couple of years we've done Whiffleball in the Fall and Volleyball in the Spring.



Allison Marianelli is making a diazonium salt



Bendorf on the “mound”, Whifflepooza 2011

As can be seen below we continue to have the Chemistree Party with all of the traditional activities and goodies. I remember going to a Chemistree party my first year at Lyco in December 1987. Who knows how long it had been going on at that point. It is a really nice tradition!



Getting ready for Chemistry Carols



Chemistree Festivities

Graduation is always a special time. Lycoming has planted flora very strategically over the years. As graduation rolls around the Quad blossoms spectacularly. As long as we have sun and keep our allergic responses in check, graduation is a fine event.



Graduation May 2011, Way2Go Kate Williamson, Sam Smith, Frank Lettieri, Rob Beamon, Jen Adams and the seductive Kyle Ruhl!



Graduation May 2012, Congrats to Phil Cook, Lis Feld, Lauren Bottorf (and the other grads)! Rob, Jen, and Jordan can't stay away.

## Graduates and Their Initial Placement

### 2011

|                 |   |
|-----------------|---|
| Jen Adams       | Bayer Health Care                                     |
| Rob Beamon      | Bayer Health Care                                     |
| Chad Lemons     | Ahlstrom Filtration                                   |
| Frank Lettieri  | Calvert Labs  |
| Emily Rogers    | George Washington University, MS program in forensics |
| Kyle Ruhl       | Colorado State University, PhD program in chemistry   |
| Samantha Smith  |   |
| Kate Williamson | Oregon State University, MS program in chemistry      |

2012

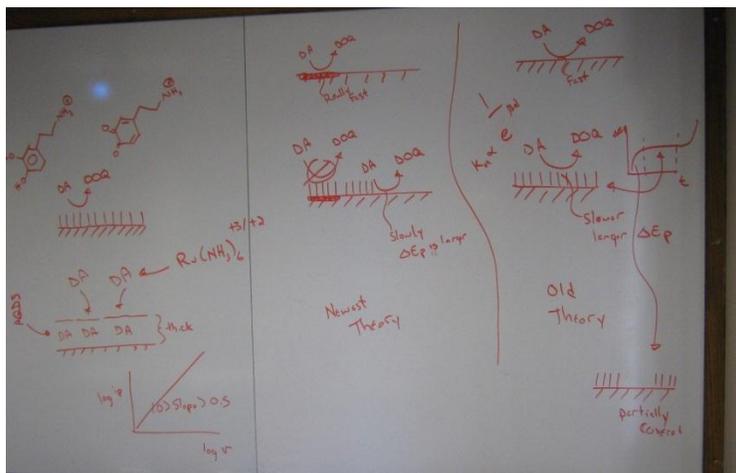
Lauren Bottorf  
Phil Cook  
Lis Feld  
Evan Holland  
Dave Sampsell

Miami University, PhD program in chemistry

Louisiana State University, PhD program in chemistry

University of Scranton, MS program in chemistry

Polyscience



Fun with electrochemistry

## 2011/12 Department of Chemistry Award Winners

|                     |   |
|---------------------|---|
| Tim Kocher          | 2011 ACS Award in First Year Chemistry            |
| Justin Cumens       | 2012 ACS Award in First Year Chemistry            |
| Tim Kocher          | 2012 Organic Chemistry Award                      |
| Caitlin DeAngelo    | 2011 Analytical Chemistry Award                   |
| Allyson Marianellis | 2012 Analytical Chemistry Award                   |
| Lauren Bottorf      | 2012 Brunstetter Award (joint award with Biology) |
| Emily Rogers        | 2011 Trask Award                                  |
| Kyle Ruhl           | 2011 American Chemical Society Award              |
| Dave Sampsell       | 2012 American Chemical Society Award              |



P Chem Students seem to have a handle on the visible portion of the electromagnetic spectrum



Spectroscopy class seems to involve lots of paperwork.....

### **2011 and 2012 Gamma Sigma Epsilon Inductees**

The Department of Chemistry at Lycoming College is home to the Rho Delta Chapter of Gamma Sigma Epsilon National Chemistry Honor Society. New student members are inducted each Fall, and the chemistry faculty and secretary are all honorary members. Here are the new members inducted over the last two years.



**New Members of ΓΣΕ Fall 2011 (pictured)**  
 Tri Do, Amanda Kinnon, Jordan Krebs, Allyson Marianelli  
 Caitlin DeAngelo, Hope Weber, Bethany Garnand



**New Members of ΓΣΕ Fall 2012 (pictured)**  
 Tim Kocher, Taylor Anspach, Laure Anderson, Katherine  
 Wrona, Ashley Gimbel, Gretchen Bartizal

## Papers, Grants, and Presentations by Lycoming Chemistry Faculty

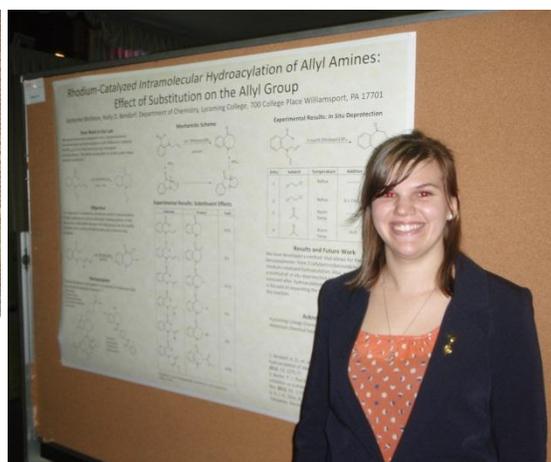
1. Bendorf, H. D.; Ruhl, K.; Shurer, A. J.; Shaffer, J. B.; Duffin, T. O.; LaBarte, T. L.; Maddock, M. L.; Wheeler, O. W. "Amine Directed Intramolecular Hydroacylation of Alkenes and Alkynes." *Tetrahedron Letters*, **2012**, *53*, 1275-1277.
2. Bendorf, Holly "Amine Heterocycle Synthesis via Rhodium(I)-Catalyzed Hydroacylation." American Chemical Society – Middle Atlantic Regional Meeting, University of Maryland, May 12, 2011.
3. Bendorf, Holly, "Rhodium(I)-Catalyzed Hydroacylation Promoted by Chelating Amines." Petroleum Research Fund, \$65,000 (2009-2012)
4. McDonald, Chriss "The Development of Novel Phosphoramides for the Activation of Samarium Diiodide." American Chemical Society – Middle Atlantic Regional Meeting, University of Maryland, May 12, 2011.
5. McDonald, C.; Ramsey, J; Sampsell, D.; Butler, J.; Cecchini, M. "Tripyrrolidinophosphoric Acid Triamide as an Activator for Samarium Diiodide Reductions." *Org. Lett.*, **2010**, *12*, 5178-5181.
6. McDonald, Chriss "The Characterization and Synthetic Utility of Complexes Made From Anionic Phosphoramides and Samarium Diiodide." Petroleum Research Fund, \$65,000 (2012-2014).
7. Ramsey, Jeremy "Using Active Learning Strategies in the Analytical Chemistry Course Series to Prepare Undergraduate Students for Laboratory Research Experiences" Biennial Conference on Chemical Education, State College, PA, July 29<sup>th</sup>, 2012.

## Outside Presentations by Lycoming Chemistry Majors

1. Lis Feld, "Using Cyclic Voltammetry to Probe the Thickness of Organic Films on Glassy Carbon Surfaces." 76<sup>th</sup> Annual Intercollegiate Student Chemists Convention, Bloomsburg University, April 14, 2012.
2. David Sampsell, "Reduction of 1-Chlorodecane and Cyclization of Haloalkenes by  $\text{SmI}_2/\text{DPMPA}^-$  Complex." 76<sup>th</sup> Annual Intercollegiate Student Chemists Convention, Bloomsburg University, April 14, 2012.
3. Lauren Bottorf "Synthesis and  $^{31}\text{P}$  NMR Studies of Organometallic Iron Phosphine Complexes." 76<sup>th</sup> Annual Intercollegiate Student Chemists Convention, Bloomsburg University, April 14, 2012.
4. Wellmon, Katherine "Rhodium-Catalyzed Hydroacylation of Allyl Amines: Effect of Substitution on the Allyl Group." 15<sup>th</sup> Annual Undergraduate Research Symposium in the Chemical and Biological Sciences, University of Maryland, Baltimore County, October 20, 2012.



Lauren Bottorf, Lis Feld, and Dave Sampsell presented at the ISC Conference at Bloomsburg in April 2012



Katie (KT) Wellmon and her poster at the UMBC undergraduate research conference, October 2012

## Student Talks in the Lycoming Chemistry Colloquium Series, Fall 2010 –Spring 2012 (Research Director)

1. Chad Lemons, "Analytical Techniques for the Determination of the Physical and Chemical Properties of Filtration Media" (Ahlstrom Filtration).
2. Lauren Bottorf, "Synthesis of Oxepines and Thiepinines via Hydroacylation of Allyl and Propargyl Sulfides and Ethers" (Bendorf).

- Kate Williams, "The Synthesis of a Di-cationic Monoradical Initiator" (University of Southern Mississippi).
- Jen Adams, "Synthesis and NMR Studies of Organometallic Ruthenium Phosphite Complexes" (Mahler).
- Rob Beamon, "Synthesis of Benzazepines via Intramolecular Hydroacylation of Allyl and Propargyl Amines" (Bendorf).
- Lis Feld, "Monitoring Film Growth from Nitrophenyl Diazonium Reduction using Cyclic Voltammetry" (Ramsey).
- Kyle Ruhl, "Synthesis of Pharmaceutical Target Molecules" (Merck).
- Dave Sampsell, "Further Characterization of the SmI<sub>2</sub>/TPPA Complex" (McDonald).
- Kyle Ruhl, "Synthesis and Hydroacylation of Tertiary Ally Amines" (Bendorf).
- Rob Beamon, "The Use of SmI<sub>2</sub>/TPPA for the Reduction of Alkyl Chlorides" (McDonald).
- Emily Rogers, "Monitoring the Growth of Films Formed by Reducing 3,5-di-*tert*-Butyldiazonium at Glassy Carbon Electrodes" (Ramsey).
- Kate Williamson, "Hydroacylation of Propargyl Sulfides" (Bendorf).
- Samantha Smith, "Synthesis of Frankensteinian Combinations of TPPA and diHMPA Ligands for SmI<sub>2</sub> Reductions" (McDonald).
- Frank Letteiri, "Determining the Stability of Diazonium Salt Solutions through Instrumental Analysis" (Ramsey).
- Caitlin DeAngelo, "Chelation-Assisted Intramolecular Hydroacylation of Allyl Sulfides" (Bendorf).
- Jordan Krebs, "Role of Extraneous Layer in Enhanced UV Resistance" (Caltech).
- Katie Wellmon, "Rhodium-Catalyzed Intramolecular Hydroacylation of Allyl Amines" (Bendorf).
- Dave Sampsell, "Optimization of SmI<sub>2</sub>/DPMPA<sup>-</sup>-Mediated Reduction of Halogenated Substrates" (McDonald).
- Eric Dingler, "Comparison of Computational and Experimental Data in Iron and Ruthenium Organometallic Phosphine Complexes" (Mahler).

20. Laura Anderson, “Demonstrating and Quantifying the Reductive Power of SmI<sub>2</sub>/DPMPA” (McDonald).
21. Kelly Andrews, “Synthesis and Electrochemistry of Diazonium Functionalities for the Formation of Monolayers at Glassy Carbon Electrodes” (Ramsey).
22. Phil Cook, “Synthesis and <sup>31</sup>P NMR Studies of Organometallic Phosphine Complexes of Group 8 Transition Metals” (Mahler).
23. Lis Feld, “Using Fast Scan Cyclic Voltammetry to Examine Organic Film Growth on Glassy Carbon Electrodes” (Ramsey).
24. Lauren Bottorf, “Synthesis and <sup>31</sup>P NMR Studies of Organometallic Iron Phosphine Complexes” (Mahler).
25. Evan Holland, “Improved Synthesis of DPMPA and its Use in the Reduction of Alkyl Chlorides” (McDonald).

### **Congratulations to:**

**Kyle Ruhl** (2011 graduate)- Haberberger Fellowship to support Honors research during the 2010-2011 academic year.

**Caitlin DeAngelo** (Lycoming Sr.)- Haberberger Fellowship to support Honors research during the 2012-2013 academic year.

**Josemar Castillo** (2006 graduate)- Just completed PhD. At Arizona State University.

**Dan Dirocco** (2007 graduate)- Just completed his Ph.D. in chemistry at Colorado State University.

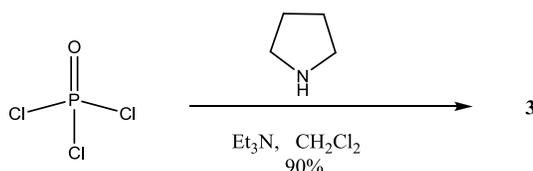
**Lindsay Welch** (2006 graduate) - Just completed her Ph.D. in chemistry at Lehigh University.

### **Update CEM**

I thought maybe it would be good to give you faculty updates, one each year. I'll go first. Life is pretty good! My two sons Mattie, now age 30 (wow...) is gainfully employed by Lutron Corporation and works on their new product design team. His new band, Tithonus, is mixing their second EP. His wife, Hannah, works for DeVry University and is a big-time slam poet. They live in Phoenixville, PA, outside of Philly. My younger son Jim (age 23, JimBob, he doesn't like it when I call him that anymore...) just graduated from PSU where he majored in electrical engineering. He's now at Case

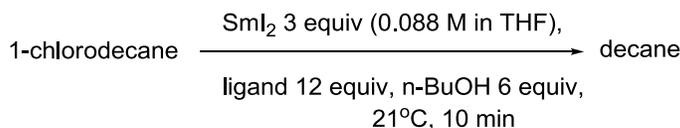


### Scheme 1



The complex formed between SmI<sub>2</sub> and four equivalents of TPPA is deep purple with the same λ<sub>max</sub> as the SmI<sub>2</sub>/HMPA complex. We have several pieces of evidence which indicate that SmI<sub>2</sub>/TriPy is substantially more reactive than SmI<sub>2</sub>/HMPA from a kinetic standpoint. Alkyl chlorides are known to be reluctant substrates for reduction by SmI<sub>2</sub>/HMPA.<sup>2</sup> Our recent reduction of 1-chlorodecane by both complexes indicates that SmI<sub>2</sub>/TPPA reduces 1-chlorodecane four times faster than SmI<sub>2</sub>/HMPA (Scheme 2).<sup>9</sup> The ligand DMPU, the most common nonmutagenic alternative to HMPA is not effective at activating SmI<sub>2</sub> to reduction of alkyl chlorides.

### Scheme 2



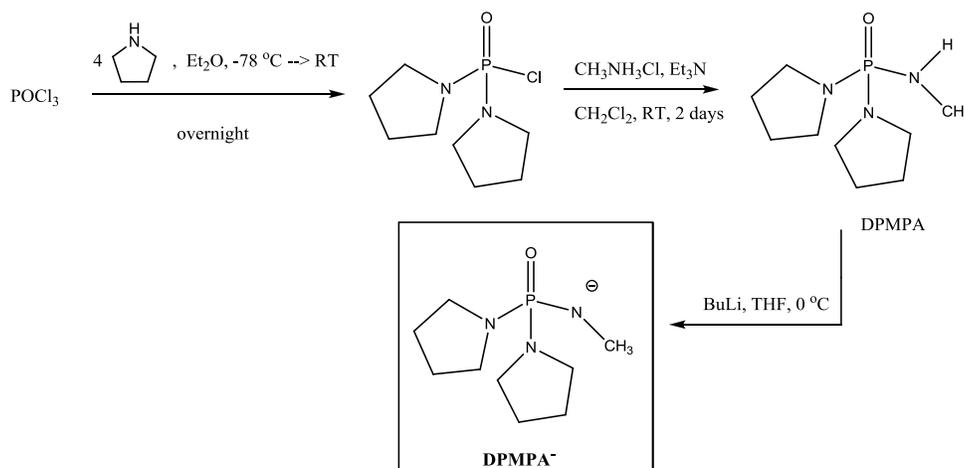
| entry | ligand | yield(%) <sup>a</sup> |
|-------|--------|-----------------------|
| 1     | HMPA   | 4                     |
| 2     | TPPA   | 16                    |
| 3     | DMPU   | 0                     |

<sup>a</sup>GC yield.

Very recently we have examined the use of anionic phosphoramides (phosphoramidates) in the hope that they will deliver even more electron density to the Sm(II) center and thus further enhance the reductive capabilities of the resultant complex. Initial efforts are illustrated in **Scheme 3**. This phosphoramidate was designed with a single *N*-methyl group, to minimize mutagenicity, and two pyrrolidino groups, because of their proven utility in the case of TPPA. Addition of four equivalents of pyrrolidine to POCl<sub>3</sub> cleanly affords dipyrrolidinophosphoryl chloride (after removal of solid pyrrolidinium hydrochloride by filtration). Addition of CH<sub>3</sub>NH<sub>3</sub>Cl and Et<sub>3</sub>N provides crystalline dipyrrolidinomethylamino phosphoric triamide (DPMPA) in multigram quantities and 77 % yield from POCl<sub>3</sub> after distillation. Addition of BuLi to DPMPA yields the desired anionic species, DPMPA<sup>-</sup>.

Addition of one equivalent of SmI<sub>2</sub> in THF to four equivalents of DPMPA<sup>-</sup> yields a deep brown (not blue or purple) THF-soluble complex. Our initial efforts at characterization of SmI<sub>2</sub>/4 DPMPA<sup>-</sup> suggest that it is a complex of extreme reactivity.

### Scheme 3



1-Chlorodecane, a reluctant substrate for reduction by most SmI<sub>2</sub> species, was chosen for these initial tests. Complexes were formed from SmI<sub>2</sub> and four equivalents of each ligand (either a neutral phosphoramidate or DPMPA<sup>-</sup>). Ten minutes after the addition of 1-chlorodecane and tetradecane (internal standard), an aliquot was removed and quenched with I<sub>2</sub>. All complexes composed of SmI<sub>2</sub> and neutral phosphoramidates produced a 0-1% yield of decane at the 10 minute mark (**Table 1**). However, the SmI<sub>2</sub>/4 DPMPA<sup>-</sup> complex afforded a **91%** yield of decane under these conditions! Inanaga has reported that SmI<sub>2</sub> with 5% HMPA requires 8 h at 60 °C to reduce 1-chlorododecane (89% yield). Dahlen and coworkers have used 7 SmI<sub>2</sub> /35 H<sub>2</sub>O/28 Et<sub>3</sub>N to reduce 1-chlorodecane (14 h, 20°C, 95%). *These results indicate that this new complex is hundreds of times more reactive than any previously known non-aquo SmI<sub>2</sub> complex.*

We are now in the process of determining the synthetic scope and limitations of this new complex. We are also attempting to characterize the new complex by visible spectroscopy, cyclic voltammetry, and X-ray analysis.

**Student Researchers: Laura Anderson, Robert Beamon, Julie Butler, Michael Cecchini, Jordan Krebs, Evan Holland, James Grant, David Sampsell, Kyle Totaro**

#### 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.
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6. Shabangi, M.; Sealy, J.; Fuchs, J.; Flowers, R. *Tetrahedron Lett.* **1998**, *39*, 4429.
7. Zijlstra, J.; Brussee, J.; van der Gen, A.; Vogel, E. *Mutation Research* **1989**, *212*, 193.
8. McDonald, C.; Ramsey, J.; Grant, J.; Howerter, K. *Tetrahedron Lett.* **2009**, *50*, 5308.
9. McDonald, C.; Ramsey, J.; Sampsell, D.; Butler, J.; Cecchini, M. *Org. Lett.*, **2010**, *12*, 5178-5181.

## Endowment Funds Benefitting the Department of Chemistry and Its Students

The Department of Chemistry is pleased to offer a wide variety of philanthropic 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 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. You will note the HPLC pictured above as an example of the sort of instrumentation that we can purchase from this fund (I contribute to this myself). 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 summer research program that the department began in 1987.

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 Brian Belz himself and benefits chemistry majors who demonstrate financial need.

### Invitation to Contact Us!

We would love to hear from you. Send us an update 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 to have a current picture of you too.** You can send your updates to: [mcdonald@lycoming.edu](mailto:mcdonald@lycoming.edu). We hope you enjoyed reading this newsletter. We promise to write more in the future.

Ta Ta for now!

