

---

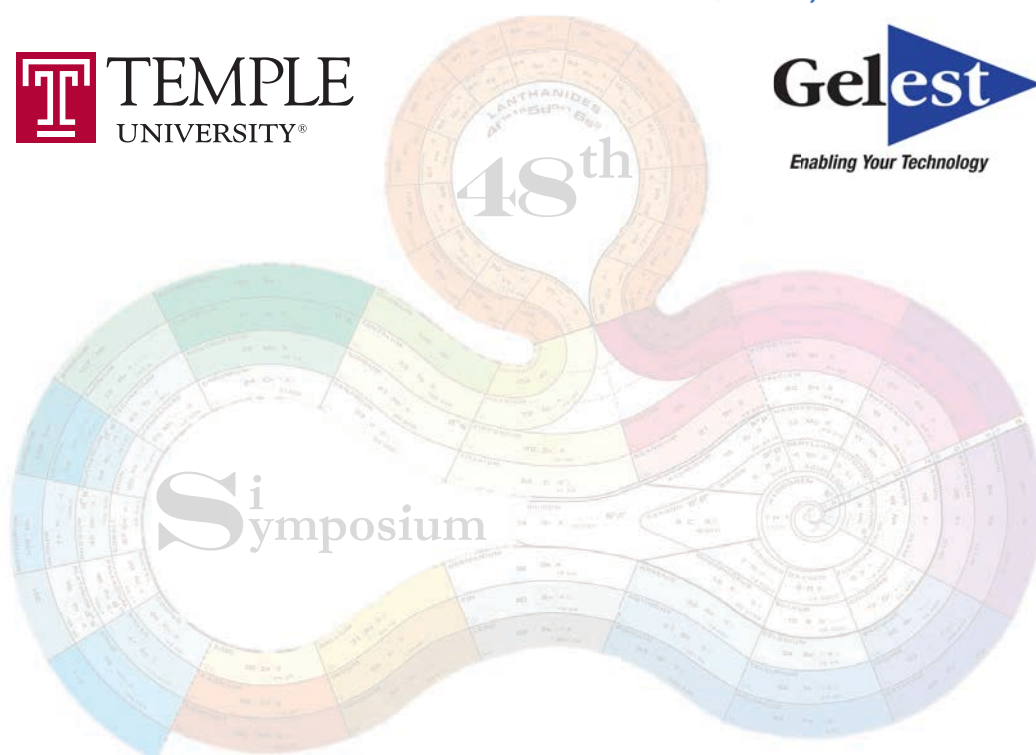
# 48<sup>th</sup> SILICON SYMPOSIUM

---

Philadelphia, Pennsylvania

HOSTED BY:

TEMPLE UNIVERSITY® and GELEST, INC.



June 7, 2017 Tutorials

Temple University® Science Education and  
Research Center  
1925 North 12<sup>th</sup> Street



June 8 and 9, 2017 Symposium

Chemical Heritage Foundation  
315 Chestnut Street

## Technical Editors

Annalese F. Maddox, Santy Sulaiman, Jonathan Goff, Jerry Larson, Scott Sieburth, Barry Arkles

*Copyright © 2017, Gelest, Inc. All copyrights are reserved by authors. All abstracts herein are printed with permission of the authors.*

---

## Table of Contents

<b>Welcome from the Committee Chairs</b>	<b>5</b>
<b>The Chemical Heritage Foundation</b>	<b>6</b>
<b>Temple University Science Education and Research Center</b>	<b>7</b>
<b>Previous Silicon Symposia</b>	<b>8</b>
<b>Conference Information</b>	<b>10</b>
<b>Detailed Symposium Schedule</b>	<b>16</b>
<b>Plenary Lecture Listing</b>	<b>25</b>
<b>Invited Lecture Listing</b>	<b>29</b>
<b>Short Lecture Listing</b>	<b>33</b>
<b>Poster Listing</b>	<b>41</b>
<b>Plenary Lecture Abstracts</b>	<b>49</b>
<b>Invited Lecture Abstracts</b>	<b>53</b>
<b>Short Lecture Abstracts</b>	<b>67</b>
<b>Poster Abstracts</b>	<b>101</b>
<b>Author Listing</b>	<b>139</b>



## Welcome from the Committee Chairs

On behalf of the Organizing Committee, it is our honor to welcome you to Philadelphia, Pennsylvania for the **48<sup>th</sup> Silicon Symposium**. The symposium brings together students and researchers in both academia and industry to discuss the latest developments and new applications of silicon chemistry. The Chemical Heritage Foundation in the “City of Brotherly Love” is an exciting venue to foster and enhance the relationships between academia and industry. The meeting aims to promote improved dialog among members of the global Silicon Community. We hope that attendees will learn about new contributions to the field of silicon chemistry while exploring the venue’s collection documenting the history of science, dating back to the 15<sup>th</sup> Century.

The two-day symposium consists of 2 Plenary Lectures, 12 Invited Lectures, and 32 Short Lectures ranging from organic synthesis and catalysis to material science. Posters submitted are from researchers in academia and industry. This year exhibited an increase in submissions from applied technologies and materials science highlighting the interdisciplinary nature of the field. We look forward to the continued growth of the conference and development of new applications for silicon-based materials.

We wish to thank Temple University® and Gelest, Inc. for their efforts in organizing and supporting this symposium. We would also like to thank Wacker, Evonik Industries AS, and Milliken for their financial assistance. Their support is essential to the success of the conference and we are most grateful to their generosity.

We are confident that the **48<sup>th</sup> Silicon Symposium** will continue the success of this outstanding series with the return to its “home” in Philadelphia for the fourth time since its inception in 1967.

Prof. Scott Sieburth  
Temple University

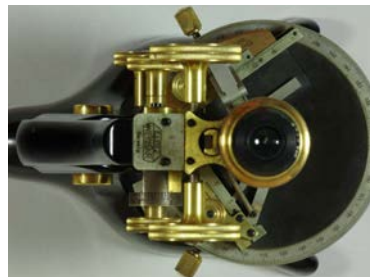
Dr. Jonathan Goff  
Gelest, Inc.



## The Chemical Heritage Foundation

The Chemical Heritage Foundation is dedicated to explaining a simple truth: *science has a past and our future depends on it.*

In 1982, the Center for the History of Chemistry was launched by the University of Pennsylvania and the American Chemical Society. The American Institute of Chemical Engineers became the third sponsor in 1984. By 1987 the center was incorporated as a nonprofit organization called the National Foundation for the History of Chemistry. It was renamed the Chemical Heritage Foundation in 1992 to better reflect its interdisciplinary nature and the widening scope of its programs and activities. CHF's mission is to foster dialogue on science and technology in society. We explore the past in order to understand the present and inform the future.



CHF is headquartered in the heart of Philadelphia's historic Old City neighborhood. It is a library, a center for scholars, as well as a museum and an archive. We focus on matter, materials, and their effects on our modern world in territory ranging from the physical sciences and industries, through the chemical sciences and engineering, to the life sciences and technologies. We collect, preserve, study, and interpret the history of chemistry, chemical engineering, and the life sciences including historical artifacts; engage communities of scientists and engineers; and tell the stories of the people behind breakthroughs and innovations.



Much of the stuff of civilization—from food to medicines to materials—was created by people familiar with matter and how to manipulate it. Often for the sheer joy of knowing, alchemists, chemists, and, later, molecular scientists sought to expand our understanding of matter from the atomic to the galactic. CHF has a rich collection of books, manuscripts, archives, photographs, scientific instruments and historical artifacts, fine art, and oral histories that document the history of science, technology, medicine, and industry.

Have you ever wondered how plastics are made? Where crayons get their colors? A visit to the Museum at CHF is a journey through the weird and wonderful world of matter and materials. Chemistry is all around us. It doesn't just begin in the laboratory, but in the water we drink, the air we breathe, and the earth beneath our feet. For centuries curious men and women have worked to unlock and master the secrets of nature—the hows and whys of chemical change. Our exhibitions profile the amazing successes, astonishing failures, and strange surprises behind the discoveries that changed our world. Visit and discover the chemistry in your life!





## Temple University<sup>®</sup> Science Education and Research Center

The Science Education and Research Center at Temple University<sup>®</sup> is a once in a lifetime opportunity to transform the College of Science and Technology (CST), enabling CST to expand scientific exploration, attract additional research funding and bring new discoveries to market. Funded by the Commonwealth of Pennsylvania capital grant and Temple University<sup>®</sup> bond issue the 247,000 sq. feet building was designed by USA Architects and Architectural Resources Cambridge. The seven-story building is LEED Gold registered and hosts 52 research labs and 16 teaching labs.

CST departments lacked appropriate space for teaching and research, making it difficult for people to collaborate. SERC's third and fourth floors house departmental research labs, break-out rooms and offices, storage and support areas, as well as seminar and conference rooms. Multidisciplinary research is key to producing scientific breakthroughs. One of the college's research cores for collaborative investigation, the Institute for Computational Molecular Science, will be on SERC's seventh floor. SERC's entire fifth floor is designed to support interdisciplinary efforts in the fast-growing materials science field.

SERC contains leading-edge labs and classrooms to attract talented scholars and to provide students with abundant opportunities for exploration and investigation. To fully support moving scientific breakthroughs from the lab to the real world, SERC will contain the latest communications, safety, HVAC and other technologies. These include vibration-free scanning tunneling microscope facility, Class 100 and Class 1000 clean rooms, where the concentration of airborne particles is controlled to specified limits, variable air volume capabilities to control air pressure in each lab, groundwater monitoring wells for student instruction and region-wide projects, and is home to 7 research centers and institutes, sparking collaborative discovery and innovation. The advanced water recovery system to recapture and reuse grey water, heat recovery wheel or energy recovery heat exchanger positioned to recover and reuse the heat energy within SERC's air handling systems, daylight harvesting via light shelves, hallways that span the structure, and interior glass walls to reduce electrical lighting costs, automated interior shades and exterior sunshades to reduce heat and reduce air conditioning costs attribute to SERC's LEED Gold registration.

### SERC Houses

Departments of Earth & Environmental Science

Department of Computer & Information  
Sciences

Center for Data Analytics & Biomedical  
Informatics

Center for Networked Computing

Department of Physics

Center for Biodiversity

Institute for Genomics and Evolutionary  
Medicine

Center for Biophysics and Computational

Biology Center for Materials Theory, Institute for Computational Molecular Science



## Previous Silicon Symposia

<i>Date</i>		<i>Site</i>	<i>Host</i>	<i>Kipping Awardee</i>
April	1967	University of Pennsylvania	A. MacDiarmid	M. Kumada
April	1968	University of Wisconsin	R. West	U. Wannagat
April	1969	Marshall, Minnesota	E. Carberry	R. A. Benkeser
May	1970	SUNY Albany	J. Zuckerman	R. West
March	1971	Carnegie Mellon University	C. Van Dyke	A. G. MacDiarmid
April	1972	University of Maryland	J. Bellama	D. Seyferth
April	1973	North Texas State University	P. Jones	A. G. Brook
March	1974	University of Missouri, St. Louis	J. Corey	H. Schmidbaur
April	1975	Case Western Reserve University	M. Kenney	H. Bock
April	1976	University of Windsor	J. Drake	M. F. Lappert
March	1977	Kansas City, Missouri	J. Connolly	
March	1978	Iowa State University	T. Barton	H. Sakurai
March	1979	University of Michigan	M. Curtis	
March	1980	Texas Christian University	R. Neilson	E. A. V. Ebsworth
March	1981	Duke University	R. Wells	
June	1982	Dow Corning, Midland, MI	C. Frye	T. J. Barton
June	1983	North Dakota State University	P. Boudjouk	
April	1984	General Electric, Schenectady, NY	R. Shade	R. J. P. Corriu
April	1985	Louisiana State University	F. Cartledge	
April	1986	Union Carbide, Tarrytown, NY	B. Kanner	P. P. Gaspar
June	1987	St. Louis, MO with VIII International	P. Gaspar, J. Corey, E. Corey	
June	1988	University of Montreal	J. Harrod	R. Calas
April	1989	Petrarch Systems, Philadelphia, PA	B. Arkles	
April	1990	Dow Corning, Midland, MI	T. Lane	J. L. Speier, Jr.
April	1991	University of Texas, El Paso	K. Pannell	
April	1992	University of Southern California	W. Weber	N. Wiberg



Date		Site	Host	Kipping Awardee
March	1993	University of Indiana, Purdue University, Indianapolis	M. Zeldin	
March	1994	General Electric, Schenectady, NY	J. Rich, J. Crivello	R. Walsh
March	1995	PCR, Inc., Gainesville, FL	PCR, Inc., U. Florida	
March	1996	Northwestern University	J. Lambert	W. Ando
May	1997	University of Western Ontario	K. Baines, M. Brook	
May	1998	Tulane University	M. Fink, K. Birdwhistell	J. B. Lambert
March	1999	Sigma-Aldrich, Milwaukee, WI	C. Recatto, M. Steinmetz	
April	2000	Dow Corning, Midland, MI	W. Schulz	P. Jutzi
May	2001	Crompton Corp., Whiteplains, NY	K. Lewis	
August	2002	Guanajuato, MX with IX International	J. Cervantes	K. Tamao
May	2003	University of Akron	C. Tessier, W. Youngs	
May	2004	University of Pennsylvania and Gelest, Inc.	D. Berry, B. Arkles, J. Larson	J. E. Mark
May	2005	University of Colorado	J. Michl	
May	2006	Dow Corning, Frankenmuth, MI	K. Brandstadt	A. Sekiguchi
May	2007	University of Victoria	L. Rosenberg, S. McIndoe	
April	2008	University of California, Berkeley, Wacker	T. D. Tilley, M. E. Boyd, R. Weidner	T. D. Tilley
June	2009	William Paterson University	B. P. S. Chauhan	
May	2010	University of Missouri, St. Louis	J. Braddock- Wilking	Y. Apeloig
June	2012	Brock University	P. M. Zelisko	M. Kira
May	2013	Texas Tech University	C. Krempner	
June	2015	University of California, Davis	A. Franz, S. Kauzlarich, P. Power	
June	2016	Portland State University	A. Goforth	M. A. Brook
June	2017	Temple University and Gelest, Inc.	S. Sieburth, B. Arkles, J. Goff	

## Organizing Committee

Prof. Scott Sieburth  
Dr. Barry Arkles  
Dr. Jerry Larson

Dr. Jonathan Goff  
Ms. Annalese Maddox  
Ms. Gabrielle Lockwood

## Special Thanks

The organizing committee would like to extend a special thank you to Barbara Fles of Temple University, Elizabeth Ries of the Hilton Philadelphia at Penn's Landing, and Laurey Andreas of CHF for their tremendous contributions to the success of this symposium.

## Sponsors

The Organizing Committee would like to thank the following companies for their generous financial support:



## Registration Tables

Registration for the tutorials will be located at the lobby of Temple University's Science Education and Research Center, 1925 N 12th St, Philadelphia, PA, prior to the tutorials on Wednesday, June 7. Additional information will be provided to the attendees.

Registration for the symposium will be located at the Chemical Heritage Foundation (CHF) Lobby, 315 Chestnut St, Philadelphia, PA, during the following times.

Wednesday, June 7, 16:30-17:30  
Thursday, June 8, 7:00 – 9:00  
Friday, June 9, 7:00 – 9:00

## Scientific Agenda

Temple University will host tutorials prior to the start of the symposium.

The Chemical Heritage Foundation will host all of the scientific lectures and poster sessions.

### Lectures

The scientific program includes 2 Plenary Lectures, one each day in Ulliyot Meeting Hall, as well as 12 Invited Lectures and 32 Short Lectures spread over Thursday, June 8 and Friday, June 9. The Invited and Short Lectures will take place in either the Franklin Rooms or Ulliyot Meeting Hall. Please refer to the session schedules for specific details.

### **Poster Session**

The poster session will occur in Ulliot Meeting Hall on the main floor of CHF on Thursday, June 8 at 17:30-19:30.

## **Contributor Guidelines**

### **Speakers**

Each room is equipped with a PC and a projector. The provided PC should be used for presentations. Please bring provide the presentation in Powerpoint on a USB flash drive. Lectures are scheduled as follows and include time for questions: Plenary Lecture – 45 minutes, Invited Lecture – 30 min, and Short Lecture – 20 min. Please respect the allotted timetable.

### **Posters**

All posters must be set up by 12:30 pm on Thursday, June 8 in Ulliot Meeting Hall. The preferred poster size is 40 in. x 32 in. Identification labels and necessary accoutrements to fix the posters will be provided. Posters must be removed at the conclusion of the poster session.

## **Social Events at the Chemical Heritage Foundation**

The **Welcome Reception** will transpire in the Jacobs Reading Room, June 7 at 17:30. **Coffee Breaks** will be hosted outside of Franklin 1 and 2 on the second floor.

### **Events Requiring Registration:**

The **Cocktail Reception** will transpire on June 9 in the Jacobs Reading Room beginning at 17:30.

**Closing Banquet** will follow the reception on June 9 in Ulliot Meeting Hall on the first floor.

## **Wireless Internet Information at Chemical Heritage Foundation**

Login: chf-conference-center

Password: 0102030405

## Tutorials at Temple University SERC

### Session 1 Registration: 7:00-7:55

#### Session 1: 8:00-10:00 – General Introduction to Silicon Chemistry and Organo-Silanes in Organic Synthesis

Alan Bassindale, Open University UK

Jerry Larson, Gelest, Inc.

**Description:** An overview of the general properties, reactivities, syntheses, and bonding characteristics of inorganic and organic chemistry of silicon will be presented. The applications of organosilicon chemistry to synthetic organic transformations will be presented. Silicon-based reductions and silicon-based cross-coupling chemistry will be emphasized.

Break: 10:00-10:15

### Session 2 Registration: 9:45-10:10

#### Session 2: 10:15-12:15 – Introduction to Silicon and Polymer Science

Judy Riffle, Virginia Tech

François Ganachaud, CNRS France

**Description:** This tutorial will focus on the fundamentals of polymer science with an emphasis on siloxane-based polymers. Topics will include: Introduction to polymer science, kinetic and thermodynamic-driven polymerization of siloxanes, functionalization of siloxane-based polymers, silicone elastomer formulation and properties.

Lunch: 12:15-14:00

### Session 3 and 4 Registration: 13:30-13:55

#### Session 3: 14:00-17:00 – Silicon Nanotechnology

Michael Sailor, UCSD

**Description:** The synthesis, properties, and applications of porous silicon-based nanomaterials will be described. Topics will include: Introduction to porous silicon—background and overview; Etching and electrochemistry of silicon; Photoluminescent Si quantum dots; Nanoparticles; Nanowires; and Applications. The tutorial will involve a hands-on experiment where participants will prepare their own photoluminescent silicon nanostructure by electrochemical etch of a silicon wafer.

#### Session 4: 14:00-16:00 – Silicones Used in Colored Cosmetic Products

Anjali Patil, Chanel

Jane Hollenberg, JCH Consulting

**Description:** Cosmetic products are a delicate balance between art and science. Silicones are used in the majority of cosmetic and personal care products due to their unique sensorial properties, such as emolliency, spreadability, non-occlusive nature, wash-off resistance and long wear. First introduced into color cosmetics in the early 1980's, silicone and later silane surface treatments have been used to improve pigment and filler performance in personal care products. Most simply, a silicone coating improves the feel of a product on the skin, a fundamental concern of any cosmetic chemist. By changing the functional groups on the treatment molecules, pigment properties such as wetting, vehicle absorption, and adhesion, can be controlled to suit a variety of vehicles and product forms. The tutorial will cover the types of personal care formulations which may contain surface treated materials, examples of the silicones and silanes used, and the effect the treatment compounds have on the formulations.

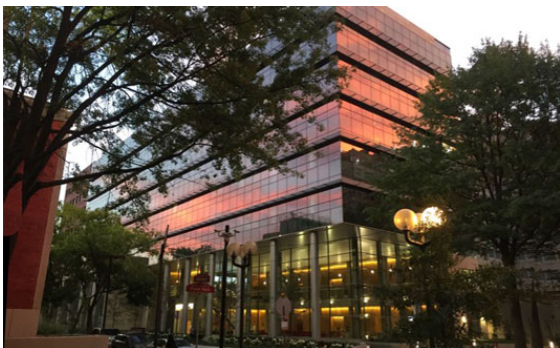
## Floor Plan of the Chemical Heritage Foundation



## Restaurants Local to the Chemical Heritage Foundation

Name	Variety	Address	Distance	Cost
Amada	Tapas	217 Chestnut St	476 ft	\$\$\$
Eulogy Tavern	Belgian	136 Chestnut St	0.1 mi	\$\$
Farmicia	New American	15 S. 3rd St	0.1 mi	\$\$
Han Dynasty	Szechuan	123 Chestnut St	0.1 mi	\$\$
Khyber Pass	Gastropub/Cajun	56 SW. 2nd St	0.1 mi	\$\$
2nd Story Brewing	New American/Brewery	117 Chestnut St	0.2 mi	\$\$
High St on Market	New American	308 Market St	0.2 mi	\$\$
Zento	Japanese/Sushi Bar	132 Chestnut St	0.2 mi	\$\$
The Gaslight	New American	120 Market St	0.3 mi	\$\$
Wedge + Fig	New American/Cheese Bistro	160 N. 3rd St	0.4 mi	\$\$
Talula's Daily	New American/Café	208 W. Washington Sq.	0.5 mi	\$\$
Pizzeria Stella	Pizza/Italian	215 Lombard St	0.6 mi	\$\$
Southwark	New American	701 S. 4th St	0.6 mi	\$\$\$
Bistrot La Minette	French	623 S. 6th St	0.8 mi	\$\$\$
Reading Terminal Market	Market/Grocery	12th and Arch St	0.9 mi	\$\$

## Navigating Philadelphia, PA



**Temple University**  
**College of Science and Technology**  
Suite 400, Carnell Hall  
1803 N. Broad Street  
Philadelphia, PA 19122  
215.204.2888



**Hilton Philadelphia at Penn's Landing**  
201 S Christopher Columbus Blvd  
Philadelphia, PA 19106  
215.521.6500



**Chemical Heritage Foundation**  
315 Chestnut Street  
Philadelphia, PA 19106  
215.925.2222  
info@chemheritage.org

### **Transportation Options:**

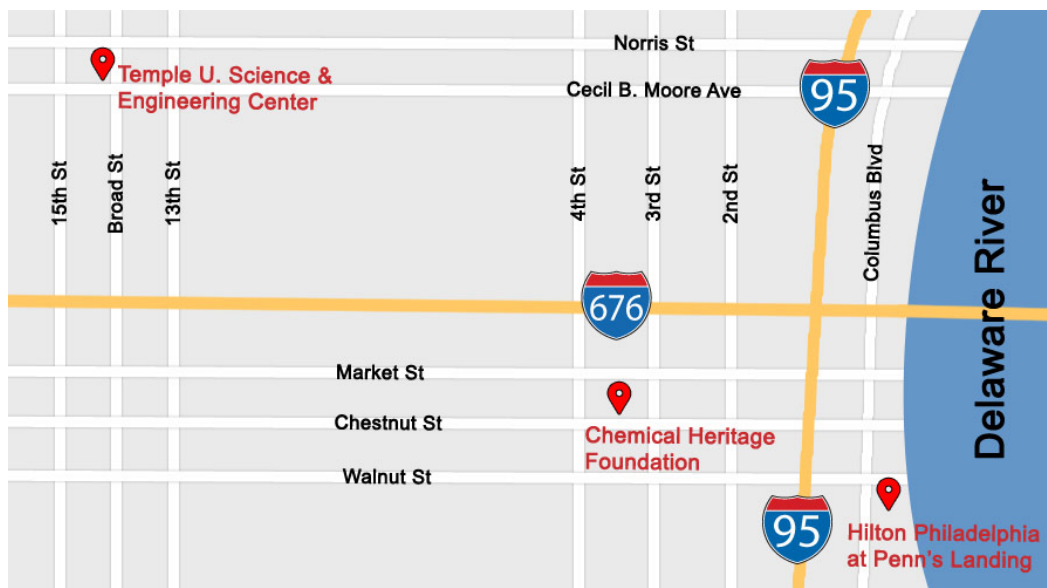
Public transportation via the Southeastern PA Transit Authority (SEPTA), cabs, Uber, and Lyft are available. A shuttle to and from the Hilton will also be available. The shuttle will operate on the following schedule:

#### Thursday:

Depart Hilton for CHF at 6:45 am and 8 am  
Depart CHF for the Hilton at 4:15 pm and 7:05 pm

#### Friday:

Depart Hilton for CHF at 6:45 am and 8 am  
Depart CHF for the Hilton at 5:05 pm and 9:45 pm



### Walking from the Hilton Philadelphia at Penn's Landing to the CHF –

Head south on S Christopher Columbus Blvd toward Dock St	240 ft
Turn right on Dock St	0.1 mi
Turn right to stay on Dock St	0.2 mi
Turn left on Walnut St	20 ft
Turn Right onto Dock St	377 ft
Turn Right onto S 3 <sup>rd</sup> St	335 ft
Turn Left onto Chestnut St, destination will be on the right	138 ft

### Driving from Temple SERC to CHF –

Drive south on Broad St towards City Hall for ~1.5 miles  
 Turn left onto Arch St.  
 Drive for ~1 miles and turn right onto 4<sup>th</sup> St.  
 Drive for ~0.4 miles and turn left onto Chestnut St.  
 Drive 300 ft to the Chemical Heritage Foundation  
 Parking information is available at: <https://www.chemheritage.org/visit/directions>

### SEPTA from Temple SERC to CHF -

Walk from SERC to Cecil B. Moore Subway station located at the corner of Broad St and Cecil B. Moore Avenue.  
 Take the southbound Broad Street Line (BSL) subway 5 stops to City Hall station  
 At City Hall station, follow signs for a free transfer to eastbound Market Frankford Line (MFL) subway  
 Take the eastbound Market Frankford Line (MFL) subway 5 stops to 2<sup>nd</sup> Street Station  
 Exit 2<sup>nd</sup> Street Station at the corner of Market St and 2<sup>nd</sup> St.  
 Walk to the Chemical Heritage Foundation

## Detailed Scientific Schedule

## Thursday, June 8, 2017 – Morning Session A

7:00	Registration - Lobby
7:00-8:15	Continental Breakfast
8:15-8:30	Opening Remarks
8:30-9:15	<p style="text-align: center;"><b>Plenary Talk</b> <b>PL-1</b> <b>Keith A. Woerpel</b> <i>New York University, New York, NY, USA</i> <b>Silylene Transfer Reactions for the Synthesis of Strained Alkenes: New Methods for Stereoselective Synthesis</b></p>
9:15-9:45	Coffee Break
<b>Franklin 1 Room</b>	<p style="text-align: center;"><b>Session A</b> <b>Low Valent/Multiple-Bonded Silicon</b> Chairperson: Scott Sieburth</p>
9:45-10:15	<p style="text-align: center;"><b>IL-1</b> <b>Matthias Driess</b> <i>Technical University Berlin, Germany</i> <b>N-Heterocyclic Silylenes: Powerful Tools in Small Molecule Activation and Homogeneous Catalysis</b></p>
10:15-10:35	<p style="text-align: center;"><b>SL-1</b> <b>Andrey Yu. Rogachev, Alexander V. Zabula</b> <i>Illinois Institute of Technology, Chicago, IL, USA</i> <b>Mechanism of Oligomerization of N-Heterocyclic Silylenes into Zwitter-ionic Silenes</b></p>
10:35-10:55	<p style="text-align: center;"><b>SL-2</b> Nada Y. Tashkandi, Sarah McOnie, Jeremy L. Bourque, <b>Kim M. Baines</b> <i>University of Western Ontario, London, ON, Canada</i> <b>The Addition of Isocyanides to Disilenes: The Never Ending Story</b></p>
10:55-11:15	Coffee Break
11:15-11:35	<p style="text-align: center;"><b>SL-3</b> <b>Kerim Samedov, Paul W. Percival, Robert West</b> <i>University of British Columbia, Vancouver, BC, Canada</i> <b>Oscillations in the mSR Spectra of Muoniated Organosilyl Free Radicals and Their Origin</b></p>
11:35-11:55	<p style="text-align: center;"><b>SL-4</b> <b>Peter P. Gaspar, Alexander Seim</b> <i>Washington University in Saint Louis, St. Louis, MO, USA</i> <b>A Computational Study of (2+4) Retro-cycloadditions of Conjugated Planar Disilenes</b></p>
11:55-13:30	Lunch



---

**Thursday, June 8, 2017 – Morning Session B**


---

07:00	Registration - Lobby
7:00-8:15	Continental Breakfast
8:15-8:30	Opening Remarks
8:30-9:15	<p style="text-align: center;"><b>Plenary Talk</b> <b>PL-1</b> <b>Keith A. Woerpel</b> <i>New York University, New York, NY, USA</i> <b>Silylene Transfer Reactions for the Synthesis of Strained Alkenes: New Methods for Stereoselective Synthesis</b></p>
9:15-9:45	Coffee Break
<b>Franklin 2 Room</b>	<p style="text-align: center;"><b>Session B</b> <b>Band Gap and Nanotechnology</b> Chairperson: Alain Kaloyeros</p>
9:45-10:15	<p style="text-align: center;"><b>IL-4</b> <b>Michael J. Sailor</b>, Dokyoung Kim, Taeho Kim, B. J. Kim, Joanna Wang, Jinyoung Kang, Youlin Pan, Barry Arkles <i>University of California - San Diego, La Jolla, CA, USA</i> <b>Surface Modification of Silicon Nanostructures Using Silane Chemistry</b></p>
10:15-10:35	<p style="text-align: center;"><b>SL-8</b> <b>Bhanu P. S. Chauhan</b> <i>William Paterson University, Wayne, NJ, USA</i> <b>Reversible Phase Transition of Silicon-Metal Nanoconjugates</b></p>
10:35-10:55	<p style="text-align: center;"><b>SL-9</b> <b>Ling Ju</b>, Nicholas C. Strandwitz <i>Lehigh University, Bethlehem, PA, USA</i> <b>Structures and Growth Behavior of MLD Films Using Cyclic Azasilanes, Maleic Anhydride, Trimethylaluminum and Water as Precursors</b></p>
10:55-11:15	Coffee Break
11:15-11:35	<p style="text-align: center;"><b>SL-10</b> <b>Prameswara Rao Chinnam</b>, Megan Van Vliet, Michael Zdilla, Stephanie L. Wunder <i>Temple University, Philadelphia, PA, USA</i> <b>Functionalization of Silica Interfacial Layer for Hybrid Lithium Ion Conducting Glass Ceramics and Polymers</b></p>
11:35-11:55	<p style="text-align: center;"><b>SL-11</b> <b>Youlin Pan</b>, Annalese F. Maddox, Taewoo Min, Jonathan Goff, Barry Arkles <i>Gelest, Inc., Morrisville, PA, USA</i> <b>Hydroxylated Surface Induced Coupling Reactions of Cyclic Azasilanes</b></p>
11:55-13:30	Lunch

---

## Thursday, June 8, 2017 – Afternoon Session A

<b>Franklin 1 Room</b>	<b>Session A Silicon Oxygen Chemistry Chairperson: Alan Bassindale</b>
13:30-14:00	<p align="center"><b>IL-2</b></p> <p><b>Joseph M. Mabry</b>, Andrew J. Guenther, Jeffrey R. Alston, Anish Tuteja, Scott T. Iacono, Raymond Campos, Sean M. Ramirez, Timothy S. Haddad <i>Edwards AFB, CA, USA</i></p> <p align="center"><b>Silicon-Hybrid Materials: Fundamental Research to Air Force Applications</b></p>
14:00-14:30	<p align="center"><b>IL-3</b></p> <p align="center"><b>Nicola Huesing</b> <i>University of Salzburg, Austria</i></p> <p align="center"><b>Functional and Flexible Materials by Sol-Gel Processes</b></p>
14:30-15:00	<p align="center"><b>SL-5</b></p> <p><b>Richard M. Laine</b>, M. Bharami, D. Hashemi, J. Kieffer, M. Moghadam, M. F. Roll, R. Tamaki, J. Furgal, T. Goodson III, J. Kampf <i>University of Michigan, Ann Arbor, MI, USA</i></p> <p align="center"><b>Electrophilic Substitution on Phenylsilsesquioxanes</b></p>
15:00-15:30	Coffee Break
15:30-15:50	<p align="center"><b>SL-6</b></p> <p><b>Masafumi Unno</b>, Kazunori Asami, Yuka Nagai, Yasunobu Egawa, Nobuhiro Takeda <i>Gunma University, Kiryu, Japan</i></p> <p align="center"><b>Synthesis and Reactios of Janus Prisms</b></p>
15:50-16:10	<p align="center"><b>SL-7</b></p> <p><b>Kayla Diemoz</b>, Jake Jagannathan, Annaliese Franz <i>University of California Davis, Davis, CA, USA</i></p> <p align="center"><b>Investigation of Hydrogen-Bonding Ability of 1,3-Disiloxanediols and Polyhedral Oligomeric Silsesquioxanes with Applications for Catalysis</b></p>
CHF Museum Open to Attendees until 17:00	
17:00-19:00 <b>Ulliyot Meeting Hall</b>	Poster Session
Dinner (on your own)	

---

**Thursday, June 8, 2017 – Afternoon Session B**


---

**Franklin 2  
Room**
**Session B  
Band Gap and Nanotechnology**  
 Chairperson: Alain Kaloyeros

13:30-14:00	<b>IL-5</b> Yixuan Yu, Adrien Guillaussier, <b>Brian A. Korgel</b> <i>The University of Texas at Austin, Austin, TX, USA</i> <b>Silicon Nanocrystal Assemblies</b>
14:00-14:30	<b>IL-6</b> Natasha Tabassum, Vasileios Nikas, Brian Ford, Edward Crawford, <b>Spyros Gallis</b> <i>SUNY Polytechnic Institute, Albany, NY, USA</i> <b>Materials Behavior of Self-Aligned Silicon Carbide Nanowire Arrays Doped with Erbium Towards Quantum Applications</b>
14:30-15:00	<b>SL-12</b> Konstantin Pokhodnya, Kenneth J. Anderson, Matthew Frohlich, Ryan Schwiderski, <b>Philip Boudjouk</b> <i>North Dakota State University, Fargo, ND, USA</i> <b>Cyclohexasilane (Si<sub>6</sub>H<sub>12</sub>, CHS) A Source of Quantum Dots (SiQDs), Nanowires (SiNWs), Nanorods (SiNRs), Conducting Inks, Highly Functionalized Rings and 1-D Polymers</b>
15:00-15:30	Coffee Break
15:30-15:50	<b>SL-13</b> <b>Andrea Goforth</b> , Christine M. Radlinger, Rylie J. Ellison <i>Portland State University, Portland, OR, USA</i> <b>Evolution of the Photoluminescence Properties of Colloidal Silicon Nanoparticles over Time and with Environmental Changes</b>
15:50-16:10	<b>SL-14</b> <b>Anis Rahman</b> , Aunik Rahman <i>Applied Research and Photonics, Harrisburg, PA USA</i> <b>Sub-Nano Scale Characterization of 1D and 2D Materials by Terahertz Technology</b>
CHF Museum Open to Attendees until 17:00	
17:00-19:00	Poster Session
<b>Ulyot Meeting Hall</b>	Dinner (on your own)

---

## Friday, June 9, 2017 – Morning Session A

07:00	Registration - Lobby
7:00-8:15	Continental Breakfast
8:15-8:30	Opening Remarks
8:30-9:15	<b>Plenary Talk</b> <b>PL-2</b>
<b>Ulyot Meeting Hall</b>	<b>Thomas J. McCarthy</b> , Pei Bian, Daniel Flagg <i>University of Massachusetts, Amherst, MA, USA</i> <b>Methylsilicones Pushed in Several Directions</b>
9:15-9:45	Coffee Break
<b>Ulyot Meeting Hall</b>	<b>Session A</b> <b>Siloxane Polymers and Elastomers</b> Chairperson: Jonathan Goff
9:45-10:15	<b>IL-7</b> Camille Spigolis, Constance Robeyns, <b>François Ganachaud</b> <i>CNRS/INSA-Lyon, Lyon, France</i> <b>New Materials Properties Through a Silicone Blend Strategy</b>
10:15-10:35	<b>SL-15</b> <b>Jennifer Morgan</b> , Tong Chen, Michael A. Brook <i>McMaster University, Hamilton, ON, Canada</i> <b>Novel Synthesis of Spirocyclic Silicones and Subsequent Branching</b>
10:35-10:55	<b>SL-16</b> <b>M. Meléndez-Zamudio</b> , A. Villegasa, J.A. Gonzáles-Calderón, R. Meléndrez, M. Meléndez-Lira, J. Cervantes <i>Universidad de Guanajato, Guanajato, México</i> <b>Study of Polydimethylsiloxane (PDMS) Elastomer Generated by <math>\gamma</math> Irradiation: Correlation Between Properties (Thermal and Mechanical) and Structure (Crosslink Density Value)</b>
10:55-11:15	Coffee Break
11:15-11:35	<b>SL-17</b> <b>Constance Robeyns</b> , Etienne Delebecq, Frédéric Lortie, François Ganachaud <i>INSA-Lyon, Lyon, France</i> <b>Microstructure Versus Mechanical Properties of Original Silicone/Thermoplastic Elastomer Blends</b>
11:35-11:55	<b>SL-18</b> <b>Scott E. Laengert</b> , Alyssa F. Schneider, Eric Lovinger, Yang Chen, Michael A. Brook <i>McMaster University, Hamilton, ON, Canada</i> <b>Sequential Functionalization of a Natural Cross-Linker Leads to Designer Silicone Networks</b>
11:55-12:15	<b>SL-19</b> <b>Chandres Surti</b> , John Bilney, Christos Angeletakis <i>Cornelius Specialties, Haverhill, Suffolk, UK</i> <b>Hydrolytic Stability of Trisiloxane Surfactants</b>
12:15-14:00	Lunch

## Friday, June 9, 2017 – Morning Session B

07:00	Registration - Lobby
7:00-8:15	Continental Breakfast
8:15-8:30	Opening Remarks
8:30-9:15	<b>Plenary Talk</b> <b>PL-2</b>
<b>Ulyott Meeting Hall</b>	<b>Thomas J. McCarthy</b> , Pei Bian, Daniel Flagg <i>University of Massachusetts, Amherst, MA, USA</i> <b>Methylsilicones Pushed in Several Directions</b>
9:15-9:45	Coffee Break
<b>Franklin Rooms</b>	<b>Session B</b> <b>Silicon Mediated Organic Synthesis</b> Chairperson: Jerry Larson
9:45-10:15	<b>IL-10</b> <b>Gregory W. O'Neil</b> , Elizabeth Cummins, Emily Schneider <i>Western Washington University, Bellingham, WA, USA</i> <b>New Methods for Tethered Carbonyl Silylations</b>
10:15-10:35	<b>SL-24</b> Hoan Q. Duong, <b>Scott McN. Sieburth</b> <i>Temple University, Philadelphia, PA, USA</i> <b>Silanediol Inhibitors of the Coagulation Cascade</b>
10:35-10:55	<b>SL-25</b> <b>Sami E. Varjosaari</b> , Vladislav Skrypai, Thomas M. Gilbert, Marc J. Adler <i>Northern Illinois University, DeKalb, IL, USA</i> <b>Controlling the Junction Switch: Asymmetric Ketone Reductions Using 1-Hydrosilatrane</b>
10:55-11:15	Coffee Break
11:15-11:45	<b>IL-11</b> <b>Donald Watson</b> <i>University of Delaware, Newark, DE, USA</i> <b>Advances in the Preparation of Organosilanes Using Palladium Catalysis</b>
11:45-12:05	<b>SL-26</b> <b>Brenden P. Derstine</b> , Buddha B. Khatri, Svitlana Kulyk, Scott McN. Sieburth <i>Temple University, Philadelphia, PA, USA</i> <b>Silanols as a Selective Proton Source for the Photochemistry of Silyl-3-enol-1-ynes</b>
12:05-12:25	<b>SL-27</b> <b>Lukas Zibula</b> , Jonathan O. Bauer, Carsten Strohmann <i>TU Dortmund, Germany</i> <b>Stepwise Substitution of Alkoxysilanes to Form Unsymmetrically Substituted Multifunctional Aminoalkoxysilanes</b>
12:25-14:00	Lunch

**Friday, June 9, 2017 – Afternoon Session A**

<b>Ulyot Meeting Hall</b>	<b>Session A Applied Technology</b> Chairperson: Barry Arkles
14:00-14:30	<b>IL-8</b> <b>Ramesh C. Kumar</b> <i>3M, Maplewood, MN, USA</i> <b>Synthesis and Applications of Silicone Copolymers Using Photoinferter and Other Silicone Macromers</b>
14:30-14:50	<b>SL-20</b> <b>Michelle R. Cummings</b> , William D. Inman, Jr. <i>The Dow Chemical Company, Midland, MI, USA</i> <b>Evolution of Liquid Silicone Rubber to Advanced Optical Moldable Silicone Materials</b>
14:50-15:10	<b>SL-21</b> <b>Kazunobu Senoo</b> , Jun Okada, Motoki Sato, Chad M. Brick <i>Sumitomo Bakelite, Kobe, Japan</i> <b>High Tear Strength Transparent Silicone Elastomers with Low Hardness and High Elongations</b>
15:10-15:30	Coffee Break
15:30-16:00	<b>IL-9</b> <b>James P. Lewicki</b> <i>Lawrence Livermore National Laboratory, Livermore, CA, USA</i> <b>Towards Controlled, Synthesis and Characterization of Complex Silicone Architectures with Tailored and Novel Physical Properties</b>
16:00-16:20	<b>SL-22</b> <b>Judith Radebner</b> , Michael Hass, Harald Stueger <i>TU Graz, Austria</i> <b>Tetraacylgermanes as Highly Efficient Photoinitiators for Dental Applications</b>
16:20-16:40	<b>SL-23</b> <b>Susan H. Tilford</b> , Jonathan Goff, Barry Arkles <i>Gelest, Inc., Morrisville, PA, USA</i> <b>Superhydrophobic Surface Coatings</b>
CHF Museum Open to Attendees until 17:00	
17:30-18:30	<b>Jacobs Reading Room</b> Cocktail Reception (Registration Required)
18:30-21:30	<b>Ulyot Meeting Hall</b> Banquet (Registration Required)

---

**Friday, June 9, 2017 – Afternoon Session B**


---

<b>Franklin Rooms</b>	<b>Session B Silicon Chemistry and Catalysis Chairperson: Joyce Corey</b>
	<b>IL-12</b> <b>Kenrick M. Lewis</b> <i>Momentive Performance Materials, Tarrytown, NY, USA</i> <b>Use of Nanocatalysis in the Direct Synthesis of Methylchlorosilanes and Alkoxysilanes</b>
14:00-14:30	
	<b>SL-28</b> Jonathan O. Bauer, Eva Barth, Christopher Golz, <b>Carsten Strohmann</b> <i>TU Dortmund, Germany</i> <b>Highly Functionalized Stereogenic Silicon Centres</b>
14:30-14:50	
	<b>SL-29</b> Eric M. Press, Eric A. Marro, Sravan K. Surampudi, Carlton P. Folster, Tapas K. Purkait, <b>Rebekka S. Klausen</b> <i>Johns Hopkins University, Baltimore, MD, USA</i> <b>Strategic Synthesis Targeting Complex Polysilanes</b>
14:50-15:10	
15:10-15:30	Coffee Break
	<b>SL-30</b> <b>Michael Haas</b> , Viktor Christopoulos, Thomas Lainer, Harald Stueger <i>Graz University of Technology, Graz, Austria</i> <b>Neopentasilane: The Ideal Building Blocks for Higher Hydrosilanes</b>
15:30-15:50	
	<b>SL-31</b> <b>Genqiang Xue</b> , Van V. Green <i>The Dow Chemical Company, Carrolton, KY, USA</i> <b>Mechanistic Aspects of the Rochow Direct Process</b>
15:50-16:10	
	<b>SL-32</b> <b>Alyssa F. Schneider</b> , Mengchen Liao, Michael A. Brook <i>McMaster University, Hamilton, ON, Canada</i> <b>The Effect of Water on the Piers-Rubinsztajn Reaction</b>
16:10-16:30	
	CHF Museum Open to Attendees until 17:00
17:30-18:30	
<b>Jacobs Reading Room</b>	Cocktail Reception (Registration Required)
18:30-21:30	
<b>Ullyot Meeting Hall</b>	Banquet (Registration Required)

---

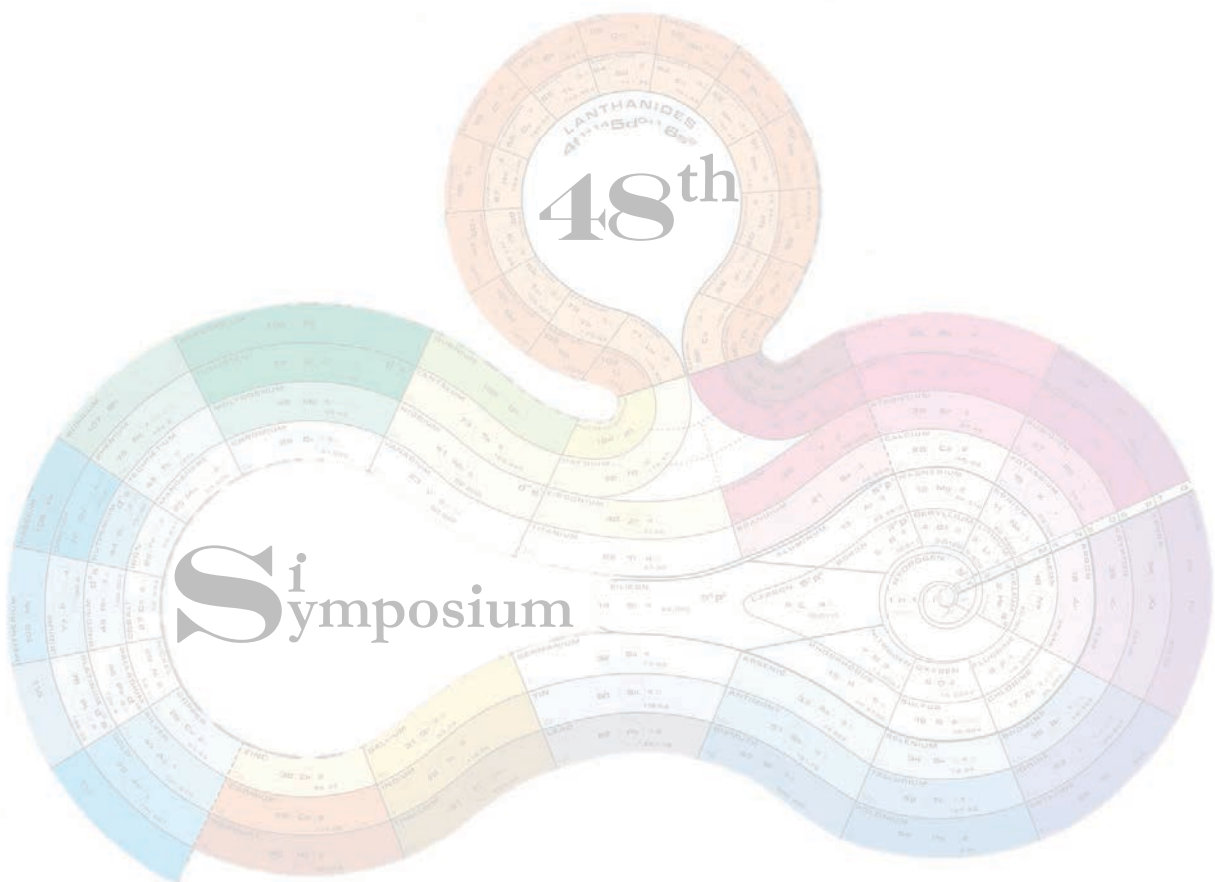




---

# Plenary Lecture Listing

---





**PL-1**

**Keith A. Woerpel\***

*New York University, New York, NY, USA*

**Silylene Transfer Reactions for the Synthesis of Strained Alkenes: New Methods for Stereoselective Synthesis**

**PL-2**

**Thomas J. McCarthy,\*** Pei Bian, Daniel H. Flagg

*University of Massachusetts, Amherst, MA, USA*

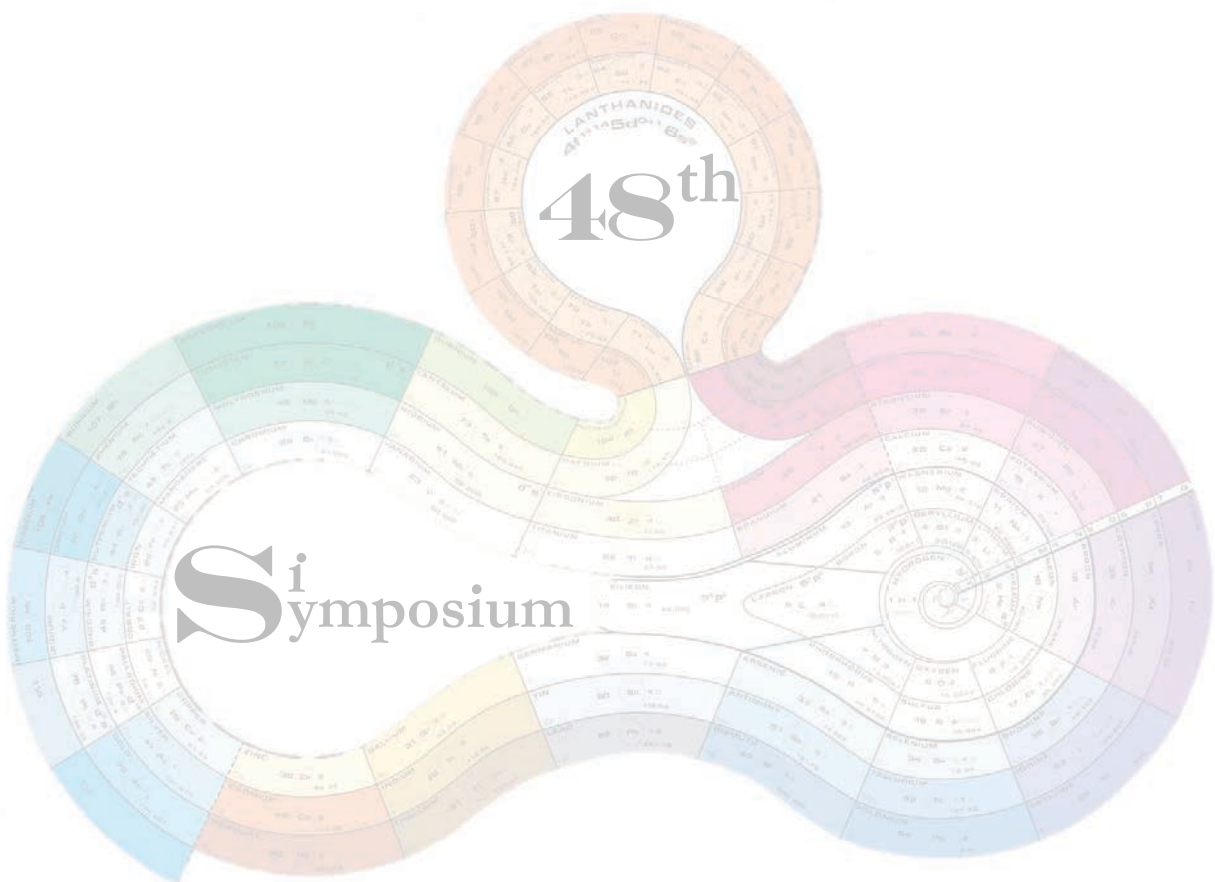
**Methylsilicones Pushed in Several Directions**



---

# Invited Lecture Listing

---





### IL-1

**Matthias Driess\***

*Technical University Berlin, Department of Chemistry: Metalorganics and Inorganic Materials, Berlin, Germany*

**N-Heterocyclic Silylenes: Powerful Tools in Small Molecule Activation and Homogeneous Catalysis**

### IL-2

**Joseph M. Mabry,\*** Andrew J. Guenther, Jeffrey R. Alston, Anish Tuteja, Scott T. Iacono, Raymond Campos, Sean M. Ramirez, Timothy S. Haddad

*Edwards AFB, CA, USA*

**Silicon-Hybrid Materials: Fundamental Research to Air Force Applications**

### IL-3

**Nicola Huesing\***

*Chemistry and Physics of Materials, Paris Lodron University Salzburg, Austria*

**Functional and Flexible Materials by Sol-Gel Processes**

### IL-4

**Michael J. Sailor,<sup>a\*</sup>** Dokyoung Kim,<sup>a</sup> Taeho Kim,<sup>a</sup> B.J. Kim,<sup>a</sup> Joanna Wang,<sup>a</sup> Jinyoung Kang,<sup>a</sup> Youlin Pan,<sup>b</sup> Barry Arkles<sup>b</sup>

<sup>a</sup> *University of California, San Diego, La Jolla, California, USA*

<sup>b</sup> *Gelest, Inc., Morrisville, PA, USA*

**Surface Modification of Silicon Nanostructures Using Silane chemistry**

### IL-5

**Brian Korgel,\*** Yixuan Yu, Adien Guillaussier

*The University of Texas at Austin, Austin, TX, USA*

**Silicon Nanocrystal Assemblies**

### IL-6

Natasha Tabassum,<sup>a</sup> Vasileios Nikas,<sup>a</sup> Brian Ford,<sup>a</sup> Edward Crawford,<sup>b</sup> **Spyros Gallis<sup>a\*</sup>**

<sup>a</sup> *Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York, USA*

<sup>b</sup> *GLOBALFOUNDRIES Corp., East Fishkill, New York, USA*

**Material Behaviors of Self-Aligned Silicon-Carbide Nanowire ARRAYS Doped with Erbium Towards Quantum Applications**

**IL-7**

**François Ganachaud**,\* Camille Spigolis, Constance Robeyns  
*CNRS, INSA-Lyon, France*  
**New Material Properties Through a Silicon Blend Strategy**

**IL-8**

**Ramesh C. Kumar**\*  
*3M Corporation, Maplewood, MN, USA*  
**Synthesis and Applications of Silicone Copolymers Using Photoinferter and Other Silicone Macromers**

**IL-9**

**James P. Lewicki**\*  
*Lawrence Livermore National Laboratory, Livermore, CA, USA*  
**Towards Controlled, Synthesis and Characterization of Complex Silicone Architectures with Tailored and Novel Physical Properties**

**IL-10**

**Gregory W. O'Neil**,\* Elizabeth Cummins, Emily Schneider  
*Western Washington University, Bellingham, WA, USA*  
**New Methods for Tethered Carbonyl Silylations**

**IL-11**

**Donald Watson**\*  
*University of Delaware, Newark, DE, USA*  
**Advances in the Preparation of Organosilanes Using Palladium Catalysis**

**IL-12**

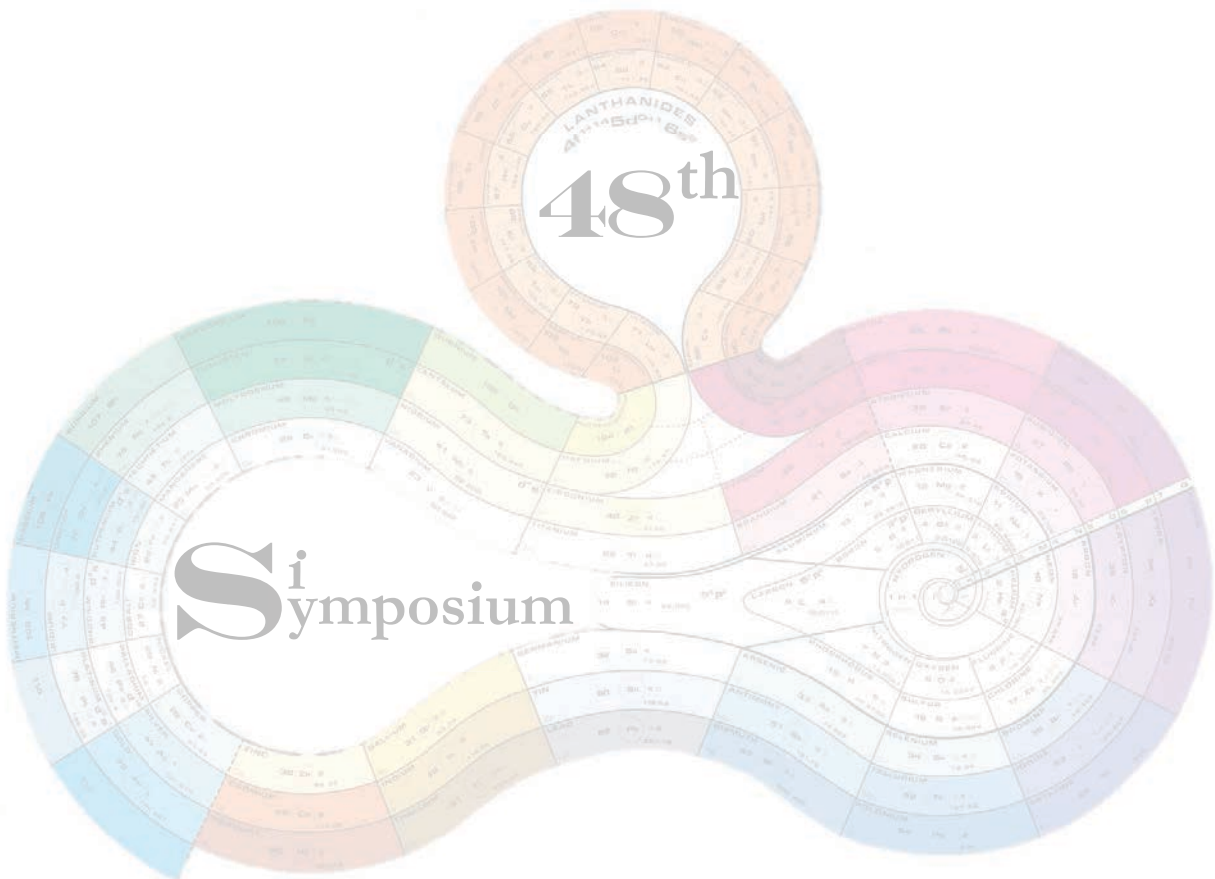
**Kenrick Lewis**\*  
*Momentive Performance Materials Inc., Tarrytown, NY, USA*  
**Use of Nanocatalysis in the Direct Synthesis of Methylchlorosilanes and Alkoxysilanes**



---

# Short Lecture Listing

---





**SL-1****Andrey Yu. Rogachev,<sup>a\*</sup>** Alexander V. Zabula<sup>b</sup><sup>a</sup>*Illinois Institute of Technology, Department of Chemistry, Chicago, IL, USA*<sup>b</sup>*University of Pennsylvania, P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, Philadelphia, PA, USA***Mechanism of Oligomerization of N-Heterocyclic Silylenes into Zwitter-ionic Silenes****SL-2****Kim M. Baines,\*** Nada Y. Tashkandi, Sarah McOnie, Jeremy L. Bourque*Department of Chemistry, University of Western Ontario, London, Ontario, Canada***The Addition of Isocyanides to Disilenes: The Never Ending Story****SL-3****Kerim Samedov,<sup>a</sup>** Paul W. Percival,<sup>b</sup> Robert West<sup>c\*</sup><sup>a</sup>*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada*<sup>b</sup>*Department of Chemistry, Simon Fraser University, Vancouver, BC, Canada*<sup>c</sup>*Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA***Oscillations in the  $\mu$ SR Spectra of Muoniated Organosilyl Free Radicals and their Origin****SL-4****Peter P. Gaspar,\*** Alexander Seim*Department of Chemistry Washington University in Saint Louis St. Louis, MO, USA***A Computational Study of (2 + 4) Retro-cycloadditions of Conjugated Planar Disilenes****SL-5****Richard M. Laine,<sup>a,c\*</sup>** M. Bharami,<sup>a</sup> D. Hashemi,<sup>a</sup> J. Kieffer,<sup>a</sup> M. Moghadam,<sup>a</sup> M. F. Roll,<sup>a</sup> R. Tamaki,<sup>a</sup> J. Furgal,<sup>b</sup> T. Goodson III,<sup>b</sup> J. Kampf<sup>b</sup><sup>a</sup>*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA*<sup>b</sup>*Department of Chemistry, University of Michigan, Ann Arbor, MI, USA*<sup>c</sup>*Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI, USA***Electrophilic Substitution on Phenylsilsesquioxanes****SL-6****Masafumi Unno,\*** Kazunori Asami, Yuka Nagai, Yasunobu Egawa, Nobuhiro Takeda*Department of Chemistry and Chemical Biology, Faculty of Science and Technology, Gunma University, Kiryu, Japan***Synthesis and Reactions of Janus Prisms**

### SL-7

**Kayla Diemoz**, Jake Jagannathan, Annaliese Franz\*

*Department of Chemistry, University of California Davis, Davis, CA, USA*

**Investigation of Hydrogen-Bonding Ability of 1,3-Disiloxanediols and Polyhedral Oligomeric Silsesquioxanes with Applications for Catalysis**

### SL-8

**Bhanu P.S. Chauhan**\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ, USA*

**Reversible Phase Transition of Silicone-Metal Nanoconjugates**

### SL-9

**Ling Ju**, Nicholas C. Strandwitz\*

*Department of Materials Science and Engineering and Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA, USA*

**Structures and Growth Behavior of MLD Films using Cyclic Azasilanes, Maleic Anhydride, Trimethylaluminum and Water as Precursors**

### SL-10

**Parameswara Rao Chinnam**, Megan Van Vliet, Michael Zdilla, Stephanie L. Wunder\*

*Department of Chemistry, Temple University, Philadelphia, PA, USA*

**Functionalization of Silica Interfacial Layer for Hybrid Lithium Ion Conducting Glass Ceramics and Polymers**

### SL-11

**Youlin Pan**,\* Annalese F. Maddox, Taewoo Min, Jonathan Goff, Barry Arkles

*Gelest, Inc., Morrisville, PA, USA*

**Hydroxylated Surface Induced Coupling Reactions of Cyclic Azasilanes**

### SL-12

Konstantin Pokhodnya, Kenneth J. Anderson, Matthew Frohlich, Ryan Schwiderski,  
**Philip Boudjouk**\*

*Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND, USA*

**Cyclohexasilane (Si<sub>6</sub>H<sub>12</sub>, CHS) A Source of Quantum Dots (SiQDs), Nanowires (SiNWs), Nanorods (SiNRs), Conducting Inks, Highly Functionalized Rings and 1-D Polymers**

**SL-13**

**Andrea M. Goforth**,\* Christine M. Radlinger, Rylie J. Ellison  
*Department of Chemistry, Portland State University, Portland, OR, USA*  
**Evolution of the Photoluminescence Properties of Colloidal Silicon Nanoparticles over Time and with Environmental Changes**

**SL-14**

**Anis Rahman**,\* Aunik Rahman  
*Applied Research and Photonics, Harrisburg, PA, USA*  
**Sub-Nano Scale Characterization of 1D and 2D Materials by Terahertz Technology**

**SL-19**

**Chandres Surti**,<sup>a</sup> John Bilney,<sup>a\*</sup> Christos Angeletakis<sup>b</sup>  
<sup>a</sup> *Cornelius Specialties, Suffolk, UK.*  
<sup>b</sup> *Proteas Technologies, Bear, DE, USA*  
**Hydrolytic Stability of Trisiloxane Surfactants**

**SL-15**

**Jennifer Morgan**, Tong Chen, Michael A. Brook\*  
*Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, Canada*  
**Novel Synthesis of a Spirocyclic Silicone and Subsequent Branching**

**SL-16**

**M. Meléndez-Zamudio**,<sup>a\*</sup> A. Villegas,<sup>a</sup> J.A. González-Calderón,<sup>a</sup> R. Meléndrez,<sup>b</sup> M. Meléndez-Lira,<sup>c</sup> J. Cervantes<sup>c</sup>  
<sup>a</sup> *Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Campus Guanajuato. Guanajuato, Gto., México*  
<sup>b</sup> *Departamento de Física, Cuerpo Académico de Física de Irradiaciones, Universidad de Sonora. Hermosillo, Son., México.*  
<sup>c</sup> *Instituto de Ingeniería y Tecnología, Departamento de Física y Matemáticas, Universidad Autónoma de Ciudad Juárez. Ciudad Juárez, Chih., México*  
**Study of Polydimethylsiloxane (PDMS) Elastomer Generated by  $\gamma$  Irradiation: Correlation Between Properties (Thermal and Mechanical) and Structure (Crosslink Density Value)**

**SL-17**

**Constance Robeyns**, Etienne Delebecq, Frédéric Lortie, François Ganachaud\*  
*INSA-Lyon, IMP, Lyon, France, Hutchinson Research Center, Chalette-sur-Loing, France*  
**Microstructure Versus Mechanical Properties of Original Silicone/Thermoplastic Elastomer Blends**

**SL-18**

**Scott E. Laengert**, Alyssa F. Schneider, Eric Lovinger, Yang Chen, Michael A. Brook\*  
*Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, Canada*

**Sequential Functionalization of a Natural Cross-Linker Leads to Designer Silicone Networks**

**SL-20**

**Michelle R. Cummings**,\* William D. Inman Jr.  
*The Dow Chemical Company, Midland, MI, USA*

**Evolution of Liquid Silicone Rubber to Advanced Optical Moldable Silicone Materials**

**SL-21**

**Kazunobu Senoo**,\* Jun Okada, Motoki Sato, Chad M. Brick  
*Sumitomo Bakelite Co, Ltd., Nishu-ku Kobe, Hyogo, Japan*

**High Tear Strength Transparent Silicone Elastomers with Low Hardness and High Elongations**

**SL-22**

**Judith Radebner**, Michael Haas, Harald Stueger\*  
*TU Graz, Institute of Inorganic Chemistry, Graz, Austria*

**Tetraacylgermanes as Highly Efficient Photoinitiators for Dental Applications**

**SL-23**

**Susan H. Tilford**,\* Jonathan Goff, Barry Arkles  
*Gelest, Inc., Morrisville, PA, USA*

**Superhydrophobic Surface Coatings**

**SL-24**

Hoan Q. Duong,<sup>a,b</sup> **Scott McN. Sieburth**<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, Temple University, Philadelphia, PA, USA*

<sup>b</sup> *Present address: Department of Chemistry, Hanoi National University of Education, Hanoi, Vietnam*

**Silanediol Inhibitors of the Coagulation Cascade**

**SL-25**

**Sami E. Varjosaari**, Vladislav Skrypai, Thomas M. Gilbert, Marc J. Adler\*  
*Department of Chemistry, Biochemistry, Northern Illinois University, DeKalb, IL, USA*

**Controlling the Junction Switch: Assymetric Ketone Reductions Using 1-Hydrosilatrane**

**SL-26**

**Brenden P. Derstine**, Buddha B. Khatri, Svitlana Kulyk, Scott McN. Sieburth\*  
*Department of Chemistry, Temple University, Philadelphia, PA, USA*  
**Silanols as a Selective Proton Source for the Photochemistry of Silyl 3-enol-1-ynes**

**SL-27**

**Lukas Zibula**, Jonathan O. Bauer, Carsten Strohmann\*  
*TU Dortmund, Anorganische Chemie, Dortmund, Germany*  
**Stepwise Substitution of Alkoxysilanes to Form Unsymmetrically Substituted Multifunctional Aminoalkoxysilanes**

**SL-28**

Jonathan O. Bauer, Eva Barth, Christopher Golz, **Carsten Strohmann\***  
*TU Dortmund, Anorganische Chemie, Dortmund, Germany*  
**Highly Functionalized Stereogenic Silicon Centres**

**SL-29**

Eric M. Press, Eric A. Marro, Sravan K. Surampudi, Carlton P. Folster, Tapas K. Purkait, **Rebekka S. Klausen\***  
*Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA*  
**Strategic Synthesis Targeting Complex Polysilanes**

**SL-30**

**Michael Haas\***, Viktor Christopoulos, Thomas Lainer, Harald Stueger  
*Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria*  
**Neopentasilane: The Ideal Building Block for Higher Hydrosilanes**

**SL-31**

**Genqiang Xue\***, Van V. Green  
*The Dow Chemical Company, Carrollton, KY, USA*  
**Mechanistic Aspects of the Rochow Direct Process**

**SL-32**

**Alyssa F. Schneider**, Mengchen Liao, Michael A. Brook\*  
*McMaster University, Department of Chemistry and Chemical Biology, Hamilton, ON, Canada*  
**The Effect of Water on the Piers-Rubinsztajn Reaction**

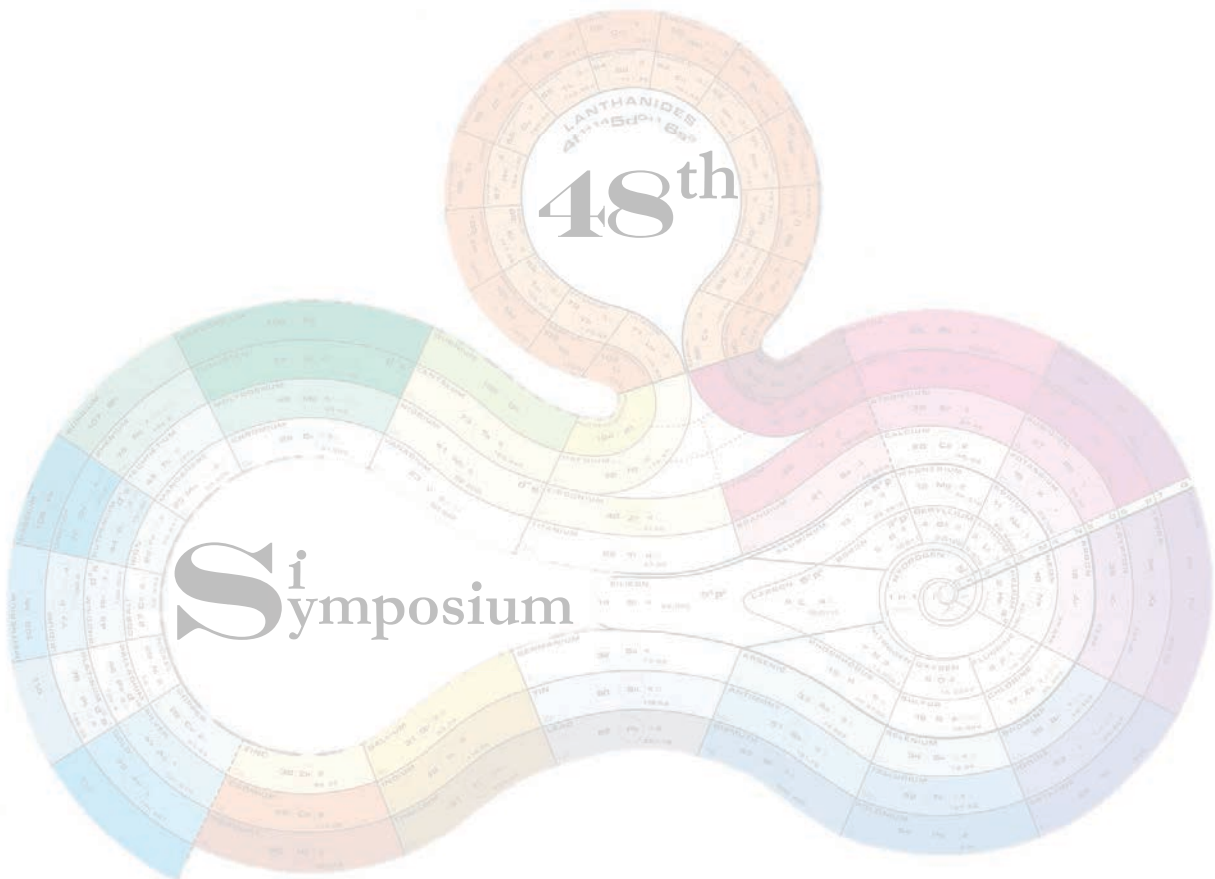




---

# Poster Listing

---





**P-1**

**Natasha Ampomah**, Kelly Moran, Qiaxian Johnson, Bhanu P. S. Chauhan\*  
*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ, USA*

**Synthesis of Noble Metal Nanoparticles Coated with Polystyrene for the Applications of Plastics**

**P-2**

**Brittany Armstrong**, Richard Saylor, Benjamin Shupe, Benjamin Wigman, R. David Britt, Annaliese K. Franz\*

*Department of Chemistry, University of California, Davis, CA, USA*

**Methodology and EPR Studies of an Enantioselective Copper(II)-Catalyzed Silyl-Spirocarbamate Formation**

**P-3**

Bhanu P. S. Chauhan,\* **Daniela Artiga**, Qiaxian Johnson, Aarti Patel  
*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ, USA*

**The Catalytic Activity of a New Generation Pt Nano-Gel Catalyst**

**P-4**

**Jonathan O. Bauer**,<sup>†</sup> Swen Weber, Carsten Strohmann\*  
*Anorganische Chemie, Technische Universität Dortmund, D-44227 Dortmund, Germany*

<sup>†</sup> *Current address: Institut für Anorganische Chemie, Universität Regensburg, Regensburg, Germany*

**Introducing the Si–F bond into Silylated Pyrrolidines**

**P-5**

**Pedro Braun Streb**, Marvin Kloss, Dominik Auer, Carsten Strohmann\*  
*TU Dortmund University, Otto-Hahn-Str. 6, 44227, Dortmund, Germany*

**Structure-reactivity Studies on Alkalimetal Silanes and Their Corresponding Solvent Separated Compounds**

**P-6**

**Viktor Christopoulos**, Michael Haas, Harald Stueger\*  
*Institute of Inorganic Chemistry, Graz University of Technology, Austria*

**The Chemistry of Nonasilane**

**P-7**

**Andrew P. Cinderella**, Bojan Z. Vulovic, Donald A. Watson\*

*University of Delaware, Newark, DE, USA*

**Palladium Catalyzed Alkylation of Silicon Electrophiles**

**P-8**

**Li Cui**\*, Shawn Chen, Mark Rickard, LaBeaume Paul, Cameron Jim, Yamada Shintaro

*The Dow Chemical Company, Marlborough, MA, USA*

**Kinetic Study of Homo-Polymerization of MTMS by *in situ* Infrared (IR) and Raman Spectroscopy**

**P-9**

**Edwin Elias**, Juan Leiva, Qiaxian R. Johnson, Bhanu P.S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ, USA*

**Three Component Coupling of Metal Nanoparticles, Stober Silica, and Functional Silanes: A New Approach to Green Catalysis**

**P-10**

**Lucile Fauvre**, Daniel Portinha, Jean-Pierre Pascault, Etienne Fleury, François

Ganachaud\*

*IMP@INSA-Lyon, CNRS UMR 5223, Villeurbanne, France*

**Supramolecular Silicones with Self-Healing Ability**

**P-11**

**Steven E. S. Fletcher**, Scott McN. Sieburth\*

*Department of Chemistry, Temple University, Philadelphia, PA, USA*

**Silicon Substitution in Benzene–Pyridone Photo-Cycloaddition**

**P-12**

**Ralph Fleurant-Jean**, Daniela Artiga, Qiaxian Johnson, Bhanu P.S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, Wayne, NJ, USA*

**Hybrid Gels of Polymethylhydrosiloxane and Polybutadienes and Their Catalytic Activity**

**P-13**

**Carlton P. Folster**, Eric A. Marro, Eric M. Press, Tapas K. Purkait, Shehani M. Mendis, Rebekka S. Klausen\*

*Johns Hopkins University, Baltimore, MD, USA*

**Synthesis of Novel Donor-Acceptor Organosilicon Materials**

**P-14**

J. Cervantes,<sup>a\*</sup> **G. González-García**,<sup>a</sup> J.A. Gutiérrez-Fuentes,<sup>a</sup> M.A. Leyva-Ramírez,<sup>b</sup> K. H. Pannell<sup>c</sup>

<sup>a</sup> *Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Campus Guanajuato. Guanajuato, Gto., México.*

<sup>b</sup> *Departamento de Química, CINVESTAV-IPN, Ciudad de México, México*

<sup>c</sup> *Chemistry Department, University of Texas at El Paso, El Paso, Texas. USA.*

**Structural Study of Complexes Obtained from Base Induced Migration of Si, Si<sub>2</sub>, and Ge Groups to the Cyclopentadienyl Ligand in the System ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO) Where M= Fe, W**

**P-15**

**Michael Haas**,\* Mario Leypold, Harald Stueger

*Institute of Inorganic Chemistry, Graz University of Technology Stremayrgasse 9/IV, 8010 Graz, Austria*

**First Sila-Aldol Reaction Enables the Synthesis of Structurally Complex Silicon-Frameworks**

**P-16**

**Junha Jeon**\*

*University of Texas at Arlington, Department of Chemistry and Biochemistry, Arlington, TX, USA*

**Catalytic C-H and C-C Bond Silylation Reactions**

**P-17**

B. Arkles,<sup>a</sup> Y. Pan,<sup>a</sup> **A. E. Kaloyeros**<sup>b\*</sup>

<sup>a</sup> *Gelest, Inc., Morrisville, PA, USA*

<sup>b</sup> *College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, NY, USA*

**Thin-Film Deposition of Silicon Nitrides from Trihydridosilanes**

**P-18**

**Austin T. Kelly**, Annaliese K. Franz\*

*Department of Chemistry, University of California, Davis, CA, USA*

**Investigations of Organometallic, Organocatalytic, and Base Mediated Methods for the Hydrolysis of 1,3-dihydro-disiloxanes**

**P-19**

**Margaret Kocherga**, Thomas A. Schmedake\*

*University of North Carolina – Charlotte, Charlotte, NC, USA*

**Luminescent Hexacoordinate Silicon Complexes**

**P-20**

**Sarah B. Krause**, Jesse R. Mcatee, Donald A. Watson\*  
*Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, USA*

**An Improved Precatalyst for Silyl-Heck Reactions**

**P-21**

**Gabriel Larribe**, François Ganachaud,\* Etienne Fleury.  
*Laboratoire Ingénierie des Matériaux Polymères, Villeurbanne, France*

**Silicone Foams from Emulsions**

**P-22**

**Konstantin Pokhodnya**, Kenneth Anderson, Svetlana Kilina, Philip Boudjouk\*  
*Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND, USA*

**Perchlorinated Cyclopentasilane (Si<sub>5</sub>Cl<sub>10</sub>) Ring Flattening Upon Donor Coordination in [Si<sub>5</sub>Cl<sub>10</sub>·2Cl]<sup>2-</sup> Dianion**

**P-23**

**A.A. Prishchenko**,\* M.V. Livantsov, O.P. Novikova, N.N. Meleshonkova, L.I. Livantsova, V.S. Petrosyan

*M.V. Lomonosov Moscow State University, Moscow, Russia*

**Organosilicon-Based Synthesis of New Azaheterocycle Derivatives of Phosphonic Acid as Perspective Bioactive Compounds**

**P-24**

**A.A. Prishchenko**,\* M.V. Livantsov, O.P. Novikova, N.N. Meleshonkova, L.I. Livantsova, V.S. Petrosyan

*M.V. Lomonosov Moscow State University, Moscow, Russia*

**New Functionalized Organophosphorus Acids with Aryl and Bicyclic Moieties Via Organosilicon-Based Synthesis**

**P-25**

**Tapas K. Purkait**,<sup>‡</sup> Jonathan G.C. Veinot\*

*Department of Chemistry, University of Alberta, Edmonton, AB, Canada*

<sup>‡</sup>Present Address: *Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA*

**Borane Initiated Functionalization of Silicon Nanocrystal Surfaces: Hydrosilylation and Ligand-Exchange Chemistry**

**P-26**

**William B. Reid**, Jesse R. McAtee, Donald A. Watson\*

*Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, USA*

**The Intramolecular Silyl-Heck Reaction and First Examples of Internal Alkene Participation**

**P-27**

**Christopher L. Rock**,<sup>a</sup> Tufan K. Mukhopadhyay,<sup>a</sup> Thomas L. Groy,<sup>a</sup> Mu-Hyun Baik,<sup>b</sup> Ryan J. Trovitch<sup>a\*</sup>

<sup>a</sup> *School of Molecular Sciences, Arizona State University, Tempe, AZ, USA*

<sup>b</sup> *Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea*

**Carbonyl Hydrosilylation Via Base Metal Catalysis**

**P-28**

**Jillian R. Sanzone**, K. A. Woerpel\*

*New York University, New York, NY, USA*

**Synthesis of Air-Stable Trialkylboranes: Uncatalyzed Carboboration of Seven-Membered-ring trans-Alkenes**

**P-29**

**Vladislav Skrypai**, Sami E. Varjosaari, Thomas M. Gilbert, Marc J. Adler \*

*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, USA*

**DRA(ma) on the 'Train': Green Direct Reductive Aminations Using 1-Hydrosilatrane**

**P-30**

**Camille Spigolis**, Mathieu Doan, François Ganachaud\*

*IMP@INSA, Villeurbanne, France*

**PDMS/Fluorosilicone Blends**

**P-31**

**Charles M. Stockdale**, Yingjian Bo, Scott McN. Sieburth\*

*Temple University, Philadelphia, PA, USA*

**Phenylsilane Oligomers from Lithiation of Phenylsilyl Ethers**

**P-32**

**Moniruzzaman Syed,<sup>a\*</sup> Caleb Glaser,<sup>b</sup> Muhtadyuzzaman Syed<sup>c</sup>**

*<sup>a</sup> Division of Natural and Mathematical Sciences, Lemoyne-Owen College, Memphis, TN, USA*

*<sup>b</sup> Sandia National Laboratories, Albuquerque, NM, USA*

*<sup>c</sup> Department of Electrical and Computer Engineering, Purdue University, IN, USA*

**Thermal Annealing of Gold Thin Films on the Structure and Surface Morphology Using RF Magnetron Sputtering**

**P-33**

**Sami E. Varjosaari, Vladislav Skrypai, Thomas M. Gilbert, Marc J. Adler\***

*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, USA*

**Controlling the Junction Switch: Asymmetric Ketone Reductions Using 1-Hydrosilatrane**

**P-34**

**Sheryl L. Wiskur\***

*University of South Carolina, Department of Chemistry and Biochemistry, Columbia, SC, USA*

**Investigating the Mechanism of Enantioselective Silylation**

**P-35**

**Alexander V. Zabula,<sup>a\*</sup> Andrey Yu. Rogachev,<sup>b</sup> Jingbai Li,<sup>b</sup> Ilia A. Guzei,<sup>c</sup> Robert West,<sup>c</sup> Rinat R. Aysin,<sup>d</sup> Larissa A. Leites,<sup>d</sup> Sergey S. Bukalov<sup>d</sup>**

*<sup>a</sup> Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA*

*<sup>b</sup> Illinois Institute of Technology, Chicago, IL, USA*

*<sup>c</sup> University of Wisconsin, Madison WI, USA*

*<sup>d</sup> Scientific and Technical Center on Raman Spectroscopy, Moscow, Russia*

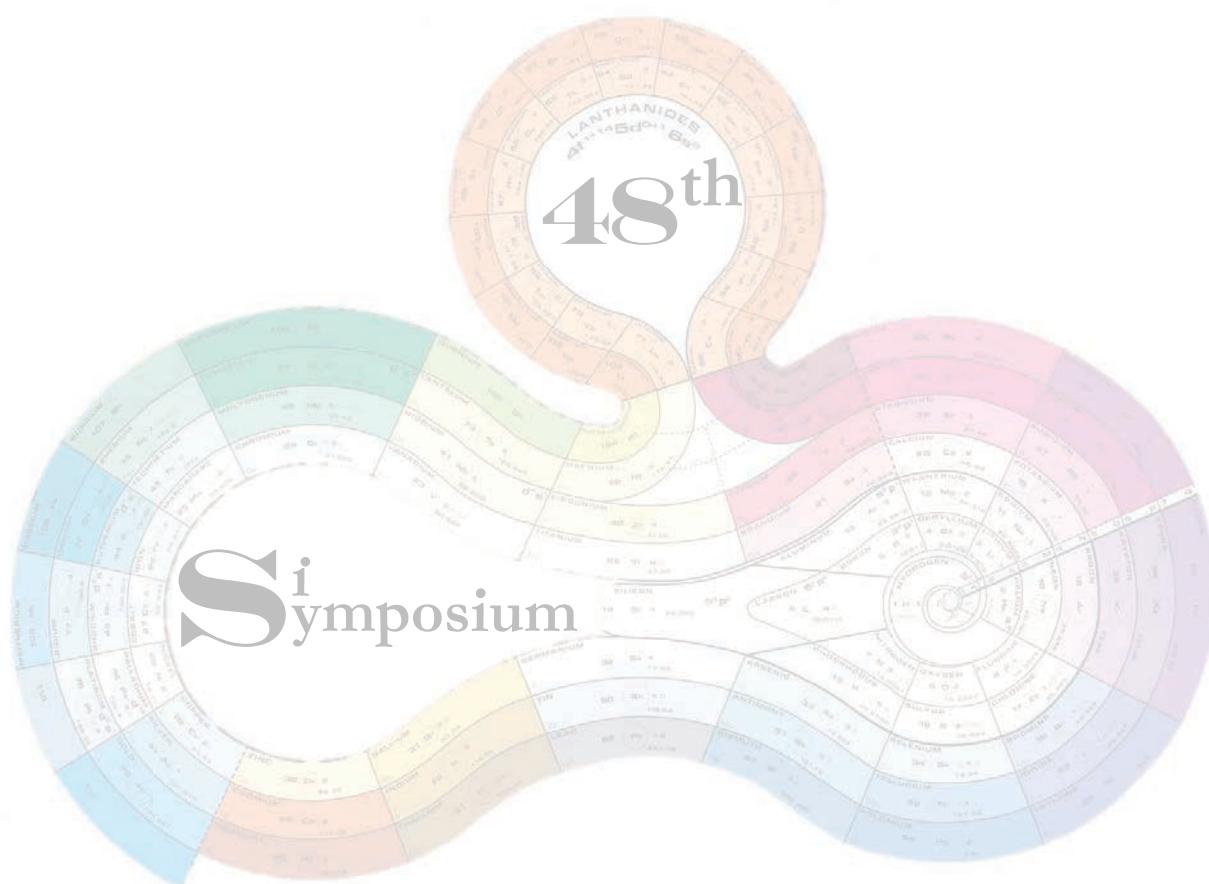
**Benz- and Pyrido-Annulated Silylenes and Their Analogs: Electronic Structure, Self-Assembly and Reactivity**



---

# Plenary Lecture Abstracts

---





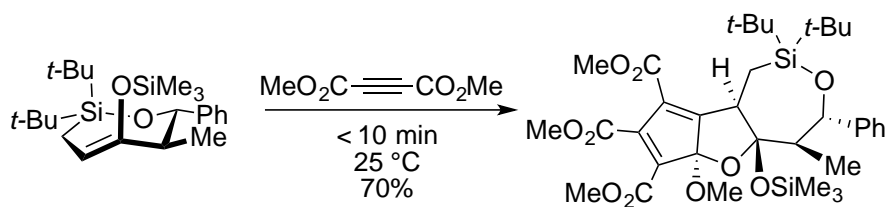
## PL-1 SILYLENE TRANSFER REACTIONS FOR THE SYNTHESIS OF STRAINED ALKENES: NEW METHODS FOR STEREOSELECTIVE SYNTHESIS

Keith A. Woerpel\*

Department of Chemistry, New York University, 100 Washington Square East, New York, NY  
10003, USA  
kwoerpel@nyu.edu

Metal-catalyzed silylene transfer reactions have proven to be useful for the conversions of simple organic substrates into synthetically useful products. For example, silylene transfer to dienes followed by insertions to alkenes results in the stereoselective synthesis of *trans*-oxasilacycloheptenes. These strained alkenes are among the most reactive alkenes reported, undergoing transformations such as cycloadditions and reactions with electron-deficient alkenes and alkynes.<sup>1</sup> Strained seven- and eight-membered ring alkenes undergo other transformations rapidly, such as additions of carbon–metal and sulfur–hydrogen bonds across the carbon–carbon double bond.

<sup>1</sup> J. R. Sanzone, K. A. Woerpel, *Angew. Chem. Int. Ed.* **2016**, *55*, 790–793.



## PL-2 METHYLSILICONES PUSHED IN SEVERAL DIRECTIONS

Thomas J. McCarthy,\* Pei Bian, Daniel H. Flagg

*Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA*

*tmcc@umass.edu, bianpei@polysci.umass.edu, dflagg21@mail.pse.umass.edu*

Silicones are perhaps the most misunderstood and the least understood class of commercial polymeric material. They are used in multiple everyday applications, but their chemistry is generally neglected and often not taught in chemistry, polymer and materials science curricula. In this talk, silicones will be overviewed, several examples of recently completed research will be described and on-going research directions will be discussed. As part of an introduction that will give some historical perspective, the preparation of Low Hysteresis Hydrophobic Surfaces and a Self Healing Silicone Polymer will be described.

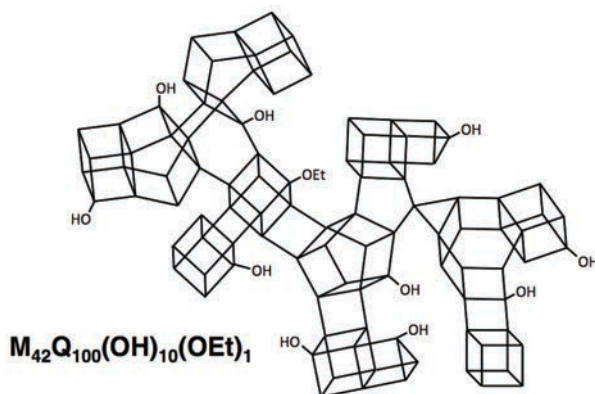
The thermal treatment of oxygen plasma - cleaned silicon wafers with trimethylsilyl- terminated linear PDMS (commercial silicone oils) will be described.<sup>1</sup> This treatment renders silicon/silica surfaces that contain covalently attached PDMS chains. The grafted layers of nanometer scale thickness are liquid-like and decrease activation barriers for contact line motion and minimize water contact angle hysteresis. Anionic siloxane equilibration as a self-healing mechanism will be discussed using examples of cross-linked network polymers that contain ethylene bridges and active silanolate end groups. We will describe that samples prepared with particular cross-link density can be cut in two and can heal by siloxane equilibration to restore the original strength of the silicone sample.

Ongoing research programs will discuss the preparation of MQ (trimethylsilylsilicate)<sup>3</sup> and MT (trimethylsilylmethylsiliconate) copolymers. In particular, vinyl- and hydrido- functionalized samples and their curing to form transparent monolithic structures with controllable properties will be described. We have specific interests in the surface properties and the permeation of water vapor through these materials and ongoing research in this direction will be presented as well.

<sup>1</sup> J. W. Krumpfer, McCarthy, T. J. *Langmuir* **2011**, 27, 11514-11519.

<sup>2</sup> P. Zheng, T. J. McCarthy, *J. Am. Chem. Soc.* **2012**, 134, 2024-2027.

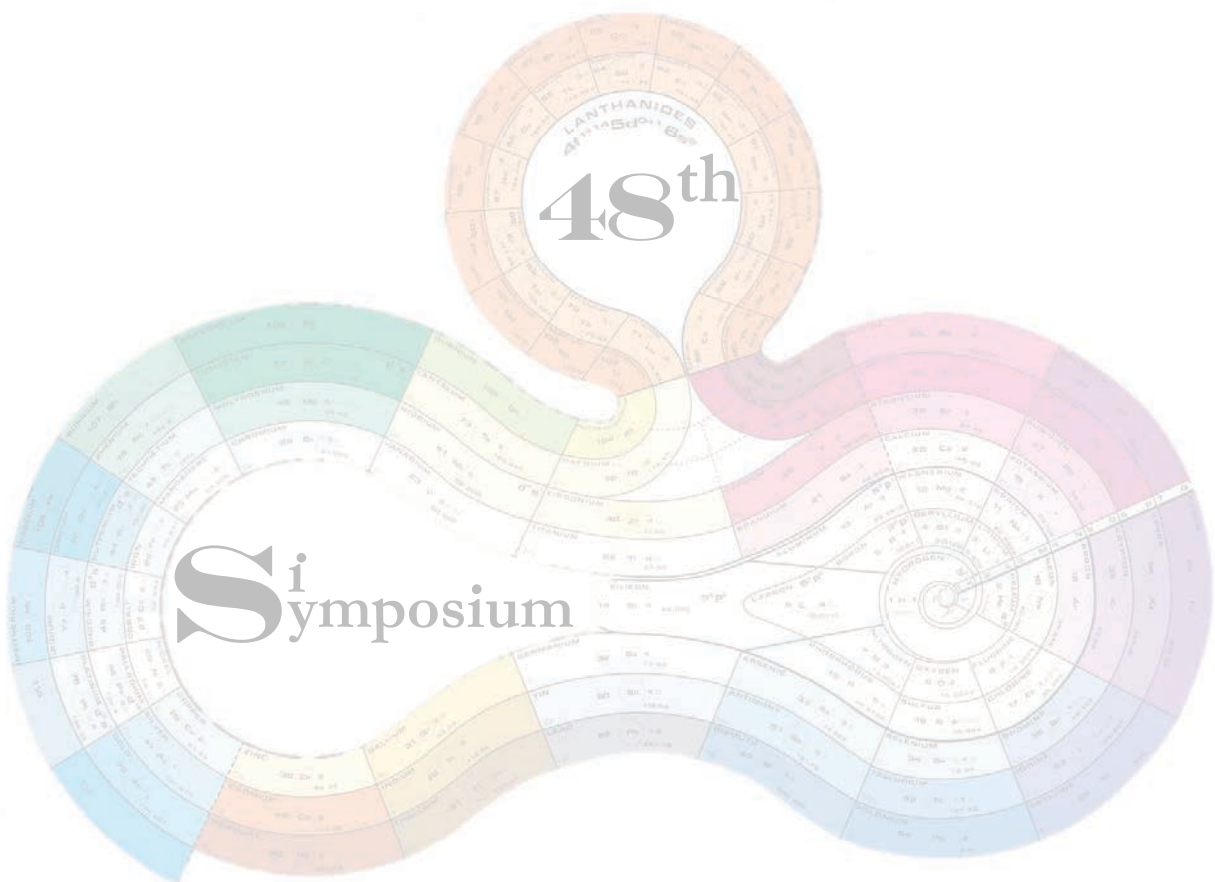
<sup>3</sup> D. H. Flagg, T. J. McCarthy, *Macromolecules*, **2016**, 49, 8581-8592.



---

# Invited Lecture Abstracts

---





## IL-1

## N-HETEROCYCLIC SILYLENES: POWERFUL TOOLS IN SMALL MOLECULE ACTIVATION AND HOMOGENEOUS CATALYSIS

Matthias Driess\*

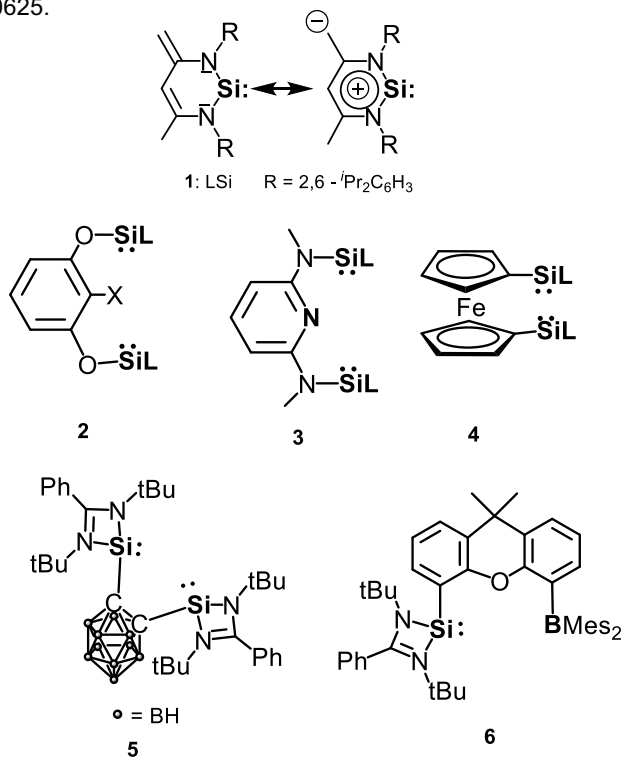
Technical University Berlin, Department of Chemistry: Metalorganics and Inorganic Materials,  
 Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin, Germany  
 matthias.driess@tu-berlin.de

The activation of small molecules by using non- and semi-metals instead of precious metals is a contemporary challenge in the molecular sciences. Ten years ago we developed the new type of zwitterionic silylene **1** which provides an unprecedented reactivity pattern with respect to small molecule activation based on divalent silicon.<sup>1</sup> The remarkably rich reactivity pattern of **1** ligated to first-row transition metals and that of the N-heterocyclic silicon(II)-based polydentate ligands **2** – **5**, which can be used as a new generation of steering ligands in homogeneous catalysis, will be briefly discussed.<sup>2</sup> This includes selected features about metal-mediated catalytic transformations, including hydrosilylation, borylations and C-N coupling reactions of hydrocarbons. In addition, the striking features of the first intramolecular silylene-borane Lewis pair **6** in metal-free activation of small molecules will also be discussed.<sup>3</sup>

<sup>1</sup> M. Asay, M. Driess, C. Jones, *Chem. Rev.* **2011**, *111*, 354; S. Yao, Y. Xiong, M. Driess, *Organometallics* **2011**, *30*, 1748

<sup>2</sup> Reviews on NHSi-metal complexes in homogeneous catalysis: B. Blom, D. Gallego, M. Driess *Inorg. Chem. Front.*, **2014**, *1*, 134; S. Raoufmoghaddam, Y. Zhou, Y. Wang, M. Driess, *J. Organomet. Chem.* **2017**, *829*, 2-10.

<sup>3</sup> Z. Mo, T. Szilvási, C. Eberle, Y. Zhou, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2017**, in press, DOI: 10.1002/anie.201700625.



## IL-2

# SILICON-HYBRID MATERIALS: FUNDAMENTAL RESEARCH TO AIR FORCE APPLICATIONS

Joseph M. Mabry,<sup>a\*</sup> Andrew J. Guenther,<sup>a</sup> Jeffrey R. Alston,<sup>b</sup> Anish Tuteja,<sup>c</sup> Scott T. Iacono,<sup>a</sup> Raymond Campos,<sup>b</sup> Sean M. Ramirez,<sup>b</sup> Timothy S. Haddad<sup>b</sup>

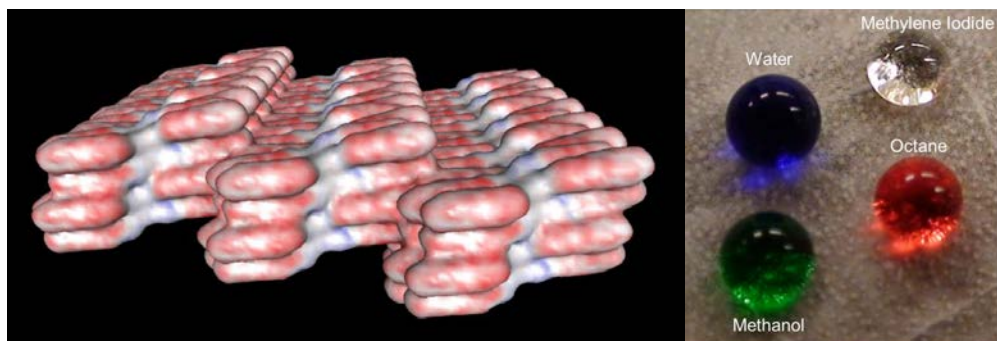
<sup>a</sup> Rocket Propulsion Division, Air Force Research Laboratory, Edwards AFB, CA 93524, USA

<sup>b</sup> ERC Incorporated, Air Force Research Laboratory, Edwards AFB, CA 93524, USA

<sup>c</sup> Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

joseph.mabry@us.af.mil, andrew.guenther@us.af.mil, scott.iacono.1@us.af.mil,  
jeffrey.alston.ctr@us.af.mil, raymond.campos.ctr@us.af.mil, sean.ramirez.ctr@us.af.mil,  
timothy.haddad.ctr@us.af.mil, atuteja@umich.edu

Studying the composition of various hybrid materials and their impact on material properties has led to a better understanding of the design and function of structured hybrid material surfaces. While the contributions of both surface energy and surface roughness to wetting-resistance and other surface properties have been known for some time, a better understanding of surface geometry was necessary in order to design and create new and unique surfaces, capable of repelling virtually all liquids, even those with extremely low surface tension values. This understanding could then be applied beyond liquids, to icing and other types of solid surface fouling. Finally, in depth understanding of these interactions has enabled the creation of functional surfaces useful in Air Force applications. The utility of these surfaces is partially due to the ability to create surface features during processing and preparation. This presentation will discuss the research and development of such surfaces at the Air Force Research Laboratory.





## IL-3 FUNCTIONAL AND FLEXIBLE MATERIALS BY SOL-GEL PROCESSES

Nicola Huesing\*

*Chemistry and Physics of Materials, Paris Lodron University Salzburg, Austria*  
*nicola.huesing@sbg.ac.at*

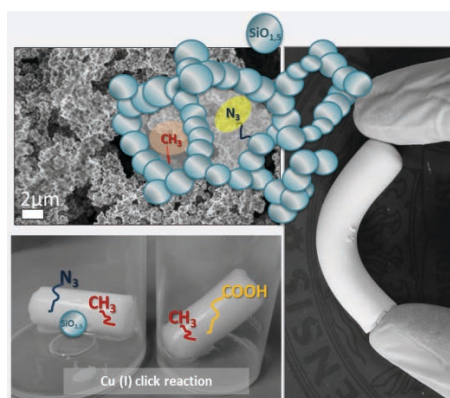
In the last years, significant research was devoted to the synthesis of hierarchically organized materials with structures that exhibit interconnected pores on different length scales from micro (<2 nm), meso- (2-50 nm), to macropores (>50 nm).<sup>1</sup> A simultaneous control over pore sizes from Angstrom to micrometers, pore shape as well as spatial distribution potentially enables the fabrication of hierarchical porous structures exhibiting novel properties and multiple functions. Simple and general methods to prepare functional monolithic materials with well-controlled pore architectures, composition and surface functionalization are therefore highly desired.

In this presentation, the deliberate design of highly porous architectures by combined sol-gel processing and phase separation strategies will be discussed. In addition, a focus will be on the synthesis of flexible and functional porous structures (see Figure 1), as well as postsynthetic modification strategies of such materials by gas-solid displacement reactions or liquid impregnation techniques to yield, e.g. quartz, carbon, silicon carbide, magnesium silicide or silicon nanostructures.<sup>2,3</sup>

<sup>1</sup> A. Feinle, M.E. Elsässer, N. Hüsing, *Chem. Soc. Rev.* **2016**, 45, 3377.

<sup>2</sup> N. Hayati-Roodbari, et. al., *Dalton Trans.* 2017, ahead of print. DOI:10.1039/c7dt00571g

<sup>3</sup> C.R. Ehgartner, S. Grandl, A. Feinle, N. Hüsing, *Dalton Trans.* **2017**, ahead of print. DOI:10.1039/C7DT00558J



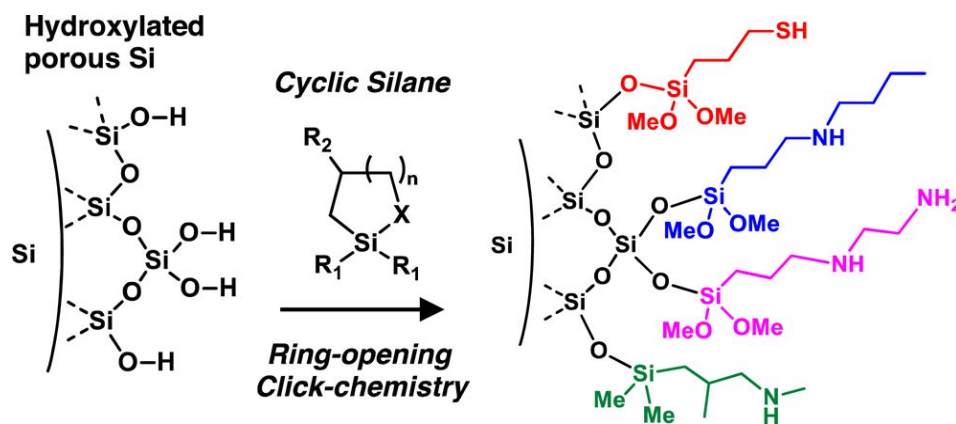
## IL-4 SURFACE MODIFICATION OF SILICON NANOSTRUCTURES USING SILANE CHEMISTRY

Michael J. Sailor,<sup>a\*</sup> Dokyoung Kim,<sup>a</sup> Taeho Kim,<sup>a</sup> B.J. Kim,<sup>a</sup> Joanna Wang,<sup>a</sup> Jinyoung Kang,<sup>a</sup>  
Youlin Pan,<sup>b</sup> Barry Arkles<sup>b</sup>

<sup>a</sup> University of California, San Diego, La Jolla, California, 92093 USA  
msailor@ucsd.edu

<sup>b</sup> Gelest, Inc, 11 East Steel Rd, Morrisville, PA 19067, USA

Whereas chemistry of porous Si has close parallels with the chemistry of crystalline silicon, silica, silanes and siloxanes, the nanostructure of porous Si leads to some unique reactivities not found in these other silicon-containing materials. This derives from several features of porous Si, including its large surface area, its increased lattice strain relative to bulk Si, the influence of microcapillary forces within the porous nanostructure, and the existence of electronic quantum confinement in the silicon skeleton. This presentation will describe some of the chemistries of Si-Si bonds, Si-H bonds, and Si-OH bonds on porous Si that can be harnessed to make interesting functional nanocomposites. In particular, silane coupling reactions and reactions of 5-membered heterocyclic silane compounds will be described. Reactions of heterocyclic silanes with silanol surfaces we refer to as "ring-opening click" reactions due to the combination of simplicity, high yield, wide scope of applicability, lack of byproducts, and use of easily removable solvents.



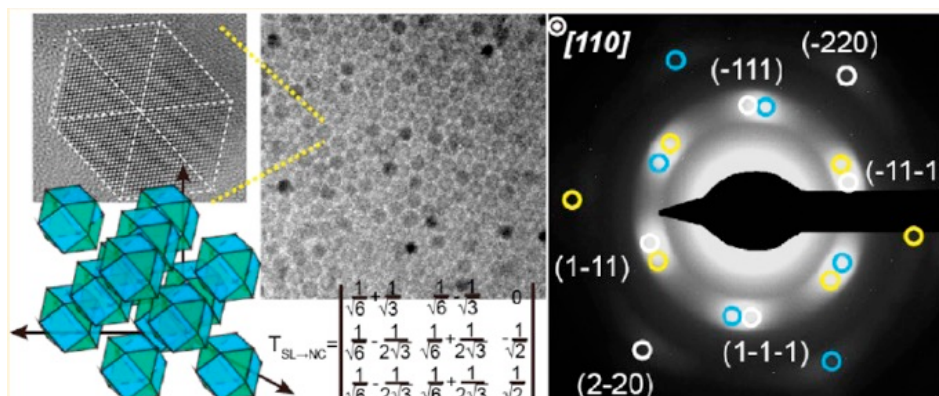
## IL-5 SILICON NANOCRYSTAL ASSEMBLIES

Yixuan Yu, Adrien Guillaussier, Brian A. Korgel\*

McKetta Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX, 78712-1062, USA  
yixuanyu@gmail.com; adrien.guillaussier@gmail.com; korgel@che.utexas.edu

Silicon nanocrystals can now be made with a high degree of uniformity and assembled into a variety of structures. For example, uniform silicon (Si) nanocrystals with cuboctahedral shape, passivated with 1-dodecene capping ligands assemble into face-centered cubic (FCC) superlattices with orientational order. Transmission electron microscopy (TEM), electron diffraction and grazing incidence wide angle and small angle X-ray scattering (GISAXS and GIWAXS) show that the preferred orientation of these soft cuboctahedra depends on the orientation of the superlattices on the substrate, indicating that the interactions with the substrate and assembly kinetics can influence the orientation of faceted nanocrystals in superlattices.<sup>1</sup> These superlattices exhibit structure-dependent solid-solid phase transitions of the Si nanocrystals under pressure. Application of a quasi-uniaxial pressure was found to induce the formation of a new Si phase with diatomic body-centered cubic (BCC) structure and a lattice constant of 4.08 Å at 9.5 GPa. We have also used Si nanocrystals to create substrate-free self-supporting bubble assemblies, which can be used to study optical phenomena in the absence of solvent and substrate effects.

<sup>1</sup> Y. Yu, X. Lu, A. Guillaussier, V. Reddy Voggu, W. Pineros, M. de la Mata, J. Arbiol, D.-M. Smilgies, T. M. Truskett, B. A. Korgel, *Nano Lett.* **2016**, *16*, 7814-7821.



## IL-6

# MATERIAL BEHAVIORS OF SELF-ALIGNED SILICON-CARBIDE NANOWIRE ARRAYS DOPED WITH ERBIUM TOWARDS QUANTUM APPLICATIONS

Natasha Tabassum,<sup>a</sup> Vasileios Nikas,<sup>a</sup> Brian Ford,<sup>a</sup> Edward Crawford,<sup>b</sup> Spyros Gallis<sup>a\*</sup>

<sup>a</sup> *Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York 12203, USA*

<sup>b</sup> *GLOBALFOUNDRIES Corp., East Fishkill, New York 12533, USA*  
*ntabassum@sunypoly.edu, vnikas@sunypoly.edu, brford@sunypoly.edu,*  
*edward.crawford@globalfoundries.com, sgalis@sunypoly.edu*

Silicon-based nanosystems with high functionality and the precise placement of single color centers with high photoluminescence (PL) yield are critical building blocks towards the practical realization of devices in the emerging field of quantum technologies.<sup>1</sup> To this end, this report focuses on the study of material behaviors of ultrathin silicon carbide (SiC:Er) nanowire (NW) arrays doped with erbium (Er<sup>3+</sup>). The arrays of the deterministically oriented SiC NWs were grown in a self-aligned manner through a novel catalyst-free chemical-vapor-deposition (CVD) synthesis route. A key enabler of this synthesis route is that the SiC NWs are engineered with tailored geometry in precise locations during nanofabrication.<sup>2</sup> This translates to an on-demand placement of Er<sup>3+</sup> ions during implantation and engineering of their PL properties in the technologically-friendly SiC NW arrays. The growth, array geometry and Er<sup>3+</sup> implantation effects on the material behaviors of SiC:Er NWs were studied. In particular, their structural and optical characteristics were investigated by means of Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopic ellipsometry (UV-VIS-SE) and Raman spectroscopy. Through a combinational and systematic micro PL (uPL), power-dependence PL (PDPL) spectroscopy, and UV-VIS-SE study, defects and architecture geometry effects on their photoluminescence yield in the near-infrared range were additionally explored. An approximately two orders of magnitude enhancement of the room-temperature Er<sup>3+</sup>-related 1540 nm emission in SiC:Er NW array, which is the telecommunication wavelength used in optical fibers, was observed compared to its thin-film analog. Furthermore the 1540 nm emission in SiC:Er NW was found to be modulated in a linear manner with the pitch of the NW array revealing the beneficial nature of using a nano-photonic crystal structure as a host template for color centers.

<sup>1</sup> A Lohrmann, B C Johnson, J C McCallum, S Castelletto: A review on single photon sources in silicon carbide. Rep. Prog. Phys. 80, 034502 (2017).

<sup>2</sup> V. Nikas, N. Tabassum, B. Ford, L. Smith, A. E. Kaloyeros, S. Gallis: Strong visible light emission from silicon-oxycarbide nanowire arrays prepared by electron beam lithography and reactive ion etching. J. Mater Res. 30, 3692 (2015).

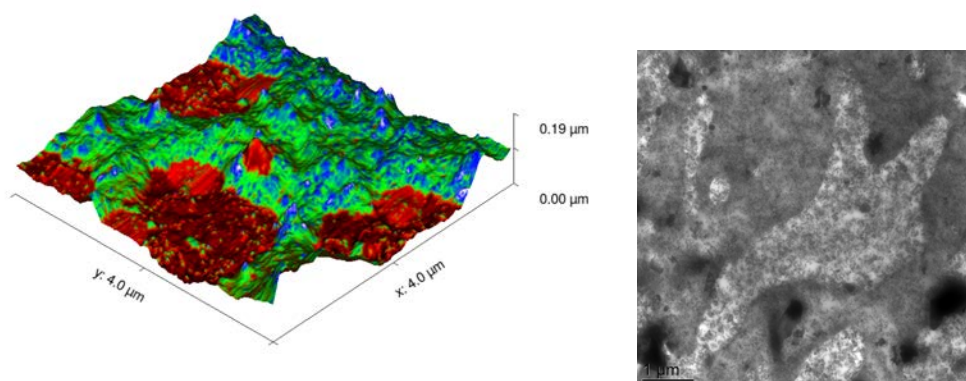
## IL-7 NEW MATERIAL PROPERTIES THROUGH A SILICONE BLEND STRATEGY

Camille Spigolis, Constance Robeyns, François Ganachaud\*

*IMP, UMR5223 CNRS, INSA-Lyon, 17 Bvd Capelle, 69621 Villeurbanne cedex, France  
francois.ganachaud@insa-lyon.fr*

Silicone HCRs are rubber materials useful in transportation applications, typically as seals in engines, rotors, connectors and so on. To generate new elastomers with reinforced properties, one practical solution is to formulate blends of various types of silicone.

Here I will present two studies that we made on the preparation of original materials, with a view to enhancing some basic properties of silicones (mainly thermal, solvent and vibration resistances). Particularly, the talk will focus on structure-properties relationships, where we correlate characterization data (e.g. electronic microscopy, thermal analyses...) and mechanical results (DMA, tensile tests...).



*AFM (left) and TEM (right) snapshots of a model fluorosilicone (FS)/silicone (PDMS) blend. AFM image: FS in red, PDMS in green, fillers as blue stains. TEM photo: FS in white, PDMS in grey, fillers as dark grey or black dots.*

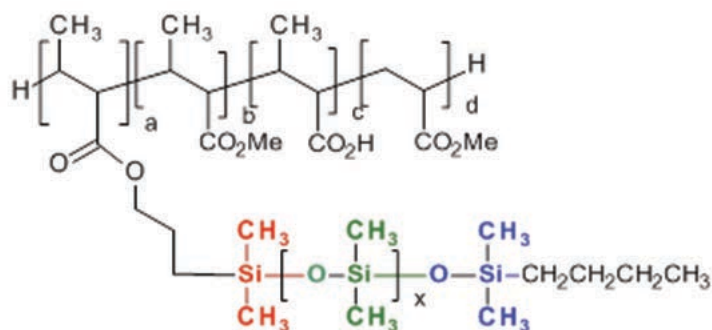
## IL-8

### SYNTHESIS AND APPLICATIONS OF SILICONE COPOLYMERS USING PHOTOINIFERTER AND OTHER SILICONE MACROMERS

Ramesh C. Kumar\*

3M Corporation, 3M Center, Building 236-3D-01, Maplewood, MN 55144-1000, USA  
rckumar0051@mmm.com

Various methods of synthesizing silicone/acrylate and other silicone copolymers such as silicone-polyurethane-polyurea, silicone polycarbonate etc. will be described. The combination of a silicone segment with wide variety of non-silicone segments provides routes to polymeric materials which combine the best features of each block without the loss of other desired properties. Useful unique property balances of these hybrid copolymers will be described.

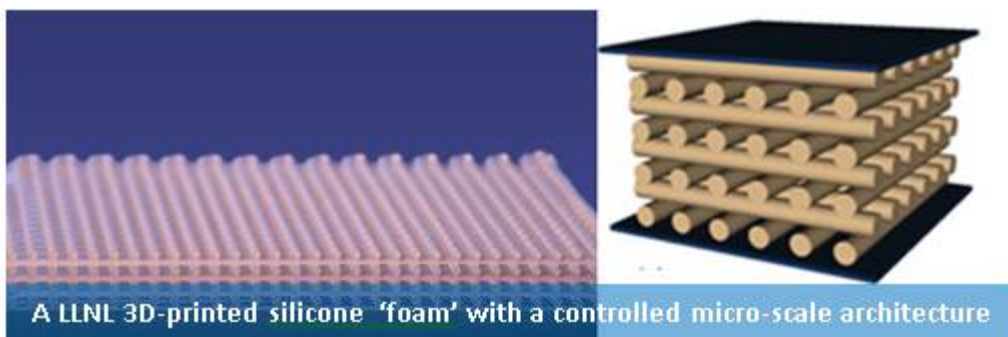


**IL-9****TOWARDS CONTROLLED, SYNTHESIS AND CHARACTERIZATION OF COMPLEX SILICONE ARCHITECTURES WITH TAILORED AND NOVEL PHYSICAL PROPERTIES**

James P. Lewicki\*

*Lawrence Livermore National Laboratory, 7000 East Ave. Livermore, CA 94550, USA*  
*lewicki1@llnl.gov*

Lawrence Livermore National Laboratory develops and utilizes silicone materials for a variety of applications and we employ a range of synthetic formulation strategies (including nanomaterial grafting, ordered network formation and precise control of crosslink density and distribution) to tailor and optimize the network architecture of these complex materials. At a very much larger, yet no less important size scale - we are also pursuing new additive manufacturing methods for the formation of silicone materials with controlled 3D micro-architected structures. The new degrees of freedom offered by both network tailoring and microstructural architecting of silicones has the potential to yield materials with improved, multifunctional, more predictable and even novel physical properties. And in this overview of our current efforts in the area of silicone materials development, we will present the results of a range of architected silicone systems which exhibit properties from - thermally controlled electrical switching behavior to negative mechanical stiffness. We will also discuss our use of a suite of experimental and modeling techniques to investigate the complex network, interfacial and micro-structures of architected silicones and their correlations with both predicted and measured macroscopic performance, including: Advanced Multiple Quantum Nuclear magnetic resonance (MQ-NMR), which may be utilized to provide in-situ information on crosslink density and motional dynamics. And at much larger size scales, X-ray Micro-CT imaging provides data on the dynamic performance of material microstructure. With multi-scale modeling, we are utilizing advanced characterization data to form predictive models of silicone materials performance and response from an atomistic to a micro-scale.



This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-675724

## IL-10 NEW METHODS FOR TETHERED CARBONYL SILYLATIONS

Gregory W. O'Neil,\* Elizabeth Cummins, Emily Schneider

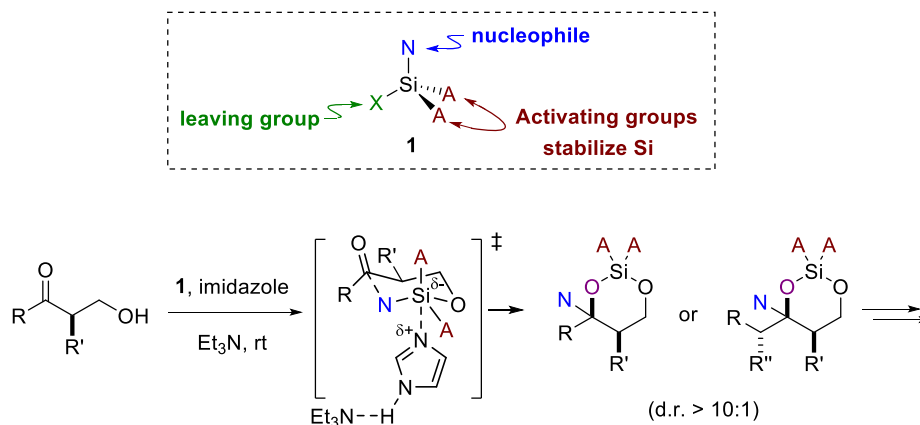
Department of Chemistry, Western Washington University, 516 High St, Bellingham, WA 98225, USA

oneilg@wwu.edu, cummine@wwu.edu, schnei3@wwu.edu

Our group recently discovered a novel cooperative-base mediated intramolecular carbonyl hydrosilylation process.<sup>1,2</sup> The reaction is proposed to occur via a six-membered chair-like transition state, delivering cyclic siloxane products with predictable and high levels of stereocontrol. Results from efforts to expand the synthetic utility of this reaction will be presented, including further manipulations to the siloxane products and the use of other nucleophilic silanes.

<sup>1</sup> O'Neil, G. W.; Miller, M. M.; Carter, K. P. "Direct Conversion of  $\beta$ -Hydroxyketones to Cyclic Disiloxanes." *Org. Lett.* **2010**, *12*, 5350-5352.

<sup>2</sup> Medina, C. R.; Carter, K. P.; Miller, M. M.; Clark, T. B.; O'Neil, G. W. "Stereocontrolled Synthesis of 1,3-Diols from Enones: Cooperative Lewis-Base Mediated Intramolecular Hydrosilylations," *J. Org. Chem.* **2013**, *78*, 9093-9101





## IL-11

## ADVANCES IN THE PREPARATION OF ORGANOSILANES USING PALLADIUM CATALYSIS

Donald Watson\*

University of Delaware, Newark, DE, 19716, USA  
 dawatson@udel.edu

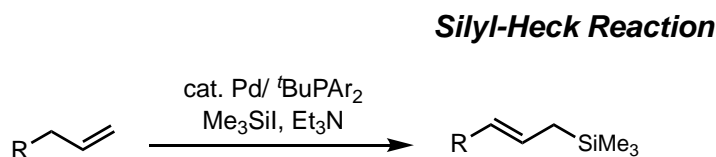
Over the last several years, our group has been active in the development of reaction conditions to prepare allyl- and vinyl-silanes from silyl halides and simple alkenes using palladium catalysis.<sup>1,2,3,4</sup> These reactions are believed to proceed via a Heck-like mechanism involving the oxidative addition of low-valent palladium complexes into the Si-X bond. I will discuss the evolution of this program, as well as some recently developed, mechanistically-related reactions that provide access to other classes of high-value organosilanes, such as secondary alkyl silanes and tetra-substituted vinyl silanes with levels of stereocontrol.

<sup>1</sup> McAtee, J. R.; Martin, S. E. S.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A., *Angew. Chem. Int. Ed.* **2012**, *51*, 3663.

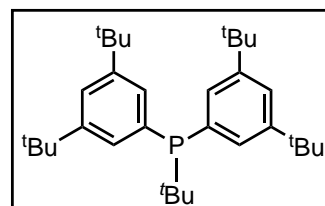
<sup>2</sup> Martin, S. E. S.; Watson, D. A., *J. Am. Chem. Soc.* **2013**, *135*, 13330.

<sup>3</sup> McAtee, J. R.; Martin, S. E. S.; Cinderella, A. P.; Reid, W. B.; Johnson, K. A.; Watson, D. A., *Tetrahedron* **2014**, *70*, 4250.

<sup>4</sup> McAtee, J. R.; Yap, G. P. A.; Watson, D. A., *J. Am. Chem. Soc.* **2014**, *136*, 10166.



- Access to allyl and vinyl silanes from inexpensive starting materials
  - Up to 98% isolated yield with E/Z selectivity of 85:15 to >95:5
    - Little to no alkene isomerization
    - Simple purification



## IL-12

# USE OF NANOCATALYSIS IN THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES AND ALKOXYSILANES

Kenrick M. Lewis\*

*Momentive Performance Materials Inc., 769 Old Saw Mill River Rd. Tarrytown, NY 10591, USA*

Nanosized materials have at least one dimension that is less than 100 nm. Nano-catalysis is the use of these materials to increase reaction rates, selectivity and stability above those shown by bulk materials.<sup>1</sup> In practice, nanocatalysis of Direct Reactions of silicon refers to the use of nanosized copper and promoter sources with micron-sized silicon to synthesize organohalosilanes and alkoxy silanes.<sup>2</sup> Owing to the disparity in escape velocities between the micron-sized and nanosized particles, these reactions are conducted in three-phase (slurry) reactors rather than in fluidized-bed reactors. This presentation will illustrate the advantageous use of nanocatalysis in the slurry-phase Direct Synthesis of methylchlorosilanes, trimethoxysilane and triethoxysilane.<sup>2-4</sup> It will also show that the catalytic instability observed when the slurry phase Direct Synthesis of trimethoxysilane is done in alkylated benzenes, paraffins and cycloparaffins is caused by the accelerated reduction of methanol on nanosized copper particles generated by the decomposition of copper hydroxide in these solvents.<sup>5</sup>

<sup>1</sup> B. Zhou, S. Hermans, G. Somorjai (Editors), *Nanotechnology in Catalysis, vol 1, chp1. Springer, NY, 2004.*

<sup>2</sup> K. M. Lewis, et al., US 7,153,991 (Dec 26, 2006); US 7,339,068 (Mar 4, 2008); US 7,429,672 (Sept. 30, 2008); US 7,652,164 (Jan 26, 2010); US 7,858,818 (Dec 28, 2010)

<sup>3</sup> K. M. Lewis, D. M. Rethwisch (Editors), *Catalyzed Direct Reactions of Silicon, Elsevier Science Publishers, 1993.* Chapter 1.

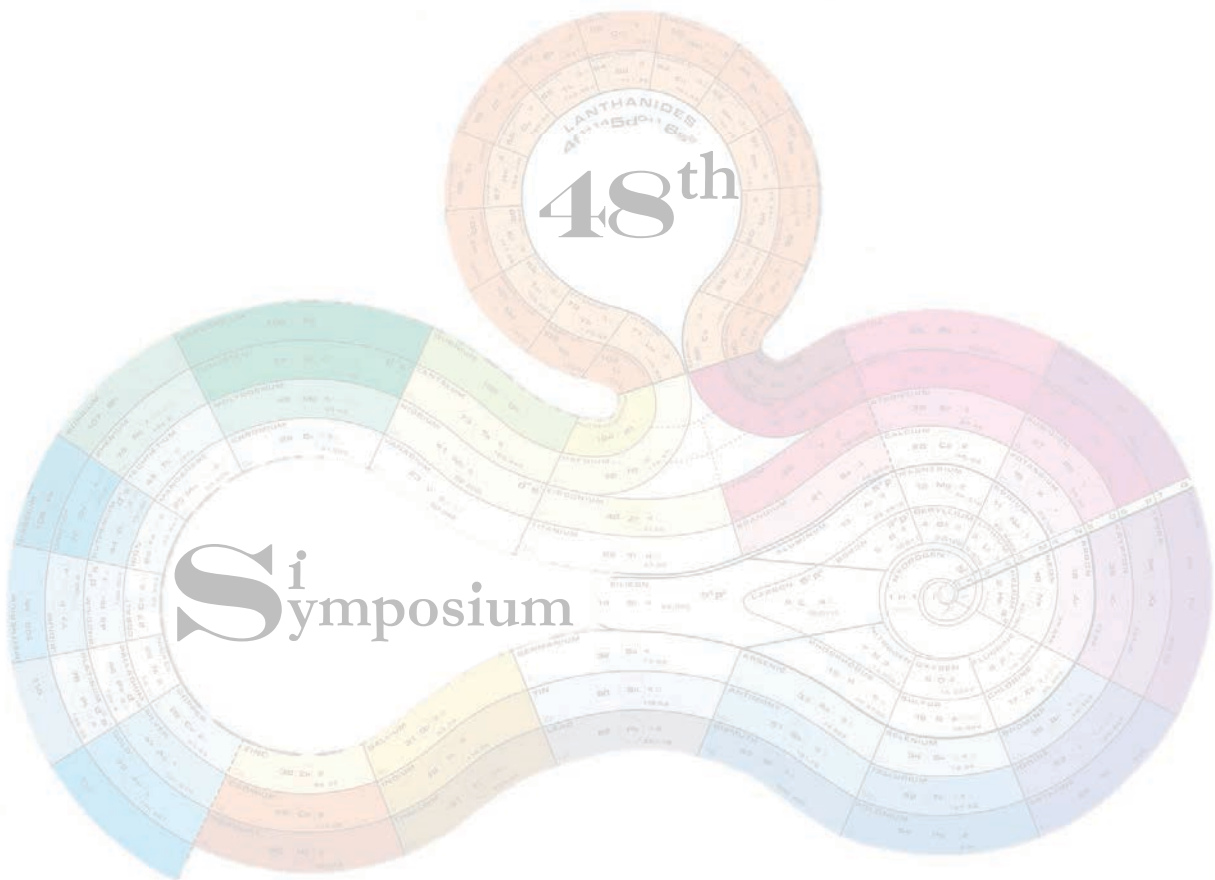
<sup>4</sup> K. M. Lewis, C-L. O'Young, A. T. Mereigh, S. R. Cromer, R. N. Eng, J. S. Ritscher, Direct Reactions of Silicon with Nanosized Copper and Copper Compounds as Catalyst Precursors, *Silicon for the Chemical Industry VI, H. Oye, et al (Editors), Tapir Press, Trondheim, Norway, 2002, pp 243-263*

<sup>5</sup> K. M. Lewis, H. Yu, R. N. Eng, T. E. Childress, F. D. Mendicino, T. A. Reed, Solvent Effects in the Direct Synthesis of Trimethoxysilane, *Silicon for the Chemical Industry IV, H. Oye, et al. (Editors), Tapir Publishers, Trondheim, Norway, 1998, pp 307 – 328, Geiranger, Norway, June 2 - 6, 1998*

---

# Short Lecture Abstracts

---





## SL-1 MECHANISM OF OLIGOMERIZATION OF N-HETEROCYCLIC SILYLENES INTO ZWITTER-IONIC SILENES

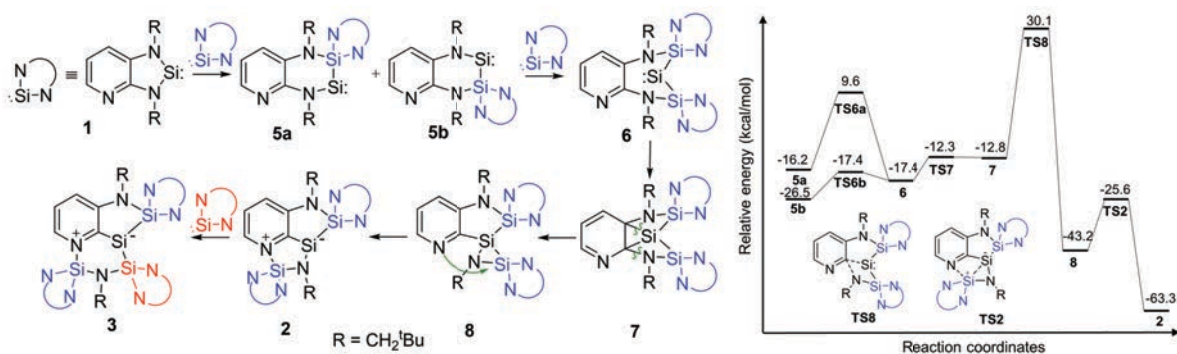
Andrey Yu. Rogachev,\* Alexander V. Zabula

Illinois Institute of Technology, Department of Chemistry, Chicago, IL, 60616  
University of Pennsylvania, P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, Philadelphia, PA 19104, USA  
andrey.rogachev@iit.edu, avzabula@gmail.com

The first representative of stable N-heterocyclic silylenes was prepared back in 1994,<sup>1</sup> shortly after the discovery of stable carbenes. Since then a great variety of cyclic systems with divalent silicon atoms has been prepared and their reactivity towards different substrates has been studied. Recently, we have found a remarkable example of thermal oligomerization of solid pyridoannulated silylene **1** at temperature above 60 °C into unprecedented tri- and tetrameric silenes **2** and **3**.<sup>2</sup> Resulting products are stabilized by zwitterionic distribution of electron density between low-valent silicon atom and adjacent pyridine ring. Here, we present comprehensive theoretical investigation of the mechanism of such an unusual transformation using tools of modern computational chemistry. Results obtained are in full agreement with available experimental observations. Fine tuning of the reaction mechanism by using other group 14 elements is also considered.

<sup>1</sup> Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. J. *Am. Chem. Soc.* **1994**, *116*, 2691.

<sup>2</sup> Zabula, A. V.; Guzei, I. A.; West, R.; Li, J.; Rogachev, A. Yu. *Angew. Chem. Int. Ed.* **2016**, *55*, 13465.



## SL-2 THE ADDITION OF ISOCYANIDES TO DISILENES: THE NEVER ENDING STORY

Nada Y. Tashkandi, Sarah McOnie, Jeremy L. Bourque, Kim M. Baines\*

*Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7  
kbaines2@uwo.ca*

One of the most important advances in inorganic chemistry over the last 30 years was the discovery of stable multiply bonded species of the heavier main group elements. The spectroscopic characterization of these unsaturated species has profoundly influenced our understanding of structure and bonding and the diverse reactivity of these compounds has provided facile entry into a number of previously unknown functional molecules. Even more exciting are the innovative applications of this chemistry that are now being explored.

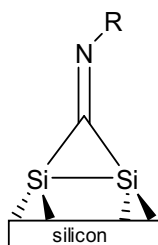
Our investigations into the chemistry of disilenes are guided by our fundamental interest in the cycloaddition chemistry of disilenes and our hypothesis that the chemistry of molecular disilenes can provide some important insights into the organic functionalization of Si(100) 2 x 1 reconstructed surfaces. In this lecture, the addition of isocyanides to tetramesityldisilene and a comparison to the addition of *t*-butyl isocyanide<sup>1,2</sup> to the Si(100) 2 x 1 surface as well as the addition of isocyanides to other molecular disilenes<sup>3,4</sup> will be presented.

<sup>1</sup> T. Kugler, C. Ziegler, W. Göpel, *J. Mol. Struct.* **1993**, 293, 257

<sup>2</sup> T. Kugler, C. Ziegler, W. Göpel, *Mater. Sci. Eng., B* **1996**, 37, 112.

<sup>3</sup> M. Majumdar, V. Huch, I. Bejan, A. Meltzer, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2013**, 52, 3516

<sup>4</sup> T. Iwamoto, N. Ohnishi, N. Akasaka, K. Ohno, S. Ishida, *J. Am. Chem. Soc.* **2013**, 135, 10606.



## SL-3 OSCILLATIONS IN THE $\mu$ SR SPECTRA OF MUONIATED ORGANOSILYL FREE RADICALS AND THEIR ORIGIN

Kerim Samedov,<sup>a</sup> Paul W. Percival,<sup>b</sup> Robert West<sup>c\*</sup>

<sup>a</sup> Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1

<sup>b</sup> Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC V5A 1S6 and TRIUMF, 4004 Wesbrook Mall, Vancouver, BC V6T 2A3

<sup>c</sup> Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison, WI 53706, USA

ksamedov@chem.ubc.ca, percival@sfu.ca, rwest@wisc.edu

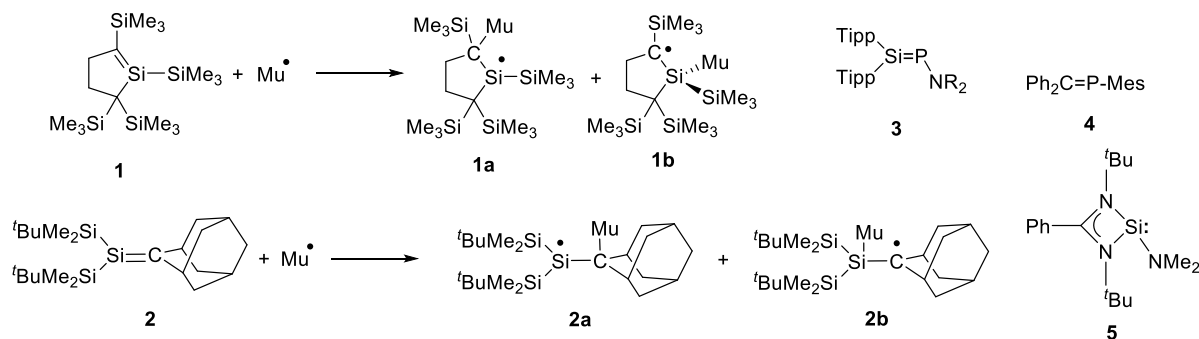
Muonium atoms (Mu), formed from positive muons generated at the TRIUMF cyclotron facility, can react with low-coordinate silicon compounds forming muoniated radicals of the latter, which are then studied by muon spin resonance spectroscopy ( $\mu$ SR). In 2008, the Kira silene **1**<sup>1</sup> was shown to react with muonium atoms (Mu) to form two radicals, **1a** and **1b**.<sup>2</sup> Adamantylidenesilene **2**<sup>3</sup> also yields a  $\mu$ SR spectrum that displays two radical species, **2a** and **2b**. A to date unprecedented oscillatory behavior was observed for the two  $\mu$ SR signals in this spectrum. Recently, similar oscillation phenomena have also been observed for a number of other compounds such as phosphasilene **3**, phosphalkene **4** and N-supported silylene **5**. A possible explanation for these remarkable observations will be offered and discussed.

<sup>1</sup> M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722–9725.

<sup>2</sup> B. M. McCollum, T. Abe, J.-C. Brodovitch, J. A. C. Clyburne, T. Iwamoto, M. Kira, P.W. Percival, R. West, *Angew. Chem. Int. Ed.* **2008**, *47*, 9772–9774.

<sup>3</sup> Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovski, *J. Am. Chem. Soc.* **1996**, *118*, 12228–12229.

<sup>4</sup> R. West, P. Percival, K. Samedov *unpublished results*.



## SL-4

### A Computational Study of (2 + 4) Retro-cycloadditions of Conjugated Planar Disilenes

Peter P. Gaspar,\* Alexander Seim

*Department of Chemistry Washington University in Saint Louis St. Louis, MO 63130-4899, USA*

(2 + 4) Cyclo adducts of planar disilenes to 1,3-butadiene tend to undergo concerted retro-additions, but the activation barriers for these reactions span a broad range of values. It has been found that those retro-additions with low barriers have transition states stabilized by delocalization in quasi-aromatic transition states. The symmetry of the butadiene adduct as well as the number of electrons delocalized in the retro-addition transition state play important roles in determining the activation barrier.

**Acknowledgment:** Financial support from the National Science Foundation under grant CHEM1213696 is gratefully acknowledged.



**SL-5****Electrophilic Substitution on Phenylsilsesquioxanes**

Richard M. Laine,<sup>a,c\*</sup> M. Bharami,<sup>a</sup> D. Hashemi,<sup>a</sup> J. Kieffer,<sup>a</sup> M. Moghadam,<sup>a</sup> M. F. Roll,<sup>a</sup> R. Tamaki,<sup>a</sup> J. Fungal,<sup>b</sup> T. Goodson III,<sup>b</sup> J. Kampf<sup>b</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

<sup>b</sup> Department of Chemistry, University of Michigan, Ann Arbor, MI, USA

<sup>c</sup> Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI, USA

talsdad@umich.edu, talsdad@umich.edu, mozhganbh100@gmail.com, hashemi@umich.edu, kieffer@umich.edu, mitrakh@umich.edu, mroll@uidaho.edu, Ryo.Tamaki@enersys.com, tgoodson@umich.edu, jkampf@umich.edu

Phenylsilsesquioxanes,  $[\text{PhSiO}_{1.5}]_{8,10,12}$  undergo a surprising number of novel electrophilic reactions that cannot be directly correlated with traditional concepts of electrophilic substitution at functionalized benzene. Although the  $T_8$ ,  $T_{10}$  and  $T_{12}$   $[-\text{SiO}_{1.5}]_x$  cages exhibit strongly electron withdrawing character equal to a traditional  $-\text{CF}_3$  group the phenyl rings can undergo electrophilic substitution at the ortho, meta or para positions depending on the reactants.

Thus, nitration, sulfonylation or acetylation give traditional meta substitution, whereas bromination goes almost exclusively ortho and iodination goes almost exclusively para providing diverse starting materials for a wide variety of hybrid materials applications. In this study, we examine the mechanisms involved that strongly suggest electronic effects not anticipated by the simple structures.

Theoretical modeling studies combined with extensive studies on the effects of electrophilic substitution on the title cage compounds, their photonic properties in particular indicate that the cage structures themselves strongly influence the electronic character of the transition state in the noted electrophilic reactions. A detailed understanding of the processes that transpire offers a facile new route to two faced (Janus) cages of potentially significant value for multiple fields of study.

## SL-6 SYNTHESIS AND REACTIONS OF JANUS PRISMS

Masafumi Unno,\* Kazunori Asami, Yuka Nagai, Yasunobu Egawa, Nobuhiro Takeda

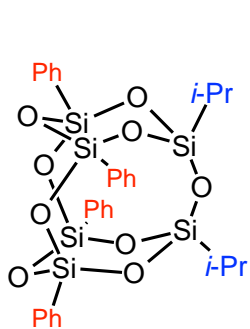
Department of Chemistry and Chemical Biology, Faculty of Science and Technology, Gunma University, Kiryu 376-8515, Japan  
unno@gunma-u.ac.jp

Following our synthesis and structure determination of Janus prism<sup>1</sup> and Janus cube<sup>2</sup>, we have investigated the synthesis of reactive cage silsesquioxanes. If we can selectively cleave bonds of cage silsesquioxanes, this could be a good precursor of well-defined materials.

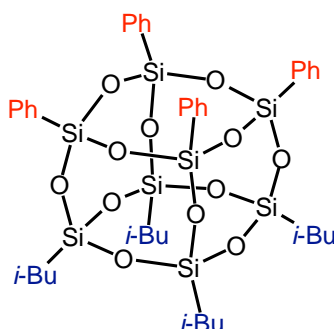
For this objective, we designed a new unsymmetrical cage hexasilsesquioxane containing a reactive part. Various reactions from this novel compound were examined, and new structures were developed.

<sup>1</sup> M. Unno, S. Tanaka, N. Takeda, 45th Silicon Symposium, Lubbock, Texas, **2013**.

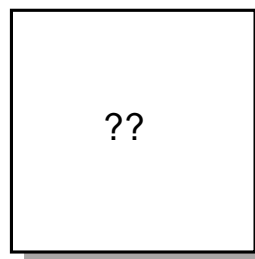
<sup>2</sup> N. Oguri, Y. Egawa, N. Takeda, M. Unno, *Angew. Chem. Int. Ed.*, **2016**, 55, 9336.



Janus prism



Janus cube



Reactive Janus prism

## SL-7

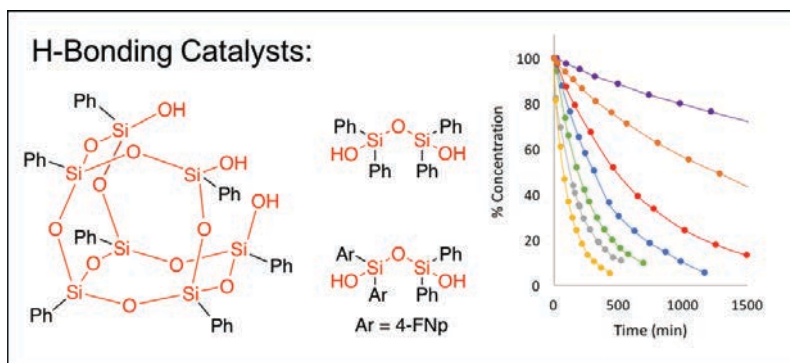
## INVESTIGATION OF HYDROGEN-BONDING ABILITY OF 1,3-DISILOXANEDIOLS AND POLYHEDRAL OLIGOMERIC SILSESQUIOXANES WITH APPLICATIONS FOR CATALYSIS

Kayla Diemoz, Jake Jagannathan, Annaliese Franz\*

Department of Chemistry, University of California Davis, One Shields Avenue, Davis, CA 95616, USA

kmdiemoz@ucdavis.edu, jrjagan@ucdavis.edu, akfranz@ucdavis.edu

The study of 1,3-disiloxanediols and incompletely condensed polyhedral oligomeric silsesquioxanes as hydrogen-bond donors is presented with applications for catalysis. Various 1,3-disiloxanediols have been synthesized in four steps or less, including naphthyl-substituted as well as unsymmetrical siloxane structures. POSS structures such as trisilanolphenyl-POSS have been previously studied for their hydrogen-bonding ability, however applications for hydrogen-bonding catalysis have remained unexplored. <sup>1</sup>H NMR spectroscopy binding studies with both neutral and ionic Lewis bases highlight the hydrogen-bonding ability of both disiloxanediols and POSS-silanols. Siloxanol-containing motifs have been demonstrated to act as catalysts through anion-binding as well as hydrogen-bonding activation. The catalytic activity of 1,3-disiloxanediols and POSS-silanols can be compared to silanols, silanediols and other disiloxanediol derivatives, providing insight into factors that can increase hydrogen-bonding ability such as Si-O-Si connectivity and cooperative hydrogen-bonding. To further probe how disiloxanediols and POSS-trisilanols act as hydrogen-bonding catalysts, reaction progress kinetic analysis (RPKA) was performed on several reactions. During kinetic studies, catalyst concentration was varied to study the effect of catalyst self-association and determine ideal reaction conditions for 1,3-disiloxanediols and POSS-trisilanols. Studying hydrogen-bonding and evaluating the degree of self-association of disiloxanediols and polyhedral oligomeric silsesquioxanes provides valuable insight into applications such as catalysis and molecular recognition.



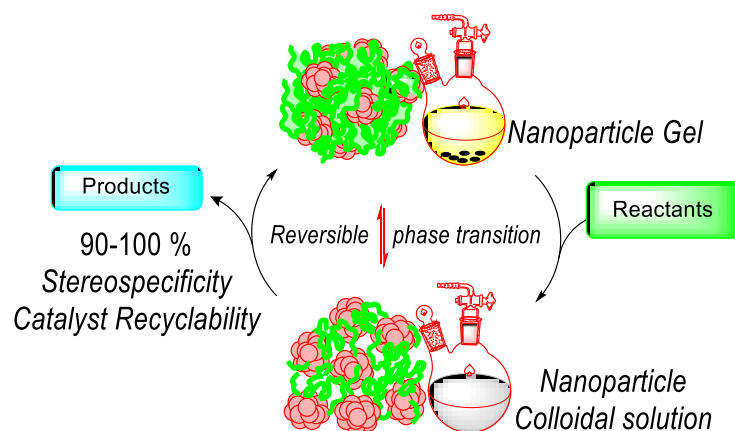
## SL-8 REVERSIBLE PHASE TRANSITION OF SILICONE-METAL NANOCONJUGATES

Bhanu P.S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University,  
300 Pompton Road, Wayne NJ, USA  
chauhanbps@wpunj.edu*

In recent years, our laboratory has been investigating new and industrially relevant routes to creating heterogeneous platforms of selectively cross-linked polysiloxanes, in which the metal nanoparticles are nucleated in desired concentration and morphology. We have observed that such “ensemble” of immobilized nanoparticles can act as highly efficient, mild and recyclable catalysts for various transformations. In these cases, during the catalysis, the air-stable solid catalyst first forms a homogeneous/dispersed phase with the reactant molecules and separates out at the end of reaction.

In this presentation, we will describe synthetic routes to mild, predictable, facile and widely applicable controlled polymerization/gelification of silicon agents to produce metal silica nanocomposites in one pot. Further reduction of the gel nucleated metals salts with functional silanes leads to the formation of silica stabilized metal nanoparticles, which can also be isolated in powder form. We will also present examples of such metal silica nanocomposites catalyzed transformations and demonstrate that such catalysts possess the advantageous attributes of both heterogeneous and homogeneous catalysts.



**SL-9****STRUCTURES AND GROWTH BEHAVIOR OF MLD FILMS USING CYCLIC AZASILANES, MALEIC ANHYDRIDE, TRIMETHYLALUMINUM AND WATER AS PRECURSORS**

Ling Ju, Nicholas C. Strandwitz\*

*Department of Materials Science and Engineering and Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA 18015, USA  
lij213@lehigh.edu, strand@lehigh.edu*

Molecular layer deposition (MLD) relies on self-limiting surface reactions for growth of organic or organic–inorganic hybrid, surface-bound polymers. Here, a four-step ABCD sequence using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), trimethylaluminum (TMA), and H<sub>2</sub>O and a three-step ABC sequence consisting of AZ, MA and H<sub>2</sub>O are reported for growing thin films.<sup>1</sup> The cyclic azasilanes possess high vapor pressure and reactivity for ring opening reactions upon exposure to -OH groups. The ABCD sequence exhibited self-limiting growth behavior with a constant growth rate of 3.5 Å/cycle at 100 °C, while the growth rate of the ABC sequence increased to 90 Å/cycle after approximately 50 cycles. The growth rate using the ABC chemistry is much larger than for MLD/ALD chemistries that involve exclusively surface reactions, and displayed a strong dependence on the substrate temperature, indicating that precursor diffusion into the ABC MLD film plays a key role in the large growth rate.

Thermal treatments in air decrease the thickness of both films. The density and dielectric constant ( $\kappa$ ) of ABCD films increased during annealing. In contrast, the ABC film exhibits a low density <1 g/cm<sup>3</sup>, and likely a high porosity after thermal treatment at 400 °C. The  $\kappa$  also remains below 3 for as-deposited and annealed ABC films. These may be useful in applications requiring porous and low- $\kappa$  films.<sup>1</sup>

In-situ quartz crystal microbalance (QCM) measurement monitors the mass gains during individual reactions, and provides detailed information of precursor diffusion behavior, such as diffusion coefficient and diffusion depth of different precursors. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements of the as-deposited and annealed films suggest the functionalities and chemical composition in the ABC and ABCD films, and provide evidence for the reaction mechanisms and structural evolution during annealing process. X-ray reflectivity (XRR) analysis indicates the density and porosity of films. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

<sup>1</sup> L. Ju, B. Bao, S. W. King, N. C. Strandwitz, J. Vac. Sci. Technol. A **35**, (2017).

## SL-10

## FUNCTIONALIZATION OF SILICA INTERFACIAL LAYER FOR HYBRID LITHIUM ION CONDUCTING GLASS CERAMICS AND POLYMERS

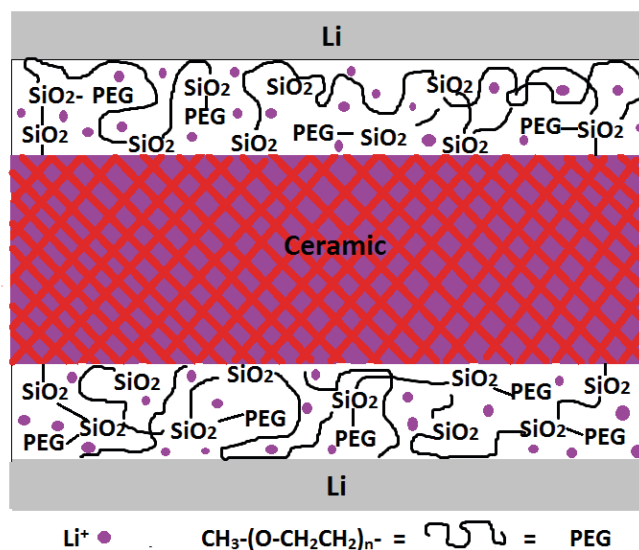
Parameswara Rao Chinnam, Megan Van Vliet, Michael Zdilla, Stephanie L. Wunder\*

Department of Chemistry, Temple University, Philadelphia, PA 19122, USA

chprbhu@temple.edu, mzdilla@temple.edu, slwunder@temple.edu

Solid electrolytes for lithium ion (LIB) and lithium metal (LMB) batteries would mitigate the safety problems associated with the flammable, volatile liquid electrolytes currently used. Both lithium ion conducting glass ceramics (LICGCs) and solid polymer electrolytes (SPEs) are currently under investigation to replace liquid electrolytes. The LICGCs have high conductivities but are brittle and often do not form good interfaces with one or both of the electrodes, while the SPEs have low conductivities but are flexible/processible and are more compatible with the electrodes. Thus, hybrid electrolytes formed from LICGCs and SPEs can benefit from their attributes and eliminate their disadvantages. However, there is typically a very high interfacial resistance between the ionic LICGC and the organic SPE, which can dramatically decrease the overall conductivity of the separator. Here we show (see Figure) that a nanometer thick silica ( $\text{SiO}_2$ ) layer deposited on the LICGC, functionalized with a polyethylene glycol (PEG)-silane containing a lithium salt ( $\text{LiX}$ ) and/or a silane with a pendant anion, dramatically reduces this interfacial resistance.<sup>1</sup> In addition, it forms a strong bond both with the LICGC and a polymer compatible with PEG. Single-ion conducting polymers (SICs) can also be directly grown from the  $\text{SiO}_2$  if there are appropriate functional groups on the silane.

<sup>1</sup> Chinnam, P. R.; Wunder, S. L. Engineered Interfaces in Hybrid Ceramic-Polymer Electrolytes for Use in All-Solid-State Li Batteries, *ACS Energy Letters* **2017**, 2, 134–138.



## SL-11 HYDROXYLATED SURFACE INDUCED COUPLING REACTIONS OF CYCLIC AZASILANES

Youlin Pan,\* Annalese F. Maddox, Taewoo Min, Jonathan Goff, Barry Arkles

Gelest, Inc., 11 East Steel Road, Morrisville, PA, 19067, USA  
ypan@gelest.com

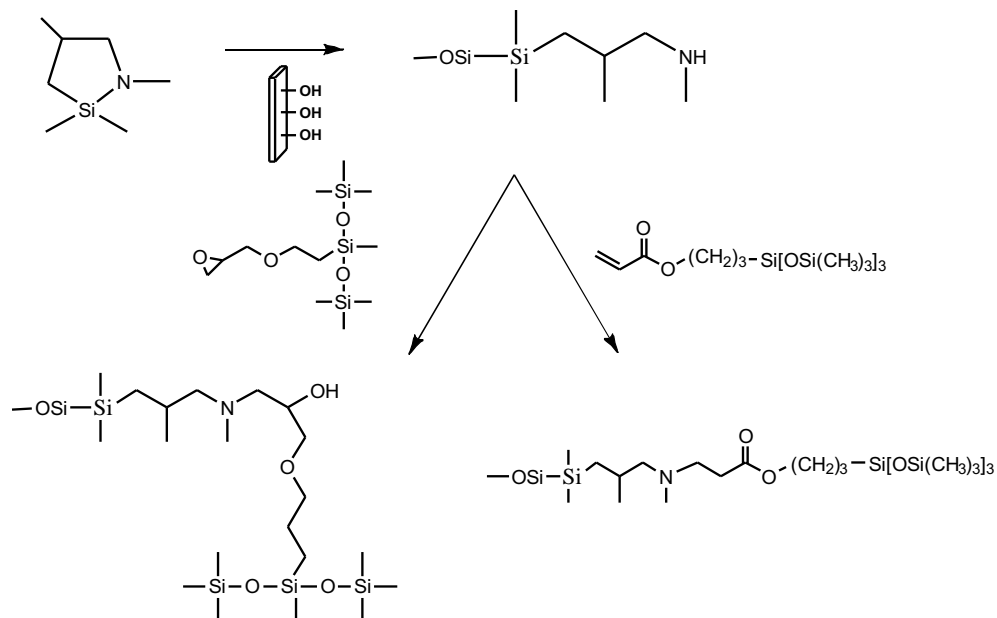
A series of cyclic azasilanes have been synthesized for the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles, nanocrystals, mesoporous materials and substrates.<sup>1,2</sup> N-methyl-aza-2,2,4-trimethylsilacyclopentane is representative of this class of compounds. Preliminary data from the treatment of hydroxylated surfaces such as fume silicas, glass, copper and oxidized silicon wafers, with cyclic azasilanes suggest high density monolayer deposition by a ring-opening reaction.<sup>3</sup>

Cyclic azasilanes contain cryptic amine functionality that can perform a subsequent 'tandem' coupling reaction with functional molecules after the surface triggered ring-opening reaction, allowing for a one-pot self-assembly route on nanostructures. Tandem coupling reactions are demonstrated via addition reactions of the cryptic amine with epoxy and acrylate systems.

<sup>1</sup> B. Arkles, Y. Pan, G. Larson, D. Berry in *Silanes and Other Coupling Agents Vol. 3* (Eds.: K. L. Mittal), VSP, 2004, p179

<sup>2</sup> D. Kim, J. Zuidema, J. Kang, Y. Pan, L. Wu, D. Warther, B. Arkles, M. Sailor, *JACS*. 2016, **118**, 1-5

<sup>3</sup> Y. Pan, A. Maddox, J. Goff, B. Arkles, *Chem. Asian J.* 2017, in print



## SL-12

### **CYCLOHEXASILANE ( $\text{Si}_6\text{H}_{12}$ , CHS) A SOURCE OF QUANTUM DOTS (SiQDs), NANOWIRES (SiNWs), NANORODS (SiNRs), CONDUCTING INKS, HIGHLY FUNCTIONALIZED RINGS AND 1-D POLYMERS**

Konstantin Pokhodnya, Kenneth J. Anderson, Matthew Frohlich, Ryan Schwiderski, Philip Boudjouk\*

*Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, USA*

*philip.boudjouk@ndsu.edu*

We present a brief overview of the utility of CHS as a useful source of a variety of materials that may point the way to a new generation of semiconducting materials, building blocks for uniquely structured materials as well as provide answers to fundamental questions surrounding the electronic structures of cyclopolysilanes.



## SL-13

**EVOLUTION OF THE PHOTOLUMINESCENCE PROPERTIES OF COLLOIDAL SILICON NANOPARTICLES OVER TIME AND WITH ENVIRONMENTAL CHANGES**

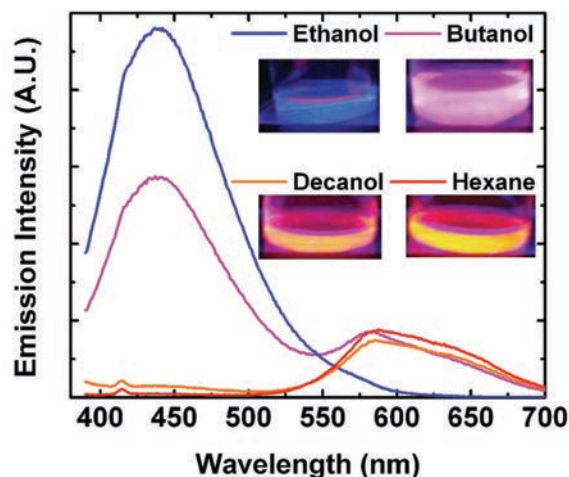
Andrea M. Goforth,<sup>\*</sup> Christine M. Radlinger, Rylie J. Ellison

Department of Chemistry, Portland State University, Portland, OR 97201, USA  
agoforth@pdx.edu

The origin of visible light emission from elemental silicon nanocrystals has been debated since the first observation of this phenomenon in the 1990's. Both porous Si (PSi), which contains matrix-embedded Si nanocrystals, and free-standing, colloidal silicon nanoparticles (Si NPs) have been synthesized using a variety of methods, and research efforts to correlate the photoluminescence (PL) properties of Si nanocrystals as a function of size and/or composition are abundant. There is general agreement that more than one luminescent decay pathway is available to the Si nanocrystal excited state, although there is ongoing debate on the assignments of these transitions to the chemical structures responsible for them. Versus PSi, reports of colloidal Si nanocrystal PL characteristics are in greater conflict as to the origins of emissive transitions, *i.e.*, the color centers that are responsible for the observed PL.

We propose that consensus concerning the variable observations and resulting assignments can be retrieved for colloidal Si NPs by accounting for the effects of surface chemical reactions that occur dynamically in solution. In this talk, we examine the reactivity of hydrogen-passivated Si NPs under a variety of solution conditions (*e.g.*, in the presence of O<sub>2</sub>, radical scavengers, radical initiators, oxidants, and UV-light), while monitoring changes to the Si NP PL spectra over time. Changes in size and surface composition are monitored using a suite of complimentary spectroscopy and microscopy techniques, and size/property and composition/property relationships are drawn. From these data and their analysis, an energy level diagram is proposed to account for the spectral and dynamic features observed, in which the role of surface states is highlighted.

<sup>1</sup> DeBenedetti, W.J.I.; Chiu, S.K; Radlinger, C.M.; Ellison, R.J.; Manhat, B.A.; Zhang, J.Z.; Shi, J.; Goforth, A.M. Conversion from Red to Blue Photoluminescence in Alcohol Dispersions of Alkyl-capped Silicon Nanoparticles: Insight into the origins of visible photoluminescence in colloidal nanocrystalline silicon. *Journal of Physical Chemistry C*, **2015**, DOI: 10.1021/acs.jpcc.5b01137.



## SL-14 SUB-NANO SCALE CHARACTERIZATION OF 1D AND 2D MATERIALS BY TERAHERTZ TECHNOLOGY

Anis Rahman,\* Aunik Rahman

Applied Research and Photonics, 470 Friendship Road, Suite 10 Harrisburg, PA 17111, USA  
a.rahman@arphotonics.net

Terahertz sub-surface imaging and spectroscopy offer an attractive solution for 1D and 2D materials for their size, defects and chemical nature. Terahertz 3D imaging with minimal sample preparation requirements and its ability to “see” below the surface with a resolution of <1 nm enables lattice level analysis. Another important property is the ability to inspect on a layer-by-layer basis via a non-contact and non-destructive route. Terahertz 3D imager designed at Applied Research and Photonics (Harrisburg, PA) has been used to demonstrate reconstructive imaging of both surface and 3D images for the analysis of silver iodide quantum dots, graphene, carbon nanotubes, and metal lines on Si wafer. Layer by layer image analysis has been outlined. Graphical analysis was used for particle size and layer thickness determinations. The results of particle size and layer thicknesses check well with those determined by TEM micrograph and powder X-ray diffraction analysis. The reported non-contact measurement system is expected to be useful for characterizing 2D and 3D nanomaterials as well as for process development and/or quality inspection at the production line. Semiconductor wafers’ defects may also be analyzed by this technique.<sup>1,2</sup> Fig. 1 exhibits the terahertz absorbance spectrum of GaN deposited on Si surface. Details of the technique along will be discussed in terms practical results.

<sup>1</sup> Anis Rahman, Aunik K Rahman, “Effective testing for wafer reject minimization by terahertz analysis and sub-surface imaging,” ASMC 2014, Saratoga Springs, NY, 978-1-4799-3944-2/14/\$31.00 ©2014 IEEE, pp. 151–155. [http://arphotonics.net/ASMC2014\\_5.8.pdf](http://arphotonics.net/ASMC2014_5.8.pdf)

<sup>2</sup> Rahman A, Rahman AK (2016), “Terahertz Spectroscopic Analysis and Multispectral Imaging of Epitaxially Grown Semiconductors with Nanometer Resolution.” J Biosens Bioelectron 7: 229. DOI: 10.4172/2155-6210.1000229.

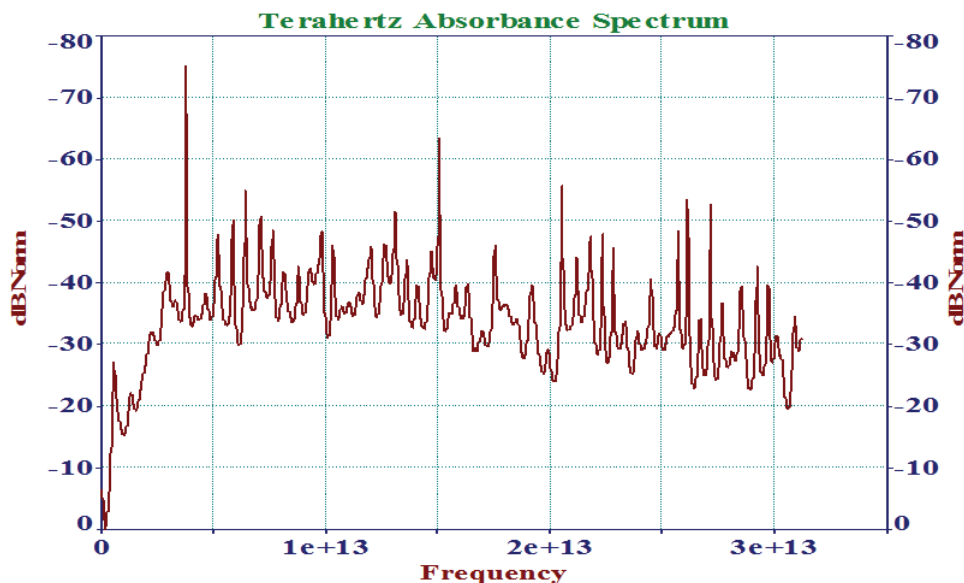


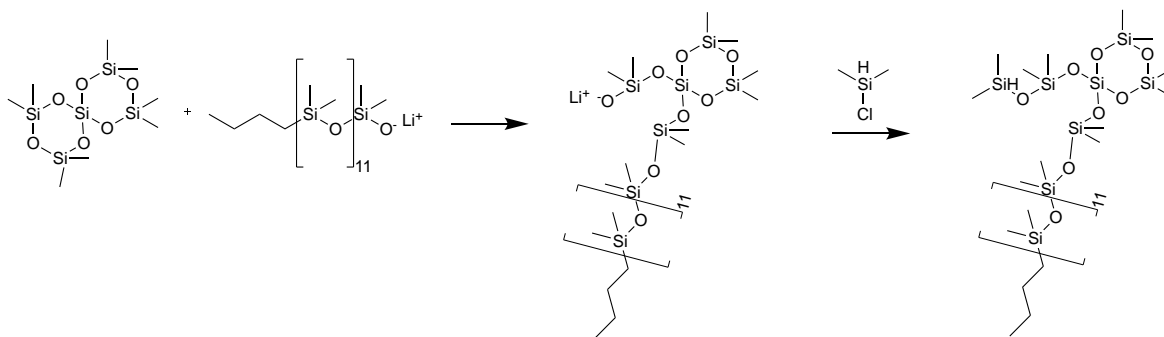
Fig. 1. Terahertz absorbance spectrum of GaN deposited on Si surface.

## SL-15 NOVEL SYNTHESIS OF A SPIROCYCLIC SILICONE AND SUBSEQUENT BRANCHING

Jennifer Morgan, Tong Chen, Michael A. Brook\*

*Department of Chemistry and Chemical Biology, McMaster University, 1280 Main St. W.,  
Hamilton ON, Canada L8S 4M1  
jmorgan@mcmaster.ca, chent38@mcmaster.ca, mabrook@mcmaster.ca*

The Piers Rubinsztajn (PR) reaction, which involves the use of a boron catalyst  $B(C_6F_5)_3$  to catalyze the condensation reaction between  $SiH$  and  $SiOR$  compounds, has been shown to be useful in synthesizing a variety of different silicone materials. In addition to dendrimers, elastomers and foams, the process has proven beneficial for the controlled preparation of highly branched silicones. During a study to use this process to create multifunctional dendrons, we instead discovered a route to the preparation of a spirocyclic silicone,  $QD_4$ , in good yield through a PR reaction with tetrakis(dimethylsiloxy)silane and water. In addition to the synthetic strategy, we will report on subsequent reactions involving  $QD_4$  and a live anionic silicone chain that is selectively able to ring-open only one of the two rings.



## SL-16

# STUDY OF A POLYDIMETHYLSILOXANE (PDMS) ELASTOMER GENERATED BY $\gamma$ IRRADIATION: CORRELATION BETWEEN PROPERTIES (THERMAL AND MECHANICAL) AND STRUCTURE (CROSSLINK DENSITY VALUE)

M. Meléndez-Zamudio,<sup>a\*</sup> A. Villegas,<sup>a</sup> J.A. González-Calderón,<sup>a†</sup> R. Meléndrez,<sup>b</sup> M. Meléndez-Lira,<sup>c</sup> J. Cervantes<sup>a</sup>

<sup>a</sup>Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Campus Guanajuato. Guanajuato, Gto., México.

<sup>a†</sup>Postdoctoral position at Universidad de Guanajuato.

<sup>b</sup>Departamento de Física, Cuerpo Académico de Física de Irradiaciones, Universidad de Sonora. Hermosillo, Son., México. rodrigo@ciencias.uson.mx

<sup>c</sup>Instituto de Ingeniería y Tecnología, Departamento de Física y Matemáticas, Universidad Autónoma de Ciudad Juárez. Ciudad Juárez, Chih., México. mlira@fis.cinvestav.mx

<sup>\*</sup>On sabbatical leave from Departamento de Física, Cinvestav-IPN.

ma.melendezzamudio@ugto.mx, vigaja@ugto.mx, amir.gonzalez@iqcelaya.itc.mx, jauregi@ugto.mx

The focus of the present investigation has been the detailed analysis of the correlation between the thermo-mechanical properties with the structure (crosslinking density value) of PDMS elastomers generated by  $\gamma$  irradiation (250, 300, 350 and 400 kGy) under O<sub>2</sub> atmosphere. The obtained elastomers show a strong structure-property dependence that is related with the crosslinking density value that is calculated by the Flory-Rehner equation<sup>1</sup>. The structural characterization of the obtained samples was performed by employing FTIR, XRD and <sup>29</sup>Si MAS NMR, showing the formation of methylene units that can serve as crosslink units (type-H) or as precursor for the formation of D<sup>OH</sup> units<sup>2</sup> (St. Pierre mechanism<sup>3</sup>) that contribute to the total population of siloxane crosslinks (type-Y) that increases with the irradiation dose. The mechanical and thermal characterizations were carried out by employing DMA, MDSC and TGA. The results showed an unexpected property (reversible change of the conformation, all-trans to gauche of the siloxane chain by effect of the temperature) related with the thermo-mechanical behavior displayed by the PDMS elastomer<sup>4</sup>. The results establish that the obtained elastomers are potential candidates to be used as Shape Changing Materials(SCM<sup>5</sup>). Such SCM are of great interest because of their potential mechanical and biocompatibility properties. This study also highlights the advantages that  $\gamma$  irradiation of PDMS can offer as an alternative route to obtain new siloxane-based materials. The authors want to thank CONACYT-México and the University of Guanajuato for financial support.

<sup>1</sup> A. M. Stricher, R. G. Rinaldi, C. Barrès, F. Ganachaud, L. Chazeau, RSC Adv. **5**, 53713 (2015).

<sup>2</sup> R. Huszank, D. Szikra, A. Simon, S. Z. Szilasi, I. P. Nagy, Langmuir **27**, 3842 (2011).

<sup>3</sup> L. E. St. Pierre, H. A. Dewhurst, J. Phys. Chem **64**, 1060 (1960).

<sup>4</sup> M. Meléndez-Zamudio, A. Villegas, J. A. González-Calderón, R. Meléndrez, M. Meléndez-Lira, J. Cervantes, J. Inorg. Organomet. Polym. Mater. **0**, 0 (2017). doi:10.1007/s10904-017-0503-2

<sup>5</sup> A. Lendlein, *Shape-Memory Polymers* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2010).

## SL-17 MICROSTRUCTURE VERSUS MECHANICAL PROPERTIES OF ORIGINAL SILICONE/THERMOPLASTIC ELASTOMER BLENDS

Constance Robeyns, Etienne Delebecq, Frédéric Lortie, François Ganachaud\*

INSA-Lyon, IMP, UMR5223, F-69621 Villeurbanne, France  
Hutchinson Research Center, Chalette-sur-Loing, France  
constance.robeyns@insa-lyon.fr, etienne.delebecq@cdr.hutchinson.fr, frederic.lortie@insa-lyon.fr, francois.ganachaud@insa-lyon.fr

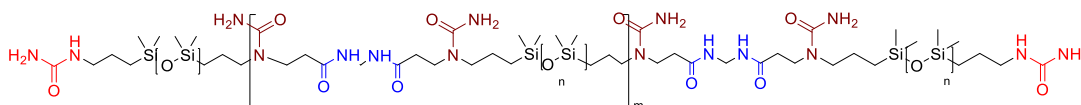
Silicones are important materials in the transportation industry for their many exceptional properties such as stiffness, damping, or linear mechanical behaviour in a broad range of temperatures. In order to improve these key material properties, specific additives such as silicone-urethane copolymers or silicone-urea copolymers<sup>1</sup> are believed to be of interest.

Here, different blends of a silicone gum and different silicone thermoplastic elastomers (TPEs) are presented. Processing, characterization and mechanical testing were done with several kinds of silicone-urea copolymers: two commercial TPEs (which have interesting damping properties<sup>2,3</sup>) and an original TPE structure, that was home-synthesized (fig. 1). The relationships between the microstructure, morphology and the mechanical properties are presented here with the help of imaging (TEM, see fig. 2) and mechanical testing (tensile tests and temperature and strain sweeps in DMA).

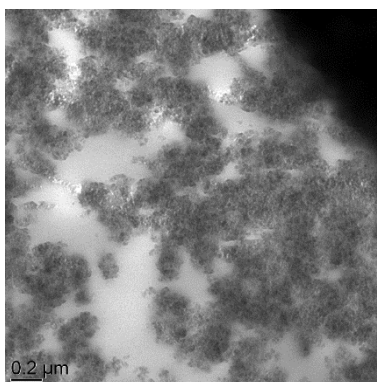
<sup>1</sup> J. Sheth et al., Polym. 45, 6919-6932 (2004)

<sup>2</sup> A. M. Stricher et al., RSC Adv. 5, 53713-53725 (2015)

<sup>3</sup> I. Yilgör, Prog. Polym. Sci., 39, 1165-1195 (2013)



**Figure 1:** Home-synthesized TPE



**Figure 2:** Morphology of a TPE-silicone base blend visible on TEM

## SL-18

## SEQUENTIAL FUNCTIONALIZATION OF A NATURAL CROSS-LINKER LEADS TO DESIGNER SILICONE NETWORKS

Scott E. Laengert, Alyssa F. Schneider, Eric Lovinger, Yang Chen, Michael A. Brook\*

McMaster University, Department of Chemistry and Chemical Biology, 1280 Main St. W, Hamilton, ON, L8S 4L8.  
laenges@mcmaster.ca

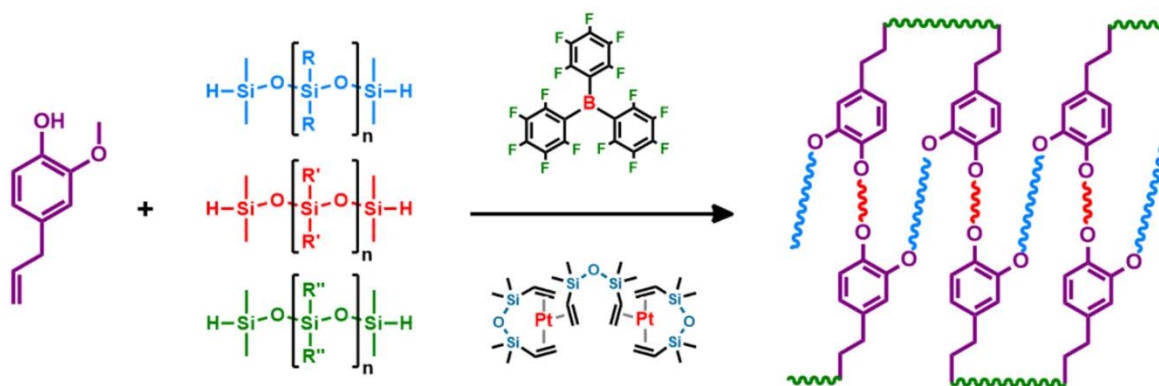
Silicone polymers, or polysiloxanes, are used in a wide variety of practical applications including medical implants, industrial sealants, and electronic insulators. Silicones can be produced in various forms, such as oils, gels, elastomers, hard plastics, and foams, but achieving precision control of network structures is challenging, since functional groups introduced in industrial processing are often randomly distributed along the silicone backbone.

We have developed a system for the construction of precise silicone networks using the natural product eugenol, an extract of cloves and other plants, by taking advantage of its triple functionality in a selective and sequential manner (Figure 1).<sup>1</sup> The boron-catalyzed Piers-Rubinsztajn reaction, using H-terminated silicones to create Si-O-C bonds, reacts fastest with the phenol group and slower with the methoxy group.<sup>2</sup> By adding a single equivalent amount of H-terminated silicone, the reaction at the phenol group takes place selectively, and subsequent addition of a second portion leads to reaction of the methoxy group. Adding a platinum catalyst and a third equivalent of Si-H leads to a hydrosilylation reaction of the silicone with the allyl group and the creation of an Si-C bond.<sup>3</sup> Remarkably, these two catalysts do not interfere with each other, and these three reactions can therefore be performed in any order, in the same reaction vessel, and without the need for workup of any kind. The result is that a variety of H-terminated polysiloxanes can be easily used to form chain extended polymers, elastomers, or foams in which the morphology of the material and its constituent parts can be manipulated at will.

<sup>1</sup> Laengert, S.; Schneider, A.; Lovinger, E.; Chen, Y.; Brook, M.A. Chemistry: An Asian Journal, In-Press.

<sup>2</sup> Grande, J.; Gonzaga, F.; Brook, M.A. Dalton Transactions, 2010, 39, 9369 – 9378.

<sup>3</sup> Grande, J.; Ulrich, T.; Dickie, T.; Brook, M.A. Polymer Chemistry, 2014, 5, 6728 – 6739.



**Figure 1:** Eugenol can react selectively with a variety of different H-terminated polysiloxanes to produce ordered silicone networks with tunable properties.

## SL-19 HYDROLYTIC STABILITY OF TRISILOXANE SURFACTANTS

Dr Chandres Surti,<sup>a</sup> John Bilney,<sup>a\*</sup> Christos Angeletakis<sup>b</sup>

<sup>a</sup> *Cornelius Specialties, 15C Rookwood Way, Haverhill, Suffolk, UK.*

<sup>b</sup> *Proteas Technologies, Bear, DE, USA*

*chandres.surti@cornelius.co.uk, john.bilney@cornelius.co.uk*

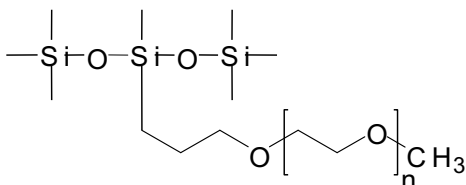
Trisiloxane surfactants (TSS) are commonly used in agriculture to improve penetration of sprayed pesticides in plants and other uses. Their unique wetting ability is due to the short siloxane backbone and the polyol fragment. However, their environmental persistence after their desired effect negatively impacts beneficial insects such as bees. The commercial materials are prepared by hydrosilylation and contain an Si-C bond. However, their preparation requires platinum catalysts and can contain significant amounts of unreacted allyl ethers and isomerized enol ethers, and these impurities are potentially toxic. As an example, Silwet L77 (Momentive, TSS1) is prepared by reaction of heptamethyl trisiloxane (HMTS) with PEG 350 allyl methyl ether. Analogs can also be prepared with an Si-O-C linkage, and these are expected to be more easily degradable since less stable toward hydrolysis than ones containing the Si-C bond. In this study, one such analog was prepared by the reaction of HMTS with PEG350 methyl ether via a solventless dehydrogenation reaction with a borane catalyst (TSS2). The relative rates toward hydrolysis of these two TSS types were measured by monitoring aqueous solutions by HPLC. Under acidic conditions TSS2 hydrolyzed much faster than TSS1. Under slightly basic conditions the hydrolysis rates for all three were similar.

<sup>1</sup> Journal of Inorganic Biochemistry 69 (1998) 203-207, Environmental degradation pathway for the breakdown of polydimethylsiloxanes.

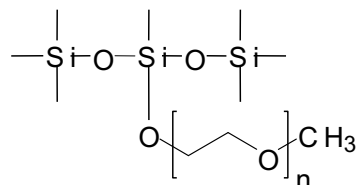
<sup>2</sup> Applied Organometallic Chemistry, 2004, 18, 28-39. Characterisation of synthetic and commercial trisiloxane surfactant materials.

<sup>3</sup> PhysOrg, 16 January 201. Common crop chemicals leaves bees susceptible to deadly viruses.

TSS1, n=ca7.5



TSS2, n=7



## SL-20

# EVOLUTION OF LIQUID SILICONE RUBBER TO ADVANCED OPTICAL MOLDABLE SILICONE MATERIALS

Michelle R. Cummings,\* William D. Inman Jr.

*The Dow Chemical Company, 2200 W. Salzburg Rd., Midland, MI 48686, USA  
michelle.cummings@dowcorning.com, william.inman.jr@dowcorning.com*

Liquid Silicone Rubber (LSR) are thermoset materials that offer properties that are not obtained by standard thermal plastic elastomers (TPE). LSR's bring long-term elasticity and toughness, excellent impact resistance, excellent dielectric properties, as well as long term stability and durability under challenging conditions such as high temperature, extreme low temperature, UV exposure, and high humidity.<sup>1</sup>

The evolution of lighting from traditional incandescent bulbs to light emitting diodes (LED) has necessitated the use of silicone materials in advanced Lamp and Luminaire applications. Optical moldable silicones incorporate the fundamental research and application understanding gained from experience in the LSR industry while bringing high optical clarity and high light transmittance. Optical clarity is achieved through the use of resin reinforced elastomer technology. Industrial lighting applications require both mechanical and optical stability under various temperatures, UV, and humidity conditions which optical moldable silicones deliver.

This paper presents the similarities and differences between the basic product composition and physical property attributes, and processing of liquid silicone rubber and optical moldable silicone materials.

<sup>1</sup> Ghanbari-Siahkali, A. and et al. (2005). "Investigation of the hydrothermal stability of cross-linked liquid silicone rubber (LSR), *Polymer Degradation and Stability*." *Polymer Degradation and Stability* **90**: 471-480

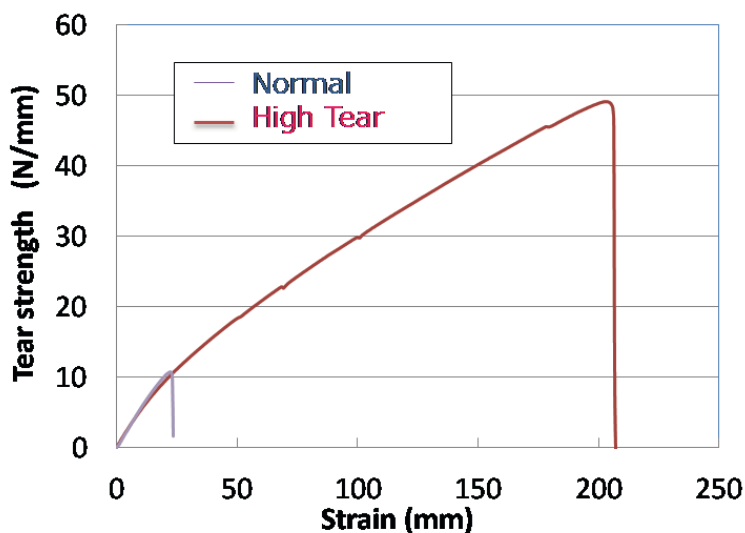


## SL-21 HIGH TEAR STRENGTH TRANSPARENT SILICONE ELASTOMERS WITH LOW HARDNESS AND HIGH ELONGATION

Kazunobu Senoo,\* Jun Okada, Motoki Sato, Chad M. Brick

Sumitomo Bakelite Co, Ltd. 1-1-5, Murotani, Nishu-ku Kobe, Hyogo, Japan 651-2241  
senoo@sumibe.co.jp

Silicone elastomers are used in countless applications because of their high thermal and chemical stability, and their flexibility over a wide range of temperatures. However, silicones are strongly susceptible to tear and have much lower tear strengths than other elastomeric polymers such as poly(ethylene) or poly(propylene). It is well known that the tear strength of silicone elastomers can readily be improved by the addition of fillers, most commonly silica, but the addition of filler also induces significant changes to other mechanical properties, such as increased hardness and modulus, and decreased elongation, that may not be desirable in all applications. In this study, we describe a series of silicone elastomers with high tear strength (>50 N/mm) maintained across the entire hardness range of 30-70 Shore A and unusually high elongation and low modulus compared to existing commercial products. Mechanical properties of the siloxanes as a function of filler loading, surface preparation, and base siloxane properties were evaluated. Dynamic Small Angle X-ray Scattering (SAXS) studies of the silicone elastomers in their highly elongated state will be discussed, as will the formation of sub-micron microparticles of these high-tear siloxanes for future use of these silicones as toughening agents in various thermosetting resin composites.



## SL-22 TETRAACYLGERMANES AS HIGHLY EFFICIENT PHOTOINITIATORS FOR DENTAL APPLICATIONS

Judith Radebner, Michael Haas, Harald Stueger\*

TU Graz, Institute of Inorganic Chemistry, Stremayrgasse 9, 8010 Graz, Austria  
j.radebner@tugraz.at, michael.haas@tugraz.at, harald.stueger@tugraz.at

Recently, acylgermanes and chemically related species attracted considerable attention due to possible applications as photoinitiators (PIs) or sources for germanium centered radicals.<sup>1-3</sup> For this purpose, we developed a novel and general approach towards the formation of these substances including the previously unknown tetraacylgermanes **3** by employing germyl anion **2** as a central intermediate (Figure 1).<sup>4</sup>

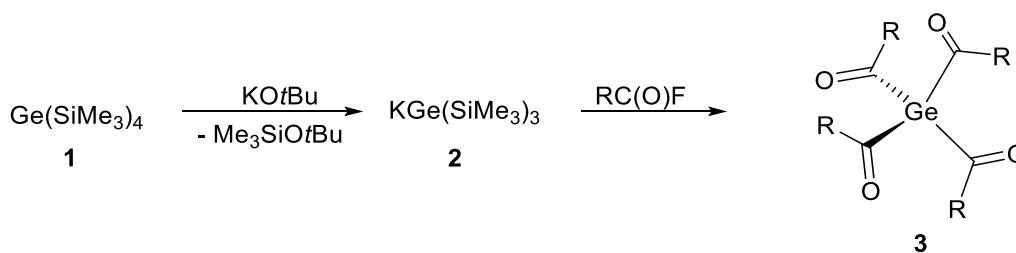
NMR-spectroscopy in combination with single crystal X-ray diffraction allowed full characterization of all prepared compounds, while UV-Vis spectroscopy revealed absorption maxima in the range of 400 nm. In this context, electronical and structural tuning of organic substituents induced bathochromic shifts as well as an increase in extinction coefficients, which are perfectly in consistence with performed TD-DFT calculations. Their low toxicity and fast photobleaching, even upon irradiation with high-wavelength visible light, demonstrate the superior potential as highly efficient photoinitiators for free-radical polymerization, especially for their use as PIs in dental filling materials.

<sup>1</sup> Neshchadin, D.; Rosspeintner, A.; Griesser, M.; Lang, B.; Mosquera-Vazquez, S.; Vauthey, E.; Gorelik, V.; Liska, R.; Hametner, C.; Ganster, B.; Saf, R.; Moszner, N.; Gescheidt, G. J. Am. Chem. Soc. **2013**, *135*, 17314.

<sup>2</sup> Lalevée, J.; Allonas, X.; Fouassier, J. P. Chem. Phys. Lett. **2009**, *469*, 298.

<sup>3</sup> Ganster, B.; Fischer, U. K.; Moszner, N.; Liska, R. Macromolecules. **2008**, *41*, 2394.

<sup>4</sup> Radebner, J.; et al. Angewan.Chem.Int.Ed. **2017**, *56*, 3103.



**Figure 1:** General approach for the step-economical formation of tetraacylgermanes **3**.

## **SL-23**

### **SUPERHYDROPHOBIC SURFACE COATINGS**

Susan H. Tilford,\* Jonathan Goff, Barry Arkles

*Gelest, Inc., 11 East Steel Road, Morrisville, PA 19067, USA*  
*stilford@gelest.com*

We are developing silane based hydrophobic and superhydrophobic surface coatings as a replacement for fluorinated surface treatments. The objective of this research is to create a line of coatings to provide tunable wettability for a variety of substrates and a wide range of applications. Using amino functionalized silanes and HMDZ treated fumed silica, we prepared coatings with excellent optical transparency and average water contact angles between 147° - 177°. The silane-silica surface treatments were applied to glass slides in a two-step process. This approach was successfully demonstrated with 1° and 2 amino functional silanes, chelating amino silanes, amino silanes with different length alkyl chains, amino functional siloxanes, and waterborne aminosilsesquioxanes. Current research efforts are focused on improving the durability of these coating systems.

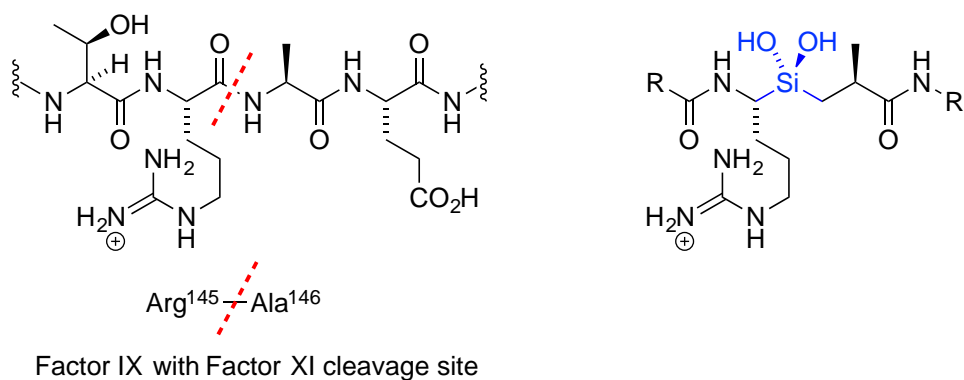
## SL-24 SILANEDIOL INHIBITORS OF THE COAGULATION CASCADE

Hoan Q. Duong,<sup>a,b</sup> Scott McN. Sieburth<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, Temple University, 1901 North 13<sup>th</sup> Street, Philadelphia, PA 19122, USA

<sup>b</sup> Present address: Department of Chemistry, Hanoi National University of Education, 136 Xuan Thuy str. Cau Giay dis., Hanoi, Vietnam  
hoandq@hnue.edu.vn, scott.sieburth@temple.edu

Coagulation is a carefully regulated biological pathway in which a cascade of serine proteases ("factors") activate other serine proteases ("factors"). This cascade activation ultimately leads to the production of thrombin, activating platelets and initiating fibrin formation. Factor XIa, an activated form of Factor XI, is a serine protease that cleaves Factor IX between alanine<sup>146</sup> and arginine<sup>145</sup>. FXIa is a prime target for therapeutic intervention. We have designed a set of Factor XIa inhibitors utilizing the central Ala-Arg dipeptide mimic. Control of stereochemistry utilized catalytic asymmetric hydrosilylation and the Davis chiral auxiliary.



## SL-25 CONTROLLING THE JUNCTION SWITCH: ASYMMETRIC KETONE REDUCTIONS USING 1-HYDROSILATRANE

Sami E. Varjosaari, Vladislav Skrypai, Thomas M. Gilbert, Marc J. Adler\*

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, 60115, USA  
svarjosaari@niu.edu, vskrypai1@niu.edu, tgilbert@niu.edu, mjadler@niu.edu

The reduction of prochiral ketones to chiral alcohols is a quintessential functional group manipulation in organic chemistry.<sup>1</sup> 1-Hydrosilatrane – a robust, inexpensive, easy to handle alkoxy silane derivative – has been shown to reduce carbonyls in the presence of Lewis base activators.<sup>2-3</sup> Therefore an appropriate chiral Lewis base could potentially induce enantioselectivity in prochiral ketones.<sup>4-6</sup> With this in mind, we have been able to obtain fair to excellent enantioselectivity using deprotonated chiral amino alcohols as activators. For example, acetophenone was reduced to (R)-phenylethanol with up to 99% yield and 85% e.e.

<sup>1</sup> Magano, J.; Dunetz, J.R. *Org. Process. Res. Dev.* **2012**, *16*, 1156-1184.

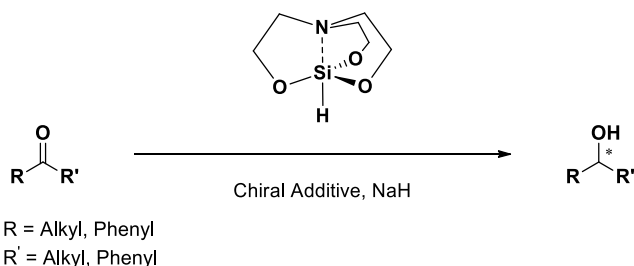
<sup>2</sup> Skrypai, V.; Hurley, J.M.; Adler, M.J. *Eur. J. Org. Chem.* **2016**, *12*, 2207-2211.

<sup>3</sup> Varjosaari, S.E.; Skrypai, V.; Suating, P.; Hurley, J.J.M.; Gilbert, T.M.; Adler, M.J. *Eur. J. Org. Chem.* **2017**, *2*, 229-232.

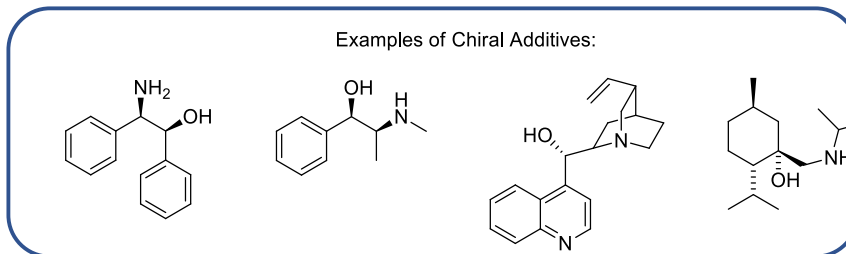
<sup>4</sup> Kohra, S.; Hayashida, H.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 89-92.

<sup>5</sup> Schiffers, R.; Kagan, H.B. *Synlett.* **1997**, 1175-1178.

<sup>6</sup> Gan, L.; Brook, M.A. *Can. J. Chem.* **2006**, *84*, 1416-1425.



Examples of Chiral Additives:



## SL-26

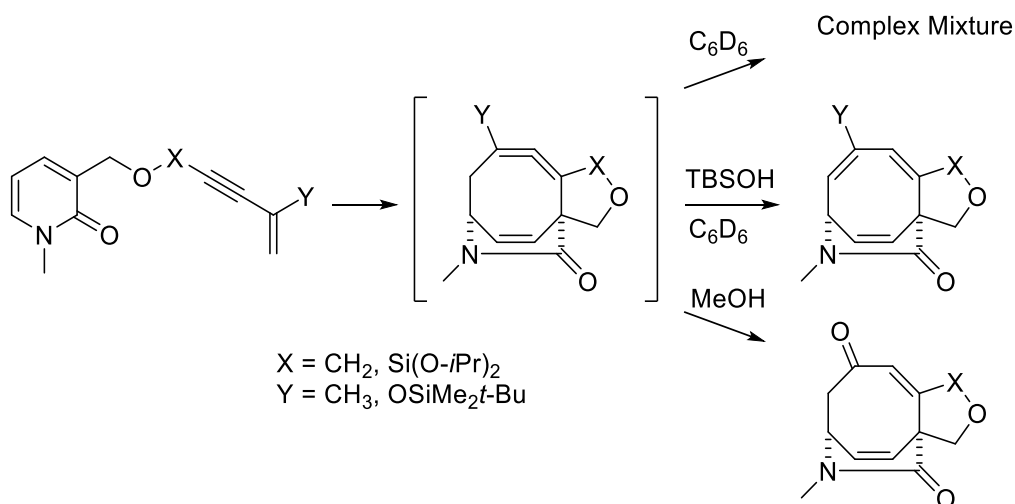
## SILANOLS AS A SELECTIVE PROTON SOURCE FOR THE PHOTOCHEMISTRY OF SILYL 3-ENOL-1-YNES.

Brenden P. Derstine, Buddha B. Khatri, Svitlana Kulyk, Scott McN. Sieburth\*

Department of Chemistry, Temple University, Philadelphia, PA 19122, USA  
 bderstine@temple.edu, sieburth@temple.edu

Intramolecular [4 + 4] photoreaction of 2-pyridones with silyl 3-enol-1-ynes yields a highly reactive 1,2,5-cyclooctatriene. In the presence of a silanol proton source the allene is converted into a 1,3-diene. Without the combination of silyl 3-enol-1-ynes and silanol, as previously reported with 1,3-enynes, complex mixture of dimers are observed.<sup>1</sup> Use of more nucleophilic solvents results in near quantitative yield of the cyclooctadienone through loss of silicon. Further manipulations of the cyclooctanoids allows for rapid scaffold diversification.

<sup>1</sup> S. Kulyk, B. B. Khatri, S. M. Sieburth; *Org. Lett.*, **2014**, *16*, 4138-4141.



## SL-27

## STEPWISE SUBSTITUTION OF ALKOXYSILANES TO FORM UNSYMMETRICALLY SUBSTITUTED MULTIFUNCTIONAL AMINOALKOXYSILANES

Lukas Zibula, Jonathan O. Bauer, Carsten Strohmann\*

TU Dortmund, Anorganische Chemie, Otto-Hahn-Str. 6, 44227 Dortmund, Germany  
 lukas.zibula@tu-dortmund.de, carsten.strohmann@tu-dortmund.de

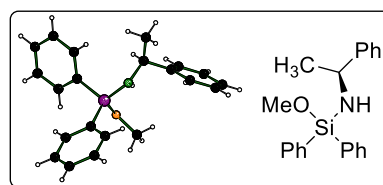
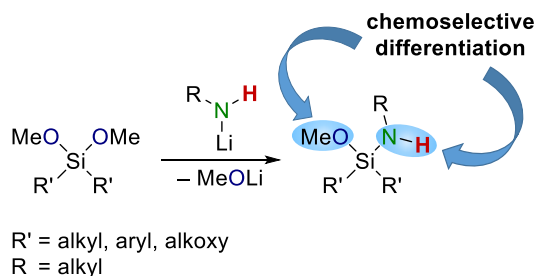
The Si–O bond is one of the most common chemical bond, which is consistent with the high affinity of oxygen for silicon. Also this is the reason for the generally known high sensitivity of Si–N bonds towards alcohols and water. In the past we developed a one-step conversion of methoxysilanes to aminosilanes. Here we present further synthetical potential of the substitution of silicon bonded alkoxygroups by lithium amides. Whereas this reaction is used very successfully with secondary amides,<sup>[1,2]</sup> a corresponding novel reaction with primary amides is hitherto unknown.

The use of primary amides leads to aminoalkoxysilanes with an acidic hydrogen atom, which allows further functionalisations and enables a variety of other applications.<sup>[3]</sup> For example, the Si–N and Si–O bonds can be chemoselectively distinguished, whereby an access to unsymmetrically disubstituted alkoxy silanes could be created. DFT calculations enable insight into the corresponding reactions. The variety of the used alkoxy silanes or amides, such as chiral amides, shows the applicability and universality of this remarkable substitution of alkoxy substituted silanes leading to N,O-functionalised organosilanes.

<sup>1</sup> J. O. Bauer, C. Strohmann, Chem. Commun., 2012, 48, 7212.

<sup>2</sup> J. O. Bauer, C. Strohmann, Angew. Chem. - Int. Ed., 2014, 53, 720.

<sup>3</sup> M. Veith, J. Böhnlein, Chem. Ber., 1989, 122, 603–607.



## SL-28 HIGHLY FUNCTIONALIZED STEREOGENIC SILICON CENTRES

Jonathan O. Bauer, Eva Barth, Christopher Golz, Carsten Strohmann\*

TU Dortmund, Anorganische Chemie, Otto-Hahn-Str. 6, 44227 Dortmund, Germany  
carsten.strohmann@tu-dortmund.de

Asymmetric synthesis and understanding the stereochemistry of silicon-chiral molecules is still a great challenge both from the preparative and the mechanistic point of view.<sup>1-4</sup> On the basis of our recently published one-step substitution of silicon-bonded methoxy groups by lithium amides,<sup>5</sup> we developed a novel highly stereoselective synthesis to form aminomethoxysilanes (**B**) with a diastereomeric ratio up to 99:1 and with silicon now being a defined stereogenic centre.<sup>6-8</sup>

This presentation will show different routes to silicon-chiral molecules bearing a complex substitution pattern, such as asymmetric siloxanes, silanols or siloxides.

<sup>1</sup> K. Kobayashi, T. Kato, M. Unno, S. Masuda, *Bull. Chem. Soc. Jpn.* **1997**, 70, 1393

<sup>2</sup> K. Igawa, J. Takada, T. Shimono, K. Tomooka, *J. Am. Chem. Soc.* **2008**, 130, 16132

<sup>3</sup> C. Strohmann, M. Bindl, V. C. Fraaß, J. Hörnig, *Angew. Chem. Int. Ed.* **2004**, 43, 1011

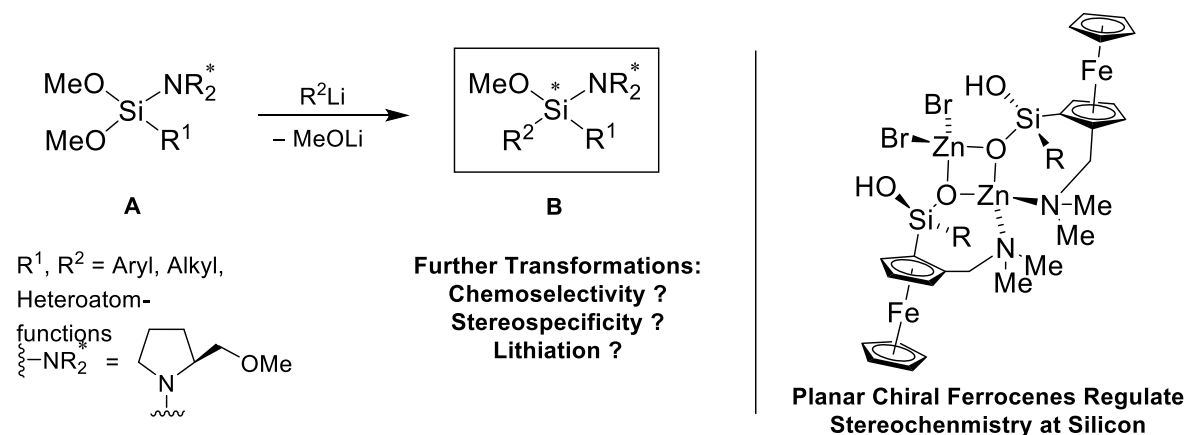
<sup>4</sup> J.O. Bauer, C. Strohmann, *Eur. J. Inorg. Chem.* **2016**, 2868.

<sup>5</sup> J. O. Bauer, C. Strohmann, *Chem. Commun.* **2012**, 48, 7212.

<sup>6</sup> J. O. Bauer, C. Strohmann, *Angew. Chem. Int. Ed.* **2014**, 53, 8167

<sup>7</sup> J.O. Bauer, C. Strohmann, *Angew. Chem. Int. Ed.* **2014**, 53, 720

<sup>8</sup> J.O. Bauer, C. Strohmann, *J. Am. Chem. Soc.* **2015**, 137, 4304.





**SL-29****STRATEGIC SYNTHESIS TARGETING COMPLEX POLYSILANES**

Eric M. Press, Eric A. Marro, Sravan K. Surampudi, Carlton P. Folster, Tapas K. Purkait, Rebekka S. Klausen\*

*Department of Chemistry, Johns Hopkins University, Baltimore, MD, 21218, USA*  
*klausen@jhu.edu*

Rational synthesis, the strategic choice of a sequence of chemical reactions that leads to a desired chemical target, is enormously powerful for the construction of complex chemical architectures. The application of rational synthesis to organic materials chemistry leads to the isolation of innovative and well-defined materials inaccessible by top-down methods, but the smaller synthetic toolkit available to the silicon chemist limits the role of strategic synthesis in the design and preparation of silicon nanomaterials for optoelectronic and biomedical applications. Yet increased structural complexity in polysilanes has great potential to lead to novel properties. We describe a synthetic approach to increasing the complexity of the polysilane framework itself. Embedded within the crystalline silicon lattice is a chair cyclohexasilane. Inspired by this structure, we target the synthesis of a class of polymers we have named poly(cyclosilane)s which contain repeating cyclosilane subunits.<sup>1</sup>

<sup>1</sup> Press, E. M., Marro, E. A., Surampudi, S. K., Siegler, M. A., Tang, J. A., Klausen, R. S. "**Synthesis of a Fragment of Crystalline Silicon: Poly(Cyclosilane)**" *Angewandte Chemie International Edition* 56, no. 2 (2017): 568–572. doi:10.1002/anie.201610208

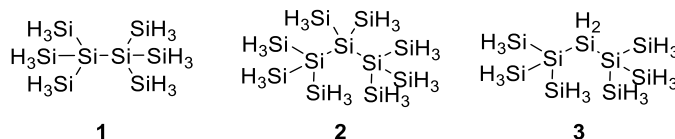
## SL-30 NEOPENTASILANE: THE IDEAL BUILDING BLOCK FOR HIGHER HYDROSILANES

Michael Haas,\* Viktor Christopoulos, Thomas Lainer, Harald Stueger

*Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria*  
michael.haas@tugraz.at

In the course of our ongoing studies on higher perhydrosilanes we recently published the selective synthesis and derivatization of the alkali-metal silanide  $\text{LiSi}(\text{SiH}_3)_3$  starting from neopentasilane  $\text{Si}(\text{SiH}_3)_4$ .<sup>1</sup> Based on this research in this lecture convenient synthetic methods to obtain 2,2,3,3-tetrakisilyltetrasilane **1**, 2,2-(trisilane-2,2-diyl)bis(2-silyltrisilane) **2** and 2,2,4,4-tetrakisilypentasilane **3** in good yields are described. Furthermore, the potential of **1**, **2** and **3** for solution based deposition of silicon films will be discussed. To the best of our knowledge, all three compounds are the first silicon hydrides  $\text{Si}_n\text{H}_{2n+2}$  with  $n \geq 8$  reported in the literature which have been synthesized and isolated in preparative amounts. All compounds were characterized by standard spectroscopic techniques including NMR spectroscopy, mass spectroscopy and X-ray crystallography. For Si-H derivatives, the coupled <sup>29</sup>Si-NMR spectra were analyzed in detail to obtain an unequivocal structural assignment. Their unique performance for silicon film deposition is demonstrated in UV-Vis studies.

<sup>1</sup> H. Stueger, T. Mitterfellner, R. Fischer, C. Walkner, M. Patz, S. Wieber *Chem. Eur. J.* **2012**, *18*, 7662–7664.



## SL-31 MECHANISTIC ASPECTS OF THE ROCHOW DIRECT PROCESS

Genqiang Xue,\* Van V. Green

*The Dow Chemical Company, 4770 Highway 42 East, Carrollton, Kentucky 41008, USA  
g.xue@dowcorning.com*

The Rochow Direct Process involves reaction of silicon with methyl chloride to synthesize methyl chlorosilanes (MCS), which are used in various silicone products. Understanding fundamental mechanisms of this reaction is critical for improving product selectivity and material efficiency. The first part of this paper surveys literature about side-reactions and by-products related to methyl group decomposition. The formation of coke deposition, hydrocarbons, hydrogen gas, and MCS containing a Si-H bond or a Si-CH<sub>2</sub>-Si moiety is discussed. The involvement of C-H bond cleavage as a rate-determining-step for methyl group decomposition is also assessed. The second part reports new methods for studying the reaction of silicon with cuprous chloride (CuCl). Silicon tetrachloride (SiCl<sub>4</sub>) yield from this reaction was measured by a GC method with short cycle-time. The onset temperature was also studied by coupling a chemisorption analyzer with a mass spectrometer.

## SL-32 THE EFFECT OF WATER ON THE PIERS-RUBINSZTAJN REACTION

Alyssa F. Schneider, Mengchen Liao, Michael A. Brook\*

McMaster University, Department of Chemistry and Chemical Biology, 1280 Main St. W.,  
Hamilton ON Canada L8S 4M1.

*schnea3@mcmaster.ca, liaom6@mcmaster.ca, mabrook@mcmaster.ca*

The Piers-Rubinsztajn reaction (PR) is one of many synthetic methods available to create silicones. The reaction involves the dehydrocarbonative condensation of a hydrosilane and an alkoxy silane catalyzed by  $B(C_6F_5)_3$  (BCF) and provides synthetic benefits to the alternative use of tin or platinum-based catalysts. The PR reaction proceeds rapidly at room temperature in an open vessel and can be used to create precise silicones,<sup>1</sup> copolymers, elastomers, foams<sup>2</sup> and resins.

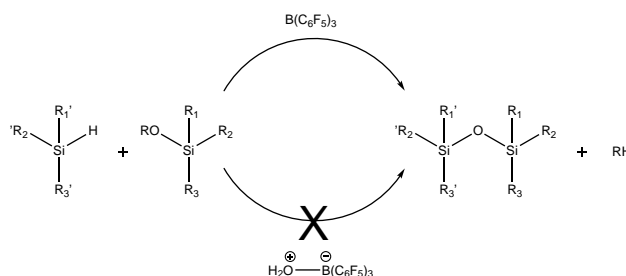
Our experience with the PR reaction shows marked difference in reactivity as a function of moisture in the atmosphere, in the reagents and particularly in the catalyst. Although  $B(C_6F_5)_3$  is generally tolerant to water,<sup>1</sup> the PR reaction proceeds much more slowly when relative humidity is high (~80%), compared to when humidity is low (~20%).

Traditionally, it is understood that the role of water in the PR reaction is to participate in the formation of a Lewis acid-base pair with  $B(C_6F_5)_3$  that must first dissociate before catalysis can occur.<sup>3</sup> It seems that the situation is somewhat more complex than that; the history of exposure of the catalyst to  $H_2O$  is much more important in this reaction than of the other reagents. A systematic study of reaction outcomes as a function of water concentration will be presented. The role of water as a competing reagent, rather than an inhibitor will be discussed.

<sup>1</sup> Grande, J. B.; Ulrich, T.; Dickie, T.; Brook, M. A., Silicone dendrons and dendrimers from orthogonal SiH coupling reactions. *Polym. Chem.* **2014**, *5*, 6728-6739.

<sup>2</sup> Grande, J. B.; Fawcett, A. S.; McLaughlin, A. J.; Gonzaga, F.; Bender, T. P.; Brook, M. A., Anhydrous formation of foamed silicone elastomers using the Piers-Rubinsztajn reaction. *Polymer* **2012**, *53*, 3135-3142.

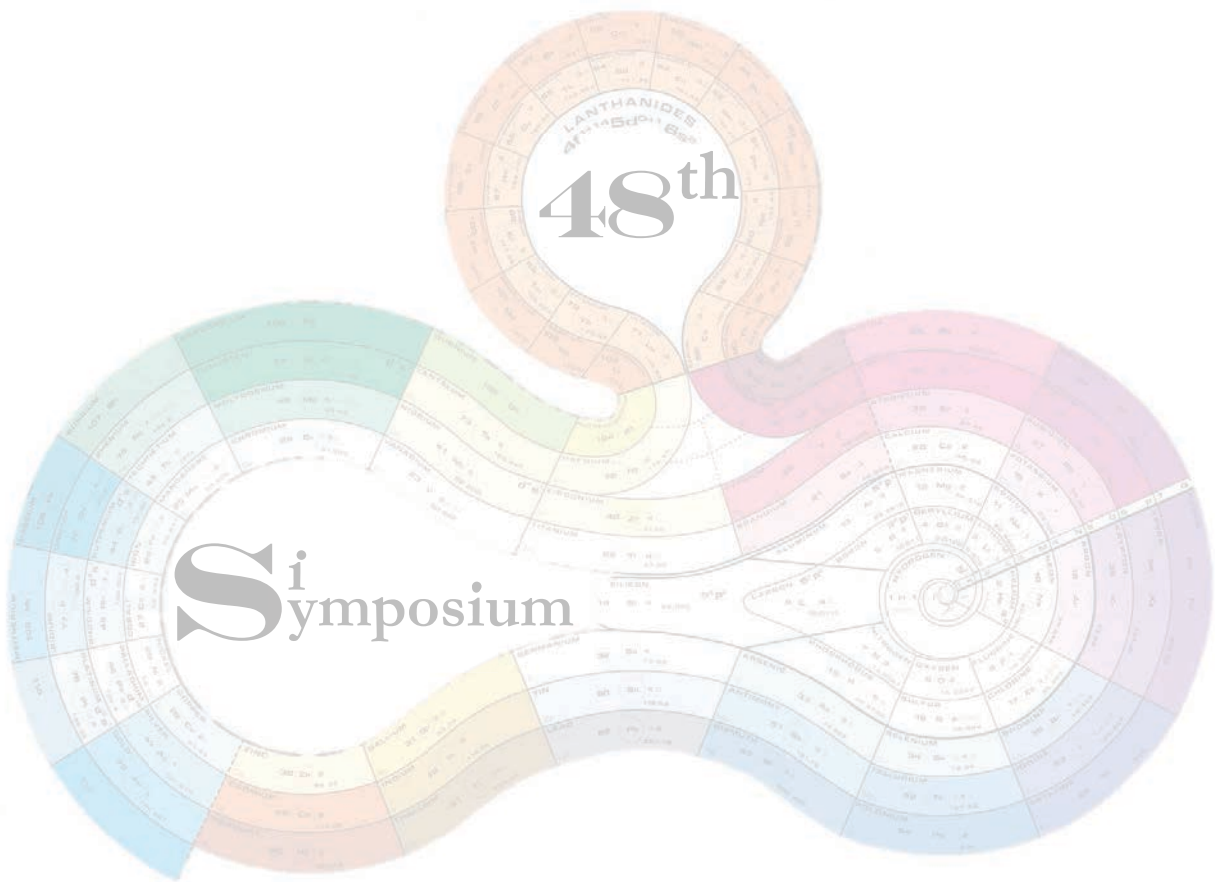
<sup>3</sup> Piers, W. E., The chemistry of perfluoroaryl boranes. *Adv. Organomet. Chem.* **2005**, *52*, 1-77.



---

# Poster Abstracts

---





**P-1****SYNTHESIS OF NOBLE METAL NANOPARTICLES COATED WITH POLYSTYRENE FOR THE APPLICATIONS OF PLASTICS**

Natasha Ampomah, Kelly Moran, Qiaxian Johnson, Bhanu P. S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, 300 Pompton Road, Wayne NJ, USA*  
*ChauhanBPS@wpunj.edu*

Applications of gold nanoparticles in today's industries have increased significantly due to their tailorable properties; such as the changing of their size, shape, surface chemistry, and aggregation state.<sup>1</sup> Their versatile surface chemistry allows one to coat the nano sized particles with small molecules, polymers, and bio macro molecules.<sup>1</sup> Recent years, we have described synthesis of highly active metal core nanoparticles decorated with functional silane, n-(2-aminoethyl)-3 aminosilanetriol (2-AST). In these systems, we have found that 2-AST complexes the metal precursors and leads to their reduction to furnish stabilized nanoparticles with high efficacy.<sup>2</sup> In this research, we have been investigating a new system where an organic community polymer is used for the production of high-end metal nanoparticles decorated and controlled with organic and inorganic hybrid polymers. For this purpose, we decided to use polystyrene, a vinyl polymer (C<sub>8</sub>H<sub>8</sub>)<sub>n</sub> which is insoluble in polar solvents and requires emulsifiers. We decided to use this polymer because of the utility of polystyrene in the production of disposable plastic, license plate frames, and other objects where rigid, economical plastics are needed.

In this research, we will describe a new approach where sonication of 2-AST stabilized gold nanoparticles, which serve as a nucleating agent with polystyrene, is investigated. We have discovered that copolymerization of 2-AST and polystyrene leads to the formation of hybrid fibers, which are reinforced with gold nanoparticles. We will present the synthetic variables for creating such new inorganic organic polymer embedded gold nanoparticles. We will describe surprising high yield formation of fibers from solution during the sonication process. One crucial advantage of this process is that it takes around 15-30 minutes to complete. We will summarize our synthetic studies and detailed characterization new products using NMR, TEM, SEM/EDS, FT-IR, and UV-Vis techniques.

<sup>1</sup> *Gold Nanoparticles: Past, Present, and Future*, Rajesh Sardar, Alison M. Funston, Paul Mulvaney, Royce W. Murray, **Langmuir**, **2009**, 25 (24), pp 13840–13851 (1B)

<sup>2</sup> *Generation of Zerovalent Metal Core Nanoparticles Using n-(2-aminoethyl)-3-aminosilanetriol* Johnson, Q.R.; Matam, S. ; Patel, A. ; Moran, K. ; Onyechi, B. ; Chauhan, B.P.S. **J. Vis. Exp.** **2016** (108): doi: 10.3791/53507

<sup>3</sup> *Upconversion Nanoparticles: Design, Nanochemistry, and Applications in Theranostics* Guanying Chen, Hailong Qiu, Paras N. Prasad, Xiaoyuan Chen **Chem. Rev.**, **2014**, 114 (10), pp 5161–5214

## P-2 METHODOLOGY AND EPR STUDIES OF AN ENANTIOSELECTIVE COPPER(II)-CATALYZED SILYL-SPIROCARBAMATE FORMATION

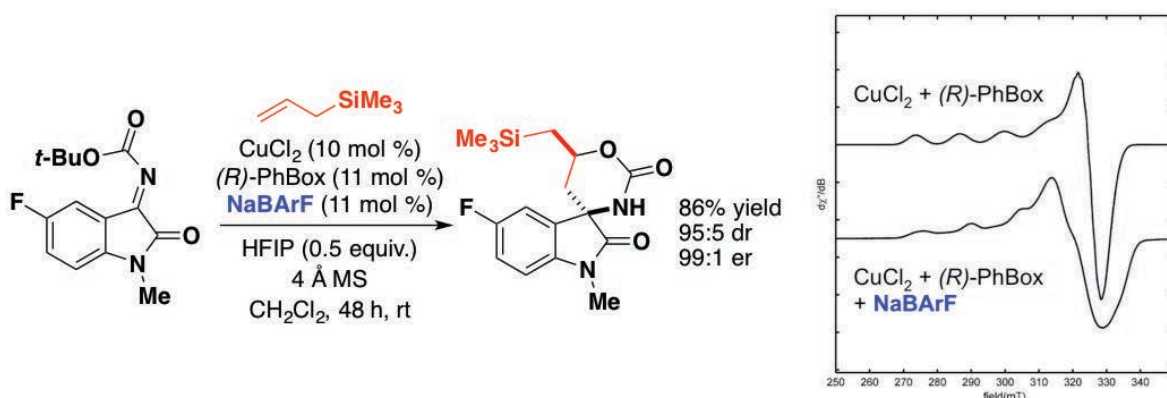
Brittany Armstrong, Richard Saylor, Benjamin Shupe, Benjamin Wigman, R. David Britt, Annaliese K. Franz\*

Department of Chemistry, University of California, Davis, California, One Shields Avenue, Davis, CA 95616, USA

barmstrong@ucdavis.edu, risaylor@ucdavis.edu, akfranz@ucdavis.edu

We have developed several stereoselective allylsilane additions to oxindole-based cores enabled by the unique reactivity of allylsilanes. Allylsilanes are versatile nucleophiles that exhibit a divergent reaction pathway based on the identity of the groups attached to silicon. We have previously demonstrated the Cu(II)-catalyzed cyclization of allylsilanes with *N*-Boc-iminooxindoles to yield spirocarbamate oxindoles.<sup>1</sup> An asymmetric variant, which proceeds with good yield and excellent diastereo- and enantioselectivity, has been developed in tandem with mechanistic studies to obtain information about the catalyst complex. The rate of reaction and overall conversion is greatly enhanced by essential additive sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (NaBARF). In addition to creating a cationic Lewis acidic complex, it is hypothesized that NaBARF contributes to the stabilization of the  $\beta$ -silyl carbocation which forms upon addition to the electrophile. Allylsilane oligomerization experiments were conducted and indicate that NaBARF plays a significant role in the stabilization of the  $\beta$ -silyl carbocation, which is an intermediate in the oligomerization process. The spiroannulation exhibits a dramatic positive nonlinear effect (+-NLE). Electron paramagnetic resonance (EPR) spectroscopy is used to study speciation of Cu(II) complex in both enantiopure and racemic conditions. EPR sheds light the role of NaBARF and other additives, and identifies the complex responsible for the (+)-NLE. This study not only sheds light on the allylsilane addition reaction and highlights EPR as a useful technique to study this system, but also provides valuable information about the Cu(II)-Box complex, a widely-utilized catalyst complex in asymmetric catalysis.

<sup>1</sup> Shupe, B. H.; Allen, E. E.; MacDonald, J. P.; Wilson, S. O.; Franz, A. K. *Org. Lett.* **2013**, *15*, 3218.





**P-3****THE CATALYTIC ACTIVITY OF A NEW GENERATION PT NANO-GEL CATALYST**

Bhanu P. S. Chauhan,\* [Daniela Artiga](#), Qiaxian Johnson, Aarti Patel

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, 300 Pompton Road, Wayne, NJ, USA*  
*ChauhanBPS@wpunj.edu*

The synthesis of hybrid nanosystems offers the opportunity to generate materials with unique properties that can be utilized in various applications such as catalysis.<sup>1,2</sup> Being able to control the shape, size, composition and porosity of a nanogel systems, can enhance their stability and efficiency.<sup>3</sup> The co-gelification of polymers with distinct functionality provides an advantage in the nanogel catalytic activity in terms of recoverability, recyclability and reusability.<sup>4</sup> We have shown the feasibility in the cross-polymerization of cis-Polybutadiene to a siloxane chain using both a palladium and platinum catalyst.<sup>5</sup> Due to the versatility, modifiability, defined microstructure and inexpensive nature of polybutadienes, makes them practicable polymer support of choice.

In this work, we will present our results on the generation and the catalytic activity of a platinum nanoparticle hybrid gel, synthesized using cis-polybutadiene and polymethylhydrosiloxane (PMHS) nanoreactors. It was observed that the polymerization of cis-PBD and PMHS via the reduction of the alkene led to the formation of a sterically stable Pt supramolecular polymer gel. The hybrid nanogels were found to have catalytic activity leading to the hydrosilylation reaction of styrene and dimethylethoxysiloxane while exhibiting recoverability and recyclability. We will present the TEM, NMR, XRD and FTIR analysis of the Pt hybrid nanogel.

<sup>1</sup> Bhanu P.S. Chauhan, Alok Sarkar, Moni Chauhan "New and Future Developments in Catalysis: Catalysis by Nanoparticles", Eds. S. Suib; 2013, Pages 375–400

<sup>2</sup> Philippot, K.; Serp, P. *Concepts in nanocatalysis. In Nanomaterials in Catalysis, 1st ed.*; Philippot, K., Serp, P., Eds.; Wiley-VCH Verlag GmbH, Co., KgaA: Weinheim, Germany, 2013;1–54.

<sup>3</sup> Rakesh K. Sharma, Manavi Yadav, Yukti Monga, Rashmi Gaur, Alok Adholeya, Radek Zboril, Rajender S. Varma, Manoj B. Gawande, *ACS Sustainable Chem. Eng.* **2016**, 4, 1123–1130 (2B) Xiao, C., Chen, S., Zhang, L., Zhou, S., Wu, W. *Chemical Communication* **2012**, 48, 11751-11753.

<sup>4</sup> Corma, A.; Garcia, H. Crossing the borders between homogeneous and heterogeneous catalysis: Developing recoverable and reusable catalytic systems. *Top Catalysis* 2008, 48, 8–31.

<sup>5</sup> Artiga, D.; Castelar, E.; Patel, A.; Matthews, S.; Chauhan, B.P.S. *The Role of Polybutadiene in the Synthesis of Novel Hybrid Metal Catalysts*. 10<sup>th</sup> Annual Undergraduate Research Symposium in the Biological and Chemical Sciences, Wayne, NJ, April, 9.

## P-4 INTRODUCING THE SI-F BOND INTO SILYLATED PYRROLIDINES

Jonathan O. Bauer,<sup>†</sup> Swen Weber, Carsten Strohmann\*

*Anorganische Chemie, Technische Universität Dortmund, D-44227 Dortmund, Germany*

*† Current address: Institut für Anorganische Chemie, Universität Regensburg, D-93053,*

*Regensburg, Germany*

*mail@carsten-strohmann.de*

In 2010, we and others reported on the enantioselective synthesis of 2-silylpyrrolidines as organocatalysts for the asymmetric Michael addition of aldehydes to nitroolefines.<sup>1,2</sup> Since then, some impressive developments in the catalyst design have been achieved, overcoming synthetic challenges and introducing pyrrolidinylsilanols as bifunctional hydrogen-bond directing organocatalysts.<sup>3,4</sup> Recently, a detailed structural and kinetic investigation gave new insight into the structure-reactivity relation in enamines derived from 2-tritylpyrrolidine (Maruoka catalyst) and 2-(triphenylsilyl)pyrrolidine (Bolm-Christmann-Strohmann catalyst).<sup>5</sup> As it was found that the C–F bond in the respective carbon-based pyrrolidines led to unique stereoelectronic and electrostatic effects,<sup>6</sup> we are interested in studying the structural and electronic properties of silylated pyrrolidines with an Si–F bond. Here, we present our preliminary results on preparation and structural elucidation of a stereochemically pure 2-(fluorosilyl)-substituted *N*-*tert*-butylpyrrolidine as precursor for potential organocatalytic applications and for convenient substitution reactions leading to new catalyst scaffolds.

<sup>1</sup> J. O. Bauer, J. Stiller, E. Marqués-López, K. Strohfeltdt, M. Christmann, C. Strohmann, *Chem. Eur. J.* **2010**, *16*, 12553-12558.

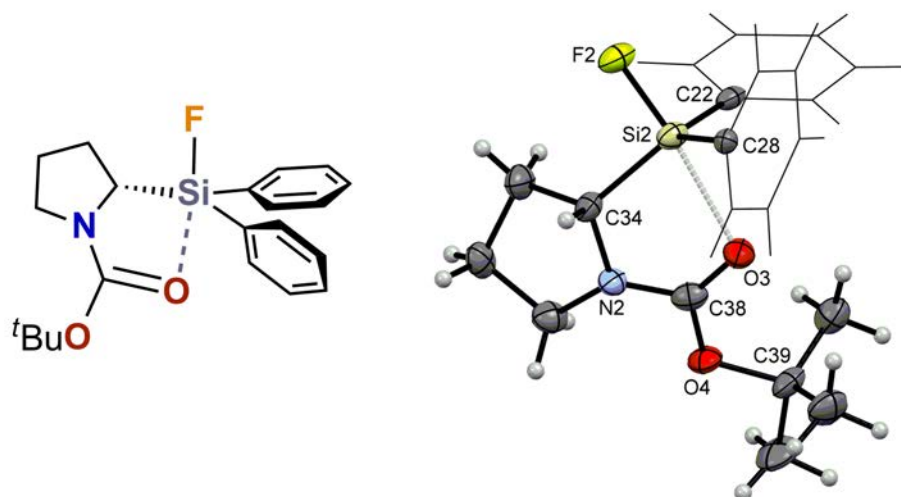
<sup>2</sup> R. Husmann, M. Jörres, G. Raabe, C. Bolm, *Chem. Eur. J.* **2010**, *16*, 12549-12552.

<sup>3</sup> K. I. Jentzsch, T. Min, J. I. Etcheson, J. C. Fettinger, A. K. Franz, *J. Org. Chem.* **2011**, *76*, 7065-7075.

<sup>4</sup> T. Min, J. C. Fettinger, A. K. Franz, *ACS Catal.* **2012**, *2*, 1661-1666.

<sup>5</sup> H. Erdmann, F. An, P. Mayer, A. R. Ofial, S. Lakhdar, H. Mayr, *J. Am. Chem. Soc.* **2014**, *136*, 14263-14269.

<sup>6</sup> C. Sparr, W. B. Schweizer, H. M. Senn, R. Gilmour, *Angew. Chem. Int. Ed.* **2009**, *48*, 3065-3068.



## P-5

## STRUCTURE-REACTIVITY STUDIES ON ALKALIMETAL SILANES AND THEIR CORRESPONDING SOLVENT SEPARATED COMPOUNDS

Pedro Braun Streb, Marvin Kloss, Dominik Auer, Carsten Strohmann\*

TU Dortmund University, Otto-Hahn-Str. 6, 44227, Dortmund, Germany  
 pedro.streb@tu-dortmund.de, carsten.strohmann@tu-dortmund.de

The reaction of organolithium reagents with electrophiles is amongst the most important reactions for the synthesis of a multitude of functionalized systems in almost all fields of chemistry.<sup>1</sup> The corresponding silyl-metal compounds are important building blocks in organosilicon chemistry.<sup>2</sup> Stereogenic lithiated silicon centers (lithiosilanes)<sup>3</sup> have been shown to be suitable for the introduction of stereoinformation and the synthesis of stereochemically enriched and pure products.<sup>2,3</sup> Preceding structural studies on lithiosilanes show small overall angles at the silicon center and a systematic bending of the phenyl groups (torsional angle < 180 °).<sup>4</sup> These effects were explained through quantum chemical calculations. The phenyl group bending is the result of a Pauli-repulsion between the electrons in the HOMO located at the silicon center and the electrons located in corresponding orbitals at the arene. These effects can be influenced through the choice of the substituents.<sup>5</sup> Of main interest is to determine if the silicon metal (M) contact has an influence on the bending or bond angles on silicon. Therefore, various metal-silanes were synthesized and analysed. Herein, we report the studies on different alkalisilanes and solvent/metal separated silylanions. It is possible to synthesize different monomeric silylanions by cleavage of disilanes using metal/metalalkoxides without the need to use overly steric substituents. The synthesized metalsilanes are stabilized using diamines and Crown-ether. The obtained experimental data show the strong ionic character of the Si-M-contact.

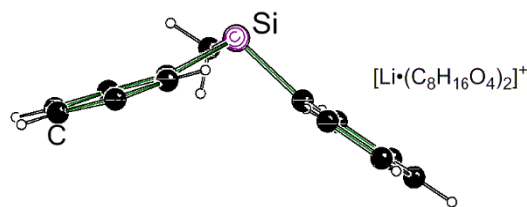
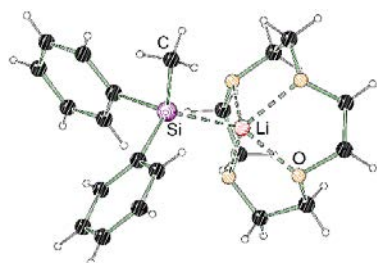
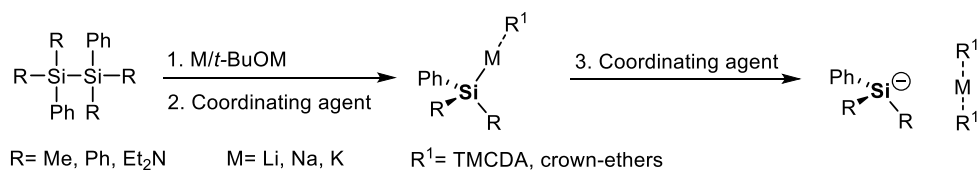
<sup>1</sup> Z. Rappoport, Y. Apeloig, *The Chemistry of Organic Silicon Compounds*, Wiley & Sons, New York, **2000**.

<sup>2</sup> P. D. Lickiss, C. M. Smith, *Coord. Chem. Rev.*, **1995**, *145*, 75–124; (b) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.*, **2000**, *210*, 11–45.

<sup>3</sup> C. Strohmann, M. Bindl, V. C. Vraaß, J. Hörnig, *Angew. Chem.* **2004**, *116*, 1029–1032.

<sup>4</sup> C. Strohmann, C. Däschlein, *Chem. Commun.* **2008**, 2791–2793.

<sup>5</sup> C. Strohmann, C. Däschlein, D. Auer, *J. Am. Chem. Soc.* **2006**, *128*, 704–705.



## P-6 THE CHEMISTRY OF NONASILANE

Viktor Christopoulos, Michael Haas, Harald Stueger\*

*Institute of Inorganic Chemistry, Graz University of Technology, Stremayergasse 9, A-8010 Graz, Austria.*

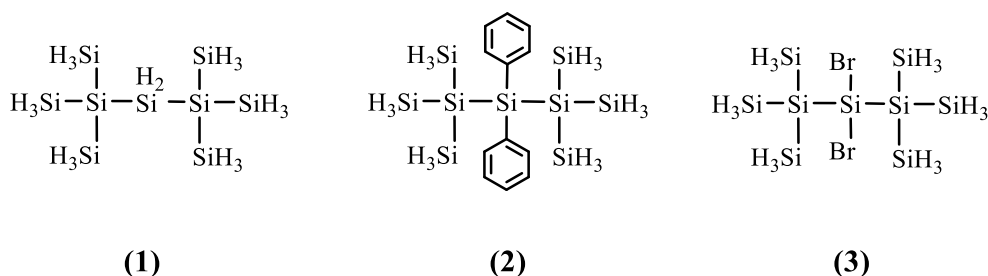
*v.christopoulos@tugraz.at; michael.haas@tugraz.at; harald.stueger@tugraz.at*

Although hydrosilane oligomers  $\text{Si}_n\text{H}_m$  ( $n > 3$ ) with linear, branched or cyclic structures are known for more than 40 years, their chemistry still remained nearly unexplored since then, which is mainly due to their limited accessibility and their disadvantageous properties. Just recently it has been found that cyclopolysilanes  $\text{Si}_n\text{H}_{2n}$  ( $n = 5,6$ ) and neopentasilane (NPS) can be used as precursors for the solution-based deposition of silicon layers allowing significant reduction of processing costs in photovoltaic applications as compared to standard vacuum-based (CVD) approaches.<sup>1,2</sup> However, these precursors entail some unfavourable properties like their unsuitable volatility and their undesirable pyrophoric character on contact with air. This contribution describes a possible synthetic pathway to the gram-scale formation of the branched nonasilane (**1**), promising an improved performance and less unfavorable characteristics. Furthermore, various functionalized derivatives of **1**, which in turn could enable the synthesis of further higher silanes will also be presented. In particular, the reaction of the recently published alkali metal silanides  $(\text{H}_3\text{Si})_3\text{SiM}^3$  with  $\text{Ph}_2\text{SiCl}_2$  leads to the generation of  $(\text{H}_3\text{Si})_3\text{SiPh}_2(\text{SiH}_3)_3$  (**2**) which in turn can be converted to bromo- and chlorohydrosilanes such as  $(\text{H}_3\text{Si})_3\text{SiBr}_2(\text{SiH}_3)_3$  (**3**).

<sup>1</sup> *Solution Processing of Inorganic Materials; Mitzi, D. B., Ed.; Wiley: Hoboken, 2009.*

<sup>2</sup> *Habas, S. E.; Platt, H. A. S.; van Hest, M. F. A. M.; Ginley, D. S. Chem. Rev. 2010, 110, 6571.*

<sup>3</sup> *Stueger, H.; Mitterfellner, T.; Fischer, R.; Walkner, C.; Patz, M.; Wieber, S. Chem. Eur. J. 2012, 18, 7662.*



## P-7 PALLADIUM CATALYZED ALKYLATION OF SILICON ELECTROPHILES

Andrew P. Cinderella, Bojan Z. Vulovic, Donald A. Watson\*

University of Delaware, Newark, DE 19716, USA  
acinder@udel.edu, bvulovic@udel.edu, dwatson@udel.edu

Alkyl silanes have a number of synthetic and industrial properties that represent an increasing field of valuable products in medicinal<sup>1-4</sup> and materials<sup>5-9</sup> chemistry. Syntheses of these compounds are typically limited to activated or sterically disencumbered nucleophile-electrophile pairings<sup>10-13</sup> and often advance under harsh reaction conditions or not at all.<sup>14-17</sup> Recent successful transformations include umpolung strategies utilizing silicon nucleophiles.<sup>18,19</sup> However, with the extensive pool of directly available silicon electrophiles, a silyl electrophile coupling would be an indispensable reaction. We now report a high yielding, general protocol for the palladium catalyzed alkylation of silyl electrophiles with zinc and magnesium nucleophiles. Features include a novel ligand, DrewPhos, which allows for secondary alkyl nucleophiles to couple with no observed isomerization of the nucleophilic group. Identification of the proper steric and electronic properties of the employed ligand was critical to obtaining high yields and suppression of isomerization. These properties were determined by X-ray crystallography and phosphine-selenide coupling constant measurements.<sup>20-21</sup>

<sup>1</sup> Franz, A. K.; Dreyfuss, P. D. et al.; *J. Am. Chem. Soc.* **2007**, *129*, 1020

<sup>2</sup> Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388

<sup>3</sup> Geyer, M.; Wellner, E. et al.; *ChemMedChem* **2015**, *10*, 911

<sup>4</sup> Tacke, R.; Dörrich, S. In *Atypical Elements in Drug Design*; Schwarz, J., Ed.; Springer Intl Publishing: Cham, 2016, p 29.

<sup>5</sup> Baum, G.; Tamborski, C. *J. Chem. Eng. Data* **1961**, *6*, 142

<sup>6</sup> Tamborski, C.; Chen, G. J. et al.; *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 172

<sup>7</sup> Bassindale, A.; Gaspar, P. P. et al.; *Frontiers of Organosilicon Chemistry*; Royal Society of Chemistry, 1991

<sup>8</sup> Cutler, J. N.; Sanders, J. H. et al.; *Tribol. Lett.* **2000**, *8*, 17

<sup>9</sup> Auner, N.; Weis, J. *Organosilicon Chemistry V*; Wiley-VCH Verlag GmbH, 2003.

<sup>10</sup> Wilt, J. W.; Chwang, W. K. et al.; *J. Am. Chem. Soc.* **1978**, *100*, 5534

<sup>11</sup> Kang, K.-T.; Yoon, U. C. et al.; *Bull. Korean Chem. Soc.* **1991**, *12*, 57

<sup>12</sup> Eiji, M.; Kei, M. et al.; *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1012

<sup>13</sup> Murakami, K.; Yorimitsu, H. et al.; *J. Org. Chem.* **2009**, *74*, 1415.

<sup>14</sup> Sommer, L. H.; Kerr, G. T. et al.; *J. Am. Chem. Soc.* **1948**, *70*, 445

<sup>15</sup> Corriu, R. J. P.; Meunier, B. *J. Organomet. Chem.* **1973**, *60*, 31

<sup>16</sup> Lennon, P. J.; Mack, D. P. et al.; *Organometallics* **1989**, *8*, 1121

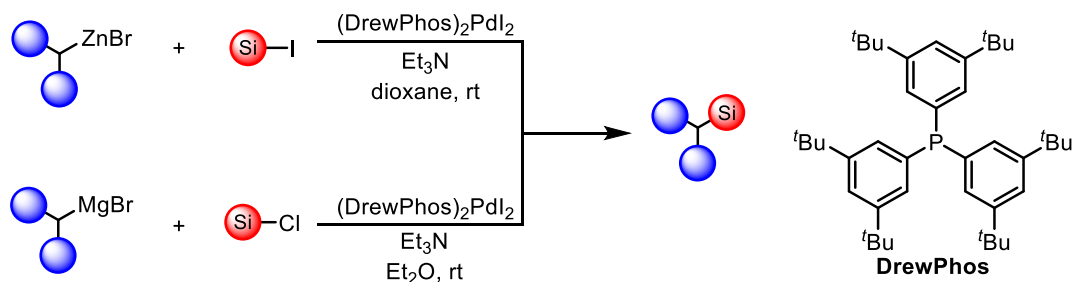
<sup>17</sup> Murakami, K.; Hirano, K. et al.; *Angew. Chem., Int. Ed.* **2008**, *47*, 5833.

<sup>18</sup> Chu, C. K.; Liang, Y. et al.; *J. Am. Chem. Soc.* **2016**, *138*, 6404

<sup>19</sup> Xue, W.; Qu, Z.-W. et al.; *J. Am. Chem. Soc.* **2016**, *138*, 14222.

<sup>20</sup> Beckmann, U.; Süslüyan, D. et al.; *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 2061

<sup>21</sup> Kawaguchi, S.-i.; Minamida, Y. et al.; *Adv. Synth. Catal.* **2015**, *357*, 2509.



**P-8**

**KINETIC STUDY OF HOMO-POLYMERIZATION OF MTMS BY *IN SITU* INFRARED (IR) AND RAMAN SPECTROSCOPY**

Li Cui,\* Shawn Chen, Mark Rickard, LaBeaume Paul, Cameron Jim and Yamada Shintaro

*The Dow Chemical Company, 455 Forest St, Marlborough, MA 01752, USA*  
*cui@dow.com*

B-staged organo polysilica solution-gel resins or silsesquioxanes (SSQs) are difficult to synthesize since the sol gel processing is known to be extremely complex and many possible structures can be formed due to the different reactivity of silane monomers. The structural and physical properties of SSQ are highly determined by the competing hydrolysis and condensation reactions.

In this study, we monitor the reaction kinetics of homo-polymerization of MTMS by *in situ* infrared (IR) and Raman spectroscopy in order to understand the SSQ polymerization. Raman spectroscopy was found to be more effective in monitoring the hydrolysis than IR since more significant Raman spectral changes were observed. In contrast, IR was found to be more effective as the formation of the Si-O-Si network had much stronger IR responses. *In situ* IR and Raman are identified to be highly useful tools that could yield process insights for designing a synthesis process for desired SSQ architecture.

**P-9****THREE COMPONENT COUPLING OF METAL NANOPARTICLES, STÖBER SILICA, AND FUNCTIONAL SILANES: A NEW APPROACH TO GREEN CATALYSIS**

Edwin Elias, Juan Leiva, Qiaxian R. Johnson, Bhanu P.S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University,  
300 Pompton Road, Wayne, NJ, USA  
ChauhanBPS@wpunj.edu*

Metallic nanoparticles are nanosized objects that can range in sizes from 1 to 100 nm and possess unique properties, which are different from their bulk material.<sup>1</sup> The spark of interest in this field of research is because new and efficient pathways can be created for their applications and field in nanotechnology. The capability of synthesizing and of customizing these metal nanoparticles to contain different functional groups can lead to new compounds for the attachment of drugs, antibodies, and ligands, which can serve the purpose as a drug or antibody carrier, and can also lead to uses in many other fields of applications such as catalysis.<sup>2</sup> We, and others, have been investigating the use of metal nanoparticles in catalysis because of their high catalytic activity and selectivity for certain reactions.<sup>1</sup>

In this work, we have synthesized noble metal nanoparticles via the reduction of the metal salts using *n*-(2-aminoethyl)-3-aminosilanetriol (2-AST) as both a reducing and stabilizing agent to generate metal core nanoparticles. These metal nanoparticles are then impregnated into a Stöber silica type matrix. In this case a three component coupling of 2-AST stabilized gold nanoparticles and highly mono dispersed 50 nm amine functionalized silica particles is carried out at room temperature. Various combinations of this three- component system were prepared and characterized by TEM, SEM, NMR, IR, and UV-Vis spectroscopy. We will also present our preliminary studies of the use of these systems in the catalysis wherein the reduction of *p*-nitrophenol to *p*-aminophenol was achieved in quantitative yield.

<sup>1</sup> *Synthesis of Polysiloxane Stabilized Palladium Colloids and Evidence of Their Participation in Silaesterification Reactions.* Chauhan, B.P.S.; Rathore, J.; Chauhan, M.; Krawicz, **A. J. Am. Chem. Soc.** 2003, 125, 2876-2877

<sup>2</sup> *Catalytic Applications of Metal Nanoparticles in Imidazolium Ionic Liquids.* P. Migowski, J. Dupont. **Chem. Eur. J.** 2007. 13, 32-39

<sup>3</sup> *Generation of Zerovalent Metal Core Nanoparticles Using *n*-(2-aminoethyl)-3-aminosilanetriol.* Johnson, Q.R. ; Matam, S. ; Patel, A. ; Moran, K. ; Onyechi, B. ; Chauhan, B.P.S. **J Vis Exp.** 2016 Feb 11;(108):

## P-10 SUPRAMOLECULAR SILICONES WITH SELF-HEALING ABILITY

Lucile Fauvre, Daniel Portinha, Jean-Pierre Pascault, Etienne Fleury, François Ganachaud\*

IMP@INSA-Lyon, CNRS UMR 5223, 17 avenue Jean Capelle, F-69621 Villeurbanne  
 lucile.fauvre@insa-lyon.fr, daniel.portinha@insa-lyon.fr, jean-pierre.pascault@insa-lyon.fr,  
 etienne.fleury@insa-lyon.fr, francois.ganachaud@insa-lyon.fr

Unlike living organisms, synthetic materials are not able to recover from damages and possess therefore a limited lifetime.<sup>1</sup> To counteract this fragility, supramolecular polymers have shown a great interest thanks to their reversibility and thus their reusability. Recent studies also focused on the emergence of new materials that self-heal without any external stimulus; to this aim supramolecular materials are of particular interest.<sup>2</sup>

Starting from published results,<sup>3,4</sup> we first set up a fundamental study by reacting  $\alpha,\omega$ -amino-PDMS with urea, to generate various functional groups likely to interact by H-bonding. Silicone-based systems were considered here for their hydrophobicity, flexibility and thermal stability. The influence of the nature of the associating groups, as well as the chain length and hydrophilic to hydrophobic ratio, on the properties of thus-prepared materials was investigated. Different analytical studies allowed correlating the chemistry (NMR, IR and SEC) and the physical chemical properties (rheology, TGA, DSC) (see Figure below).

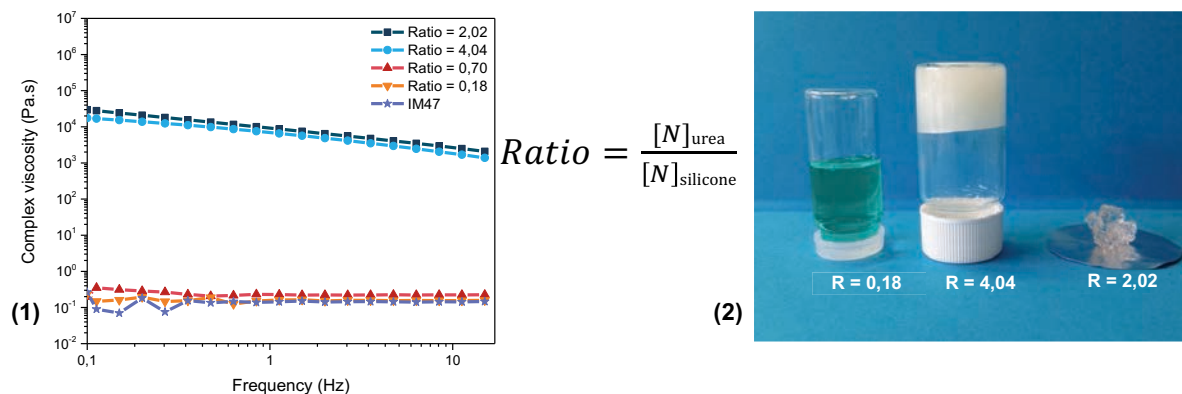
With a complete understanding of those supramolecular interactions, we look for generating polydimethylsiloxanes with autonomous self-healing abilities.

<sup>1</sup> Y. Yang, X. Ding, M.W. Urban, *Progress in Polymer Science*, 2015, 49, 34-59

<sup>2</sup> P. Zhang, G. Li, *Progress in Polymer Science*, 2016, 57, 32-63

<sup>3</sup> P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, *Nature*, 2008, 451, 977-980

<sup>4</sup> A. Zhang, L. Yang, Y. Lin, L. Yan, H. Lu, L. Wang, *J. Appl. Polym. Sci.*, 2013, 129, 2435-2442



**Figure 1:** Influence of the initial urea/amine molar ratio on rheological behaviour –Complex viscosity increase with ratio.

**Figure 2:** Upside down test – t = 21 min. R=4,04 slowly flows while R=0,18 does it instantaneously. R=2,02 is solid.

**Acknowledgements:** Agence Nationale de la Recherche (ARCADE project, contract N°ANR-15-CE08-0022)

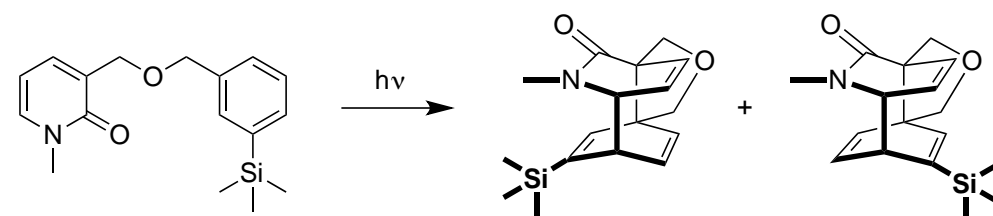


## P-11 SILICON SUBSTITUTION IN BENZENE-PYRIDONE PHOTO- CYCLOADDITION

Steven E. S. Fletcher, Scott McN. Sieburth\*

Department of Chemistry, Temple University, 1901 North 13th St, Philadelphia, PA 19122 USA  
sfletcher@temple.edu, sieburth@temple.edu

Benzene will reluctantly undergo [4+4] (a.k.a. *para*) photocycloaddition with 2-pyridones, but when the benzene carries substituents, this cycloaddition can be a preferred pathway. Silicon substitution promotes this higher-order cycloaddition. In this presentation, we explore all of the benzene silicon's substitutions, silicon's effect on stereoselectivity and the rearrangements of these strained products.



## P-12

### HYBRID GELS of POLYMETHYLHYDROSILOXANE AND POLYBUTADIENES AND THEIR CATALYTIC ACTIVITY

Ralph Fleurant-Jean, Daniela Artiga, Qiaxian Johnson, Bhanu P.S. Chauhan\*

*Engineered Nanomaterials Laboratory, Department of Chemistry, William Paterson University, 300 Pompton Road, Wayne, NJ, USA*  
*ChauhanBPS@wpunj.edu*

Hybrid materials possess different physical and chemical properties, which can be found very advantageous in applications compared to their single constituent. In recent years in our laboratory we have been investigating formation of hybrid gels via catalytic carbon-silicon bond formation using polymethylhydrosiloxane (PMHS), and polyalkenes. The experimental route makes use of a platinum complex (1, 5-cyclooctadiene)dimethylplatinum(II), as a catalyst in order to facilitate the cross-linkage of the reduction of the Si-H bond with the alkene, cis-Polybutadiene. In this work we will present the reaction scheme of generating a stabilized polymeric gel impregnated with the Pt-nanoparticles complex. Alcoholic functionalization of these gels were tested in the presence of isopropanol, benzyl alcohol, which will be discussed.

Previous experimental research as shown that using Wilkinson's catalyst efficiently promotes coupling of polymeric Si-H bonds with alcohols and give well-defined silicones.<sup>1,2</sup> The research in our laboratory will promote a new well-defined stabilized nano-gel that can be used as a green-catalyst and the future studies of these gels can be done in order to promote different inorganic-organic functionalities that will eventually exhibit different chemical and physical properties.<sup>3</sup> FTIR, NMR were used to identify the precursor's peak of PMHS, cis-Polybutadiene, and the alcohols used. Our first experimental protocol discussed the route used to generate the stabilized gel using PMHS with Cis-polybutadiene (alkene system) embedded with the platinum-complex. The second part discussed the functionalization of the obtained stabilized platinum gel with the different alcohols mentioned in this scientific work. The detailed analysis of these materials were carried out using FTIR, NMR, X-ray, TEM, and SEM.

<sup>1</sup> *A Catalytic Route to Grafted Silicones*, Bhanu P. S. Chauhan, Thomas E. Ready, Zoha AL-Badri, Philip Boudjouk, *Organometallics*, **2001**, 20 (13), pp 2725–2729

<sup>2</sup> Bhanu P. S Chauhan, Philip Boudjouk. *Tetrahedron letters*. **2000**, Volume 41(8), 1127-1130.

<sup>3</sup> *Functionalized polysilalkylene siloxanes (polycarbosiloxanes) by hydrosilylation—Catalysis and synthesis*, Sophie Putziena, Oskar Nuykenb, Fritz E. Kühna, *Progress in Polymer Science*, volume 35(6), **2010**. pp 687-713.

## P-13 SYNTHESIS OF NOVEL DONOR-ACCEPTOR ORGANOSILICON MATERIALS

Carlton P. Folster, Eric A. Marro, Eric M. Press, Tapas K. Purkait, Shehani M. Mendis, Rebekka S. Klausen\*

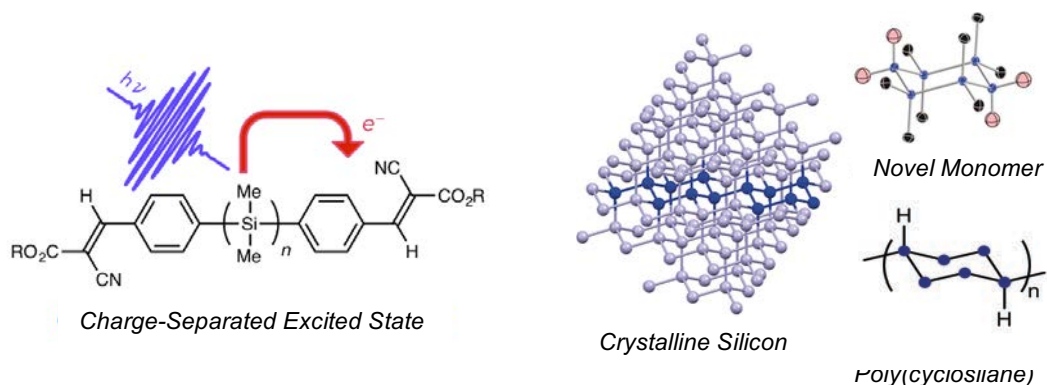
Johns Hopkins University, 3400 N Charles St, Baltimore, MD 21218, USA  
 cfolste1@jhu.edu, emarro1@jhu.edu, epress2@jhu.edu, tpurkai1@jhu.edu,  
 namanthi\_mendis@yahoo.com, klausen@jhu.edu

The Klausen group uses strategic synthesis to construct complex silicon-based chemical architectures. A novel class of hybrid materials containing both  $\pi$ -conjugated carbon blocks and  $\sigma$ -conjugated silane blocks represents a promising new direction for molecular semiconductors. Thin film transistors based on these materials exhibit high carrier mobilities. Interrogation of photophysical properties by both steady state and ultrafast spectroscopies support intramolecular photoinduced charge transfer from silicon to carbon.<sup>1,2</sup> Novel donor-acceptor polymers are synthesized by post polymerization modification of a novel and complex poly(cyclosilane) mimic of crystalline silicon.<sup>3</sup> Dimensions of poly(cyclosilane) formation are dictated by the strategic placement of reactive Si-H bonds and inert Si-Me bonds on a cyclohexasilane monomer. Our findings suggest new opportunities to control charge separation in silicon based materials.

<sup>1</sup> *Chem. Eur. J.*, **2016**, 22, 6204-6207.

<sup>2</sup> *Dalton Trans.*, **2017**, DOI:10.1039/CFDT0038F.

<sup>3</sup> *Angew. Chem. Int. Ed.*, **2017**, 56, 568-572.



## P-14

## STRUCTURAL STUDY OF COMPLEXES OBTAINED FROM BASE INDUCED MIGRATION OF Si, Si<sub>2</sub>, AND Ge GROUPS TO THE CYCLOPENTADIENYL LIGAND IN THE SYSTEM (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)M(CO) WHERE M= Fe, W

J. Cervantes,<sup>a\*</sup> G. González-García,<sup>a</sup> J.A. Gutiérrez-Fuentes,<sup>a</sup> M.A. Leyva-Ramírez,<sup>b</sup> K. H. Pannell<sup>c</sup>

<sup>a</sup> Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Campus Guanajuato. Guanajuato, Gto., México.

<sup>b</sup> Departamento de Química, CINVESTAV-IPN, Ciudad de México, México.

<sup>c</sup> Chemistry Department, University of Texas at El Paso, El Paso, Texas. USA.

jauregi@ugto.mx, gerardog@ugto.mx, jagutier@ugto.mx, mleyva@cinvestav.mx, kpannell@utep.edu.

Revisiting the chemistry of the system of the type (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>n</sub> (M=Fe, W, n= 2, 3), the structures of three organometallic complexes of group 14 elements Me<sub>3</sub>Si(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>SnPh<sub>3</sub> (**1**), Me<sub>4</sub>Si<sub>2</sub>[η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>(SnPh<sub>3</sub>)<sub>2</sub> (**2**, Figure 1) and Me<sub>3</sub>Ge(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>Me (**3**) have been determined by using X ray-single crystal diffraction analysis. Such complexes were obtained previously by base induced migration with lithium diisopropylamide (LDA) of the corresponding original system (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>SiMe<sub>3</sub>, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>](Si<sub>2</sub>Me<sub>4</sub>)<sub>2</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>GeMe<sub>3</sub>, respectively.<sup>1,2</sup> In the specific case of Me<sub>3</sub>Si-, and Me<sub>3</sub>Ge- migration complexes, the structures obtained represent some of the few examples reported from the synthetic procedure used (base induced migration to cyclopentadienyl ligand). In the migration complex of the Me<sub>3</sub>Si- the intermediate anion Me<sub>3</sub>Si(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>Li<sup>+</sup> was quenched with Ph<sub>3</sub>SnCl. Details of the structures characteristics will be discussed. The authors wish thanks to the University of Guanajuato for financial support (project CIIC 1,105/2016-2017) and CONACYT (INFRA-2014-01-225496).

<sup>1</sup> J. Cervantes, S. P. Vincenti, R. N. Kapoor, K. H. Pannell. *Organometallics*, 1989, 8, 744-748

<sup>2</sup> S. Sharma, J. Cervantes, J. L. Mata-Mata, M. C. Brun, F. Cervantes-Lee, K.H. Pannell. *Organometallics* 1995, 14, 4269-4274

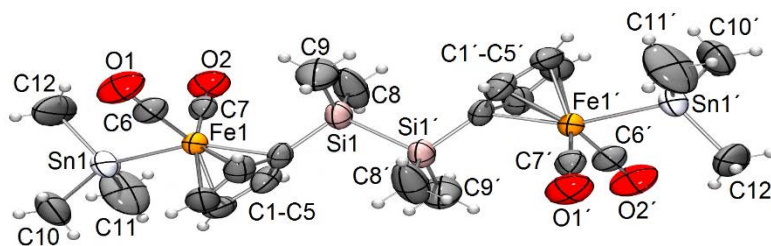


Figure 1: Ortep view of Me<sub>4</sub>Si<sub>2</sub>[η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>(SnPh<sub>3</sub>)<sub>2</sub> in the crystal structure.

## P-15

## FIRST SILA-ALDOL REACTION ENABLES THE SYNTHESIS OF STRUCTURALLY COMPLEX SILICON-FRAMEWORKS

Michael Haas,\* Mario Leypold, Harald Stueger

*Institute of Inorganic Chemistry, Graz University of Technology Stremayrgasse 9/IV, 8010 Graz, Austria*  
*michael.haas@tugraz.at*

The classical aldol reaction and in particular its power in the reversible formation and breaking of carbon-carbon bonds is one of the most important biosynthetic tools for the evolution of life on earth.<sup>1,2</sup> For silicon-based compounds, however, this type of silicon-carbon bond formation was previously unknown, although it must be considered as a powerful alternative to the standard coupling techniques, such as Wurtz reaction and related methods,<sup>3-5</sup> hydrosilylation<sup>6</sup> as well as transition metal catalyzed silicon-carbon coupling reactions.<sup>7</sup> We considered the intramolecular sila-aldol reaction as an optimal starting point for the development of this transformation, as it should be entropically favored and should provide highly symmetric starting materials. Therefore,  $\alpha,\omega$ -bisacylsilanes were synthesized and reacted with equimolar amounts of KOtBu. In contrast to the classical carbon-based aldol reaction, no stable addition products could be isolated yet. However, in the case of the bisacylsilanes, the sila-aldol product reacted further in a highly selective rearrangement cascade by a directed breakup of the cyclohexasilane backbone and the insertion of an oxygen atom into the ring to give **1**. This novel transformation introduces a pioneering strategy for the formation of silicon-carbon bonds by establishing a further link between the two related fields of silicon- and carbon-Chemistry.

<sup>1</sup> for example: A. Szekrenyi, X. Garrabou, T. Parella, J. Joglar, J. Bujons, P. Clapes, *Nat. Chem.* **2015**, *7*, 724-729

<sup>2</sup> M. Rueping, *Angew. Chem. Int. Ed.* **2006**, *45*, 1838-1840.

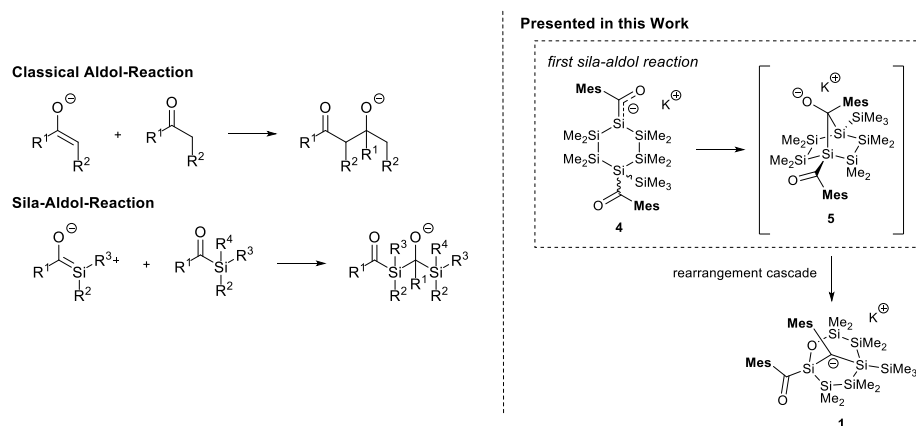
<sup>3</sup> D. J. Atkinson, J. Sperry, M. A. Brimble, *Synthesis* **2010**, 911-913;

<sup>4</sup> T. Kobayashi, K. H. Pannell, *Organometallics* **1991**, *10*, 1960-1964

<sup>5</sup> L. E. Guseynikov, Y. P. Polyakov, E. A. Volnina, N. S. Nametkin, *J. Organomet. Chem.* **1985**, *292*, 189-203.

<sup>6</sup> for example: Y. Liu, L. Deng, *J. Am. Chem. Soc.* **2017**, *139*, 1798-1801.

<sup>7</sup> for example: Y. Hua, P. Asgari, T. Avullala, J. Jeon, *J. Am. Chem. Soc.* **2016**, *138*, 7982-7991;



## P-16 CATALYTIC C-H AND C-C BOND SILYLATION REACTIONS

Junha Jeon\*

*University of Texas at Arlington, Department of Chemistry and Biochemistry, Arlington, TX  
76092, USA  
jjeon@uta.edu*

Transition metal-catalyzed silylation reactions have been useful methods for synthesis of small organosilicon compounds and large molecular weight materials. We have been recently developed several mechanistically intriguing transition metal-catalyzed alkene hydrosilylation and dehydrogenative silylation, as well as C-H and C-C bond silylation reactions to synthesize diverse organosilanes and organosilanols.<sup>1,2,3</sup> In detail, the progress toward design and application of single-pot, catalytic reductive C-H and C-C bond silylations with silyl acetals, as traceless directing groups, for synthesis of a new class of organosilanes will be presented.

<sup>1</sup> Y. Hua, P. Asgari, T. Avullala, J. Jeon, *J. Am. Chem. Soc.* **2016**, *138*, 7982-7991.

<sup>2</sup> Y. Hua, P. Asgari, U. S. Dakarapu, J. Jeon, *Chem. Commun.* **2015**, *51*, 3778-3781.

<sup>3</sup> Y. Hua, S. Jung, J. Roh, Jeon, J. *J. Org. Chem.* **2015**, *80*, 4661-4671.

**P-17****Thin-Film Deposition of Silicon Nitrides from Trihydridosilanes**B. Arkles,<sup>a</sup> Y. Pan,<sup>a</sup> A. E. Kaloyeros<sup>b\*</sup><sup>a</sup> *Gelest, Inc., 11 East Steel Rd. Morrisville, PA 19067, USA*<sup>b</sup> *College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Fuller Rd, Albany, NY 12203, USA*

Organotrihydridosilanes can provide a route for generating self-assembled monolayers (SAMs) on metal substrates. Under mild processing conditions, these precursors can readily interact with a variety of clean, hydrogenated and fresh metal and metalloid surfaces, including titanium, silicon and gold. All classes of hydridosilanes have minimal interaction with anhydrous oxide surfaces. Following monolayer assembly, SAMs formed from 2-chloroethyltrihydridosilane may be converted to silicon nitride by pulsing with ammonia or silicon dioxide by pulsing water vapor or an oxygen-bearing reactant<sup>1</sup>. A proposed mechanism for the initial steps of deposition involves the dissociative adsorption of trihydridosilanes with the release of hydrogen, followed by topmost atom layer insertion and concomitant surface reconstruction.

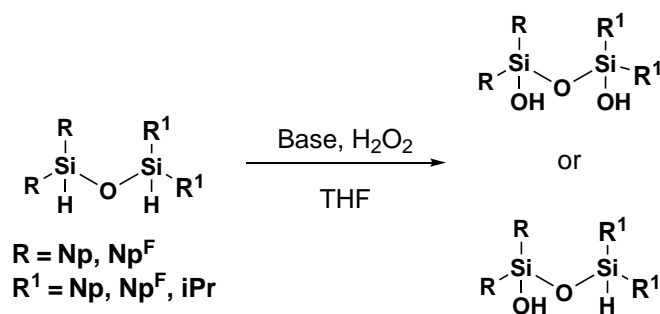
<sup>1</sup> B. Arkles, Y. Pan, A. E. Kaloyeros, Atomic Layer Deposition Applications, 10, ECS Transactions, 2014 64(9), 243-249

**P-18****INVESTIGATIONS OF ORGANOMETALLIC, ORGANOCATALYTIC, AND BASE MEDIATED METHODS FOR THE HYDROLYSIS OF 1,3-DIHYDRO-DISILOXANES**

Austin T. Kelly, Annaliese K. Franz\*

*Department of Chemistry, University of California, Davis, CA 95616, USA  
athkelly@ucdavis.edu, akfranz@ucdavis.edu*

Our group has shown the 1,3-disiloxanediol structure to be a scaffold for the development of anion-binding and hydrogen-bonding catalysts, as well as monomers for silicones. As such the development of efficient, green, and catalytic methods for the synthesis of 1,3-disiloxanediols is needed. An initial investigation of organometallic and organocatalytic methods of silane hydrolysis showed the organocatalytic method to be the highest yielding. The optimization of this organocatalytic method for the hydrolysis of 1,3-dihydro-disiloxanes to the corresponding 1,3-disiloxanediols with catalyst loadings of 0.01 mol% is presented. Also, base-mediated methodology for the preparation of tetra-aryl 1,3-disiloxanediols and a chemoselective hydrolysis of unsymmetrical 1,3-dihydro-disiloxanes is described.



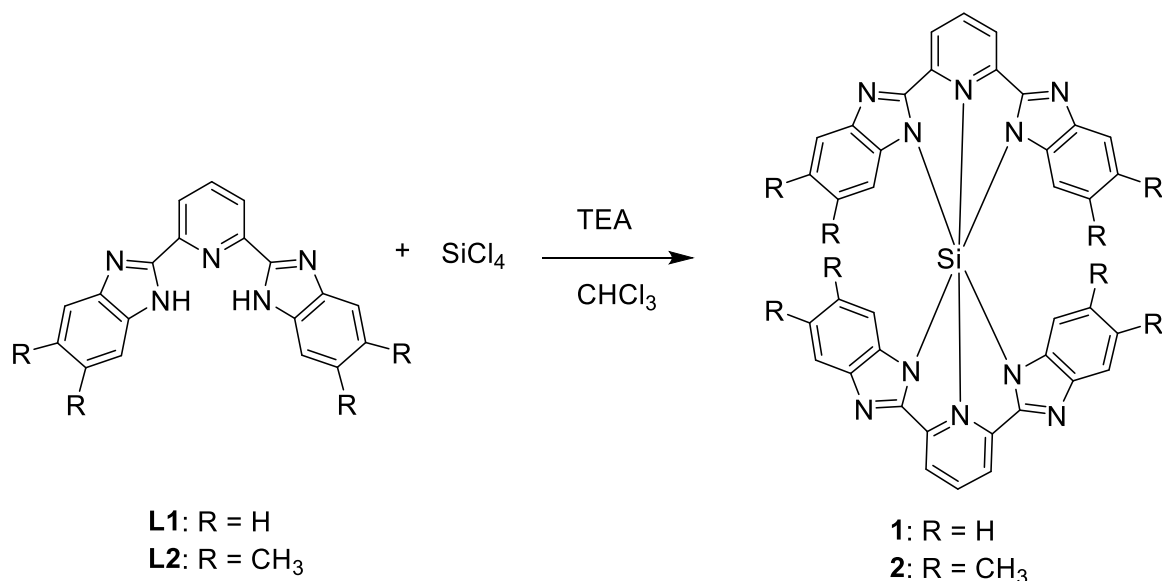


## P-19 LUMINESCENT HEXACOORDINATE SILICON COMPLEXES

Margaret Kočergera, Thomas A. Schmedake\*

University of North Carolina – Charlotte, 9201 University City Blvd. Charlotte, NC 28223  
mkočergera@uncc.edu; tschmeda@uncc.edu

Hexacoordinate silicon complexes based on dianionic pincer ligands are attractive candidates for luminescent applications. The wide variety of pincer ligands provides tailorability of the electronic properties, and the hexacoordinate silicon center enforces a rigid planar environment to minimize rotational relaxation modes. Reaction of silicon tetrachloride with two equivalents of 2,6-bis(2-benzimidazolyl)pyridine (bzimpy, **L1**) in chloroform with triethylamine produces  $\text{Si}(\text{bzimpy})_2$ , **1**.  $\text{Si}(\text{bzimpy})_2$  is stable in air and is luminescent in solution and the solid state. However, the solubility is low in most solvents. The methylated analog, **2**, is significantly more soluble and still fluorescent. The synthesis and spectroscopic properties of **1** and **2** and other  $\text{Si}(\text{pincer})_2$  species will be presented.



## P-20

### AN IMPROVED PRECATALYST FOR SILYL-HECK REACTIONS

Sarah B. Krause, Jesse R. Mcatee, Donald A. Watson\*

*Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA*  
*skrause@udel.edu, jesse.mcatee@gmail.com, dawatson@udel.edu*

Previous work from our group has shown that allyl and vinyl silanes can be prepared from terminal alkenes via the silyl-Heck reaction. Mechanistic studies aimed at identifying the active palladium complexes in this reaction have revealed a new complex by <sup>31</sup>P NMR and mass spectrometry. This complex has been isolated and a crystal structure has been solved, confirming the identity of an iodide dimer of the palladium complex, (LPdI<sub>2</sub>)<sub>2</sub>. This complex has been found to be a competent single component precatalyst for the silyl-Heck reaction, giving comparable yields to previous precatalysts. However, this precatalyst offers several advantages over previous systems. The complex can be readily prepared from PdI<sub>2</sub> and is temperature, moisture, and air stable for long periods of time. Additionally, this catalyst gives more reproducible results when compared to the Pd<sub>2</sub>dba<sub>3</sub> precatalyst.

## P-21 SILICONE FOAMS FROM EMULSIONS

Gabriel Larribe, François Ganachaud,\* Etienne Fleury.

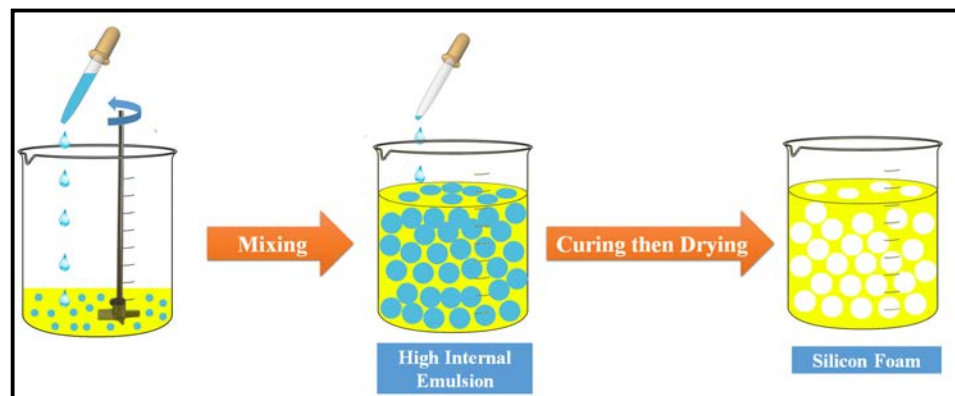
Laboratoire Ingénierie des Matériaux Polymères, 17 Avenue Jean Capelle Ouest, 69621  
Villeurbanne, France  
gabriel.larribe@insa-lyon.fr, francois.ganachaud@insa-lyon.fr, etienne.fleury@insa-lyon.fr

Cellular materials are widely used in applications such as thermal and sound insulations, absorbent for liquids and low density foams. Solid foams are materials containing gaseous voids called cells, surrounded by a dense matrix. They differ in their composition, cell morphology (open or closed porosity) and physical properties. In the closed-cell materials, the voids are isolated from each other and the cavities are surrounded by a continuous wall polymer; whereas, in open-cell materials, bridges between cells allow gas or liquid diffusion. Open foams are widely seen in Nature, for example in cork, wood, sponges and corals.

Recently cellular synthetic materials were developed through chemical or physical foaming. The control of cell size and morphology is difficult to achieve with these techniques, e.g. to generate totally interconnected structures. The approach of using highly concentrated emulsions (with a fraction of at least 70% water) to prepare controlled microcellular polymers and 100% interconnected porosity, represents an attractive alternative for many applications<sup>1</sup>. The materials thus obtained, known as polyHIPE (High Internal Phase Emulsion), are of great interest for academic and industrial researchers, because of their easy preparation and their high application potential (**Figure1**). In particular, Grosse et al.<sup>2</sup> showed that it is possible to get silicone foams crosslinked by hydrosilylation, starting from highly concentrated water-in-silicone emulsions. Using such technique, we aim at developing silicone foam elastomers, which exhibit low flammability and good mechanical properties as potential candidates for sound insulation in buildings. Foams with good mechanical properties were obtained in a simple and fast way, especially, at low densities (of 0.20) and narrow cells diameters (around 90  $\mu\text{m}$ ).

<sup>1</sup> Lissant, K. J. *Emulsions and Emulsion Technology*; Dekker, M., Ed.; New-York, 1974.

<sup>2</sup> Grosse, M. T.; Lamotte, M.; Birot, M.; Deleuze, H. *J. Polym. Sci. Part A Polym. Chem.* **2008**, 46 (1), 21–32.



**Figure 1:** General Principle of preparation of a silicone foam by HIPE

## P-22

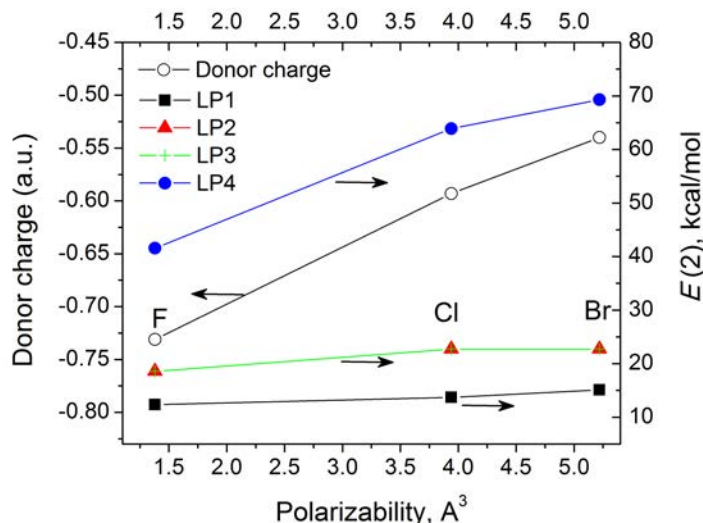
PERCHLORINATED CYCLOPENTASILANE (Si<sub>5</sub>Cl<sub>10</sub>) RING FLATTENING UPON DONOR COORDINATION IN [Si<sub>5</sub>Cl<sub>10</sub>·2Cl]<sup>2-</sup> DIANION

Konstantin Pokhodnya, Kenneth Anderson, Svetlana Kilina, Philip Boudjouk\*

Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, USA

konstantin.pokhodnya@ndsu.edu; philip.boudjouk@ndsu.edu

We report the detailed computational study of flattening of the puckered Si<sub>5</sub> ring by suppression of the pseudo-Jahn-Teller (PJT) effect through coordination of two Cl<sup>-</sup> anions to the molecule forming an inverse sandwich dianion [Si<sub>5</sub>Cl<sub>10</sub>·2Cl]<sup>2-</sup> complex. The PJT effect which causes nonplanarity of the Si<sub>5</sub>Cl<sub>10</sub> structure (C<sub>s</sub>) results from vibronic coupling of pairs of occupied molecular orbitals (OMOs) and unoccupied molecular orbitals (UMOs). It was shown that filling the intervenient molecular orbitals of puckered Si<sub>5</sub>Cl<sub>10</sub> with valent electron pairs of Cl<sup>-</sup> donors suppresses the PJT effect, with the Si<sub>5</sub> ring becoming planar (D<sub>5h</sub>) upon complex formation. In this paper the stabilization energy *E*(2) associated with donor-acceptor charge transfer (delocalization) was estimated using NBO analysis for all studied inverse sandwich compounds [Si<sub>5</sub>Cl<sub>10</sub>·2X]<sup>2-</sup> (where X= F, Cl, Br). It was found that the polarizabilities of the donor ions significantly affect the stabilization energy value and should be taken into account when choosing the ligands suitable for forming Si-based one-dimensional compounds and other nanoscale materials (**Figure1**).



**Figure 1:** The donor charge (-○-) as well as the sums of all *E*(2) contributions due to LP (lone pair) donor→BD\*(Si-Cl) acceptor NBO delocalization (-■- LP1; -▲- LP2; -+ LP3; -●- LP4) vs. donor polarizability.

## P-23

## ORGANOSILICON-BASED SYNTHESIS OF NEW AZAHETEROCYCLE DERIVATIVES OF PHOSPHONIC ACID AS PERSPECTIVE BIOACTIVE COMPOUNDS

A.A. Prishchenko,\* M.V. Livantsov, O.P. Novikova, N.N. Meleshonkova, L.I. Livantsova, V.S. Petrosyan

M.V. Lomonosov Moscow State University, Moscow, 119991, Russia  
aprishchenko@yandex.ru

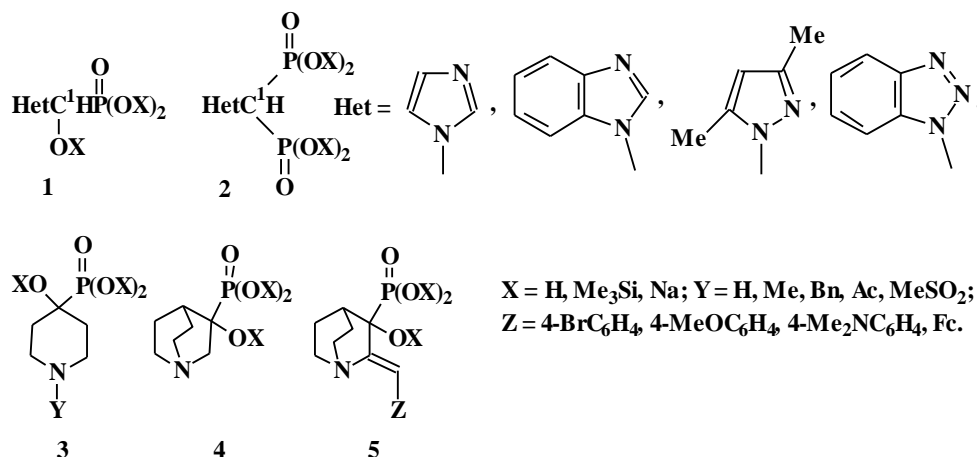
Functionalized organophosphorus acids and their derivatives with heterocyclic moieties are of great interest as effective chelating ligands and perspective bioactive substances with various properties. These acids are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine.<sup>1</sup> We have synthesized the new functionalized phosphonic acids and their derivatives 1-5 including azaheterocycles *via* addition of tris(trimethylsilyl) phosphite to azaheterocyclic formamides and ketones. Trimethylsilyl-containing organophosphorus compounds easily react with methanol excess or with sodium methylate in methanol giving water soluble acids or their sodium salts in high yields.<sup>2,3</sup>

The resulting compounds are the perspective biologically active substances and polydentate ligands with versatile properties as well as the promising precursors for multitarget drug discovery. This work was financially supported by the RFBR (grants numbers 15-03-00002 and 17-03-00169).

<sup>1</sup> V.P. Kukhar, H.R. Hudson, *Aminophosphonic and Aminophosphinic Acids. Chemistry and Biological Activity*. New York: Wiley, **2000**. 634 p.

<sup>2</sup> A.A. Prishchenko, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Heteroat. Chem.*, **2016**, *27*, 381-388.

<sup>3</sup> A.A. Prishchenko, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Mendeleev Commun.*, **2017**, *27*, 90-92.



## P-24 NEW FUNCTIONALIZED ORGANOPHOSPHORUS ACIDS WITH ARYL AND BICYCLIC MOIETIES VIA ORGANOSILICON-BASED SYNTHESIS

A.A. Prishchenko,\* M.V. Livantsov, O.P. Novikova, N.N. Meleshonkova, L.I. Livantsova, V.S. Petrosyan

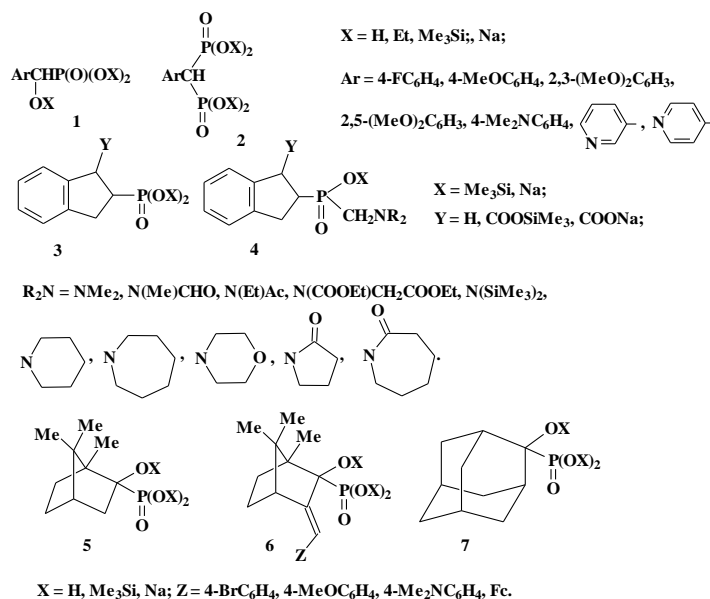
M.V. Lomonosov Moscow State University, Moscow, 119991, Russia  
aprishchenko@yandex.ru

Functionalized organophosphorus acids and their derivatives with aryl and bicyclic moieties are widely used in organic synthesis and may be considered as promising biologically active compounds and efficient ligands. We proposed the convenient synthesis of new these acids using trimethylsilyl esters of trivalent organophosphorus acids containing highly reactive PH and POSi moieties and starting indene, aldehydes or ketones with aryl and bicyclic moieties. Thus a number of functionalized compounds **1-7** as structural organophosphorus biomimetics of important hydroxy or amino acids are synthesized by us. Also trimethylsilyl-containing organophosphorus compounds easily react with methanol excess or sodium methylate in methanol giving water soluble acids or their sodium salts in high yields.<sup>1,2</sup> The resulting compounds are the perspective precursors for multitarget drug discovery.

This work was financially supported by the RFBR (NN 15-03-00002 and 17-03-00169).

<sup>1</sup> A.A. Prishchenko, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Heteroat. Chem.*, **2016**, *27*, 381-388.

<sup>2</sup> A.A. Prishchenko, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Mendeleev Commun.*, **2017**, *27*, 90-92.



P-25

## BORANE INITIATED FUNCTIONALIZATION OF SILICON NANOCRYSTAL SURFACES: HYDROSILYLATION AND LIGAND-EXCHANGE CHEMISTRY

Tapas K. Purkait,<sup>‡</sup> Jonathan G.C. Veinot\*

Department of Chemistry, University of Alberta, Edmonton, AB, Canada

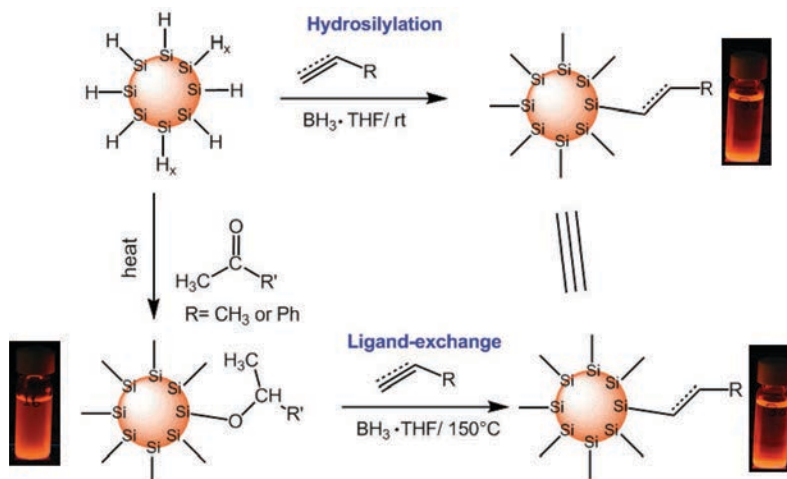
<sup>‡</sup>Present Address: Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA.

tpurkai1@jhu.edu, jveinot@ualberta.ca.

Hydrosilylation is one of the most common and effective ways to passivate H-terminated Si surfaces through robust Si-C bonds. Most of the current functionalization methods either require heating, exposure to intense UV light, addition of a radical initiator, or use of an expensive and toxic metal catalyst. Each of these methods has its own challenges including inefficient surface passivation, oligomerization of surface ligands, or difficulty in metal catalyst separation. This presentation will outline the development of an efficient, borane initiated functionalization methods developed for Si nanocrystal (SiNC) surfaces. Hydrosilylation of alkynes/alkynes on hydride-terminated SiNCs is catalyzed by Lewis acidic borane ( $\text{BH}_3 \cdot \text{THF}$ ) at room temperature.<sup>1</sup> Whereas alkoxy-terminated SiNC surfaces undergo an unprecedented ligand exchange reaction of the alkoxy-surface groups with alkyl or alkenyl-surface groups in the presence of  $\text{BH}_3 \cdot \text{THF}$ .<sup>2</sup>

<sup>1</sup> T. K. Purkait et. al., *J. Am. Chem. Soc.* **2014**, *136*, 17914–17917.

<sup>2</sup> T. K. Purkait et. al., *J. Am. Chem. Soc.* **2016**, *138*, 7114–7120.



## P-26

## THE INTRAMOLECULAR SILYL-HECK REACTION AND FIRST EXAMPLES OF INTERNAL ALKENE PARTICIPATION

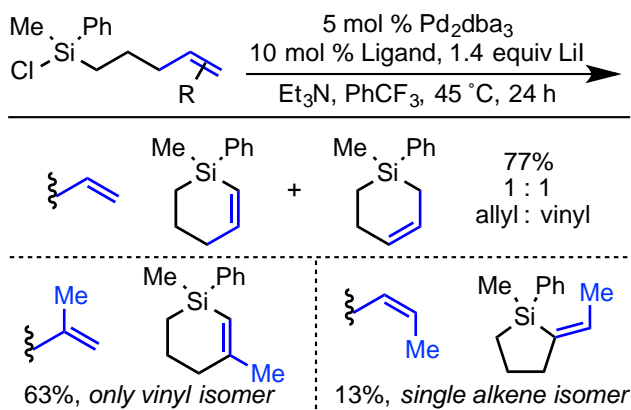
William B. Reid, Jesse R. McAtee, Donald A. Watson\*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA  
 wreid@udel.edu, jesse.mcatee@gmail.com, dawatson@udel.edu

Unsaturated silanes have widespread applications in various fields of chemistry.<sup>1</sup> In 2012, our group published a palladium-catalyzed method for the synthesis of allyl- and vinyl-silanes directly from unfunctionalized alkenes and trimethylsilyliodide (TMSI).<sup>2</sup> We sought to develop an analogous intramolecular variant and saw this as an opportunity to better study and understand the silyl-Heck reaction. By tethering an alkene to an electrophilic silane, we are able to form cyclic unsaturated silanes with interesting cyclization patterns. Surprisingly, the simplest silyl analogue proceeded with complete selectivity for the 6-endo cyclization product forming both allyl and vinyl products. However, we found that the starting alkene geometry and alkyl chain length have a pronounced effect on the selectivity of the ring closure. Additionally, many of the products formed were vinyl silanes, which contrasts earlier studies where the allyl isomer is preferred. For the first time, we have shown that internal alkenes will participate in the silyl-Heck reaction with interesting selectivity.

<sup>1</sup> Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631.

<sup>2</sup> McAtee, J. R.; Martin, S. E. S.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 3663.





## P-27

## CARBONYL HYDROSILYLATION VIA BASE METAL CATALYSIS

Christopher L. Rock,<sup>1</sup> Tufan K. Mukhopadhyay,<sup>1</sup> Thomas L. Groy,<sup>1</sup> Mu-Hyun Baik,<sup>2</sup> Ryan J. Trovitch\*<sup>1</sup>

<sup>1</sup> School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA

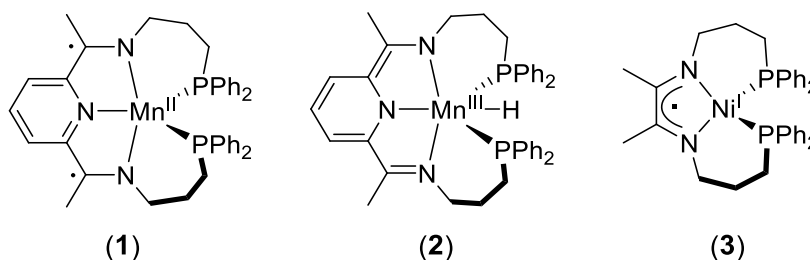
<sup>2</sup> Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, South Korea

clrock@asu.edu, tmukhopa@asu.edu, tgroy@asu.edu, mbaik2805@kaist.ac.kr, ryan.trovitch@asu.edu

Seeking to replace existing precious metal hydrosilylation catalysts, our group has focused on the development of base metal replacement that are supported by a redox non-innocent ligand framework. Recently,<sup>1</sup> our efforts have yielded (<sup>Ph</sup><sub>2</sub>PP<sup>Pr</sup>PDI)Mn (**1**) that promotes ambient temperature aldehyde and formate hydrosilylation at turnover frequencies of up to 4900 min<sup>-1</sup> and 330 min<sup>-1</sup>, respectively. During catalysis, evidence for a new species, (<sup>Ph</sup><sub>2</sub>PP<sup>Pr</sup>PDI)MnH (**2**), was observed. Complex **2** was independently synthesized to determine its catalytic activity and was found to be comparable to **1**, although mechanistic investigations revealed **2** to have superior carboxylate hydrosilylation ability, while **1** is more efficient at carbonyl hydrosilylation. Kinetic studies also revealed divergent mechanisms; **1** operates via a modified Ojima mechanism, while **2** follows an insertion pathway. Additionally, (<sup>Ph</sup><sub>2</sub>PP<sup>Pr</sup>PDI)Ni (**3**)<sup>2</sup> has shown the ability to hydrosilylate aldehydes and ketones at turnover frequencies of 41.6 h<sup>-1</sup> (ambient temperature) and 4.1 h<sup>-1</sup> (60 °C), respectively. Variation of the phosphine substituents (R = Ph (**3**), <sup>i</sup>Pr (**4**), <sup>t</sup>Bu (**5**)) resulted in a decrease in activity for carbonyl hydrosilylation.

<sup>1</sup> Mukhopadhyay, T. K.; Rock, C. L.; Hong, M.; Ashley, D. C.; Groy, T. L.; Baik, M-H.; Trovitch, R.J. *J. Am. Chem. Soc.* **2017**, Articles ASAP.

<sup>2</sup> Porter, T. M.; Hall, G. B.; Groy, T. L.; Trovitch, R. J. *Dalton Trans.* **2013**, 42, 14689-14692.



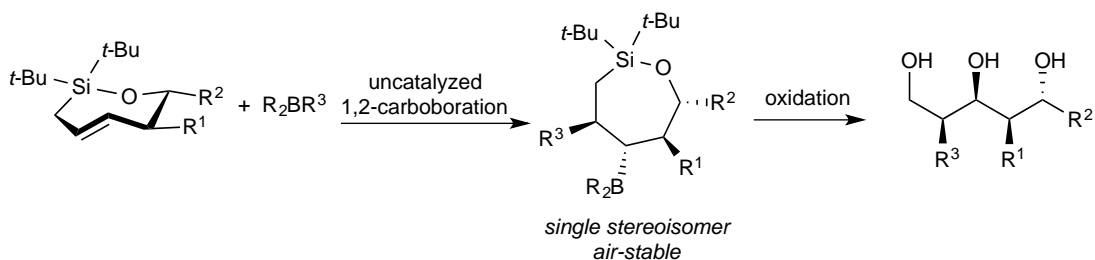
## P-28

**SYNTHESIS OF AIR-STABLE TRIALKYLBORANES: UNCATALYZED CARBOBORATION OF SEVEN-MEMBERED-RING *TRANS*-ALKENES**

Jillian R. Sanzone, K. A. Woerpel\*

New York University, 100 Washington Square East, 10<sup>th</sup> Floor, New York, NY 10003, USA  
jrs564@nyu.edu, kwoerpel@nyu.edu

Seven-membered-ring *trans*-alkenes undergo rapid, uncatalyzed carboboration reactions to form trialkylboranes as single diastereomers. Products formed from this reaction are air-stable, contrasting with other trialkylboranes, which can ignite in the presence of oxygen. Up to four consecutive stereocenters can be constructed around the ring and a variety of functional groups are tolerated under the reaction conditions. Ring strain is an important factor in this reaction, as a larger *trans*-cyclooctene did not react with triethylborane. Control experiments and computational studies support a concerted mechanism for the migratory insertion of the *trans*-alkene into the carbon–boron bond. Hindered trialkylboranes can undergo reverse hydroboration reactions to form allylic silanes or can be fully oxidized to afford triol products.



## P-29

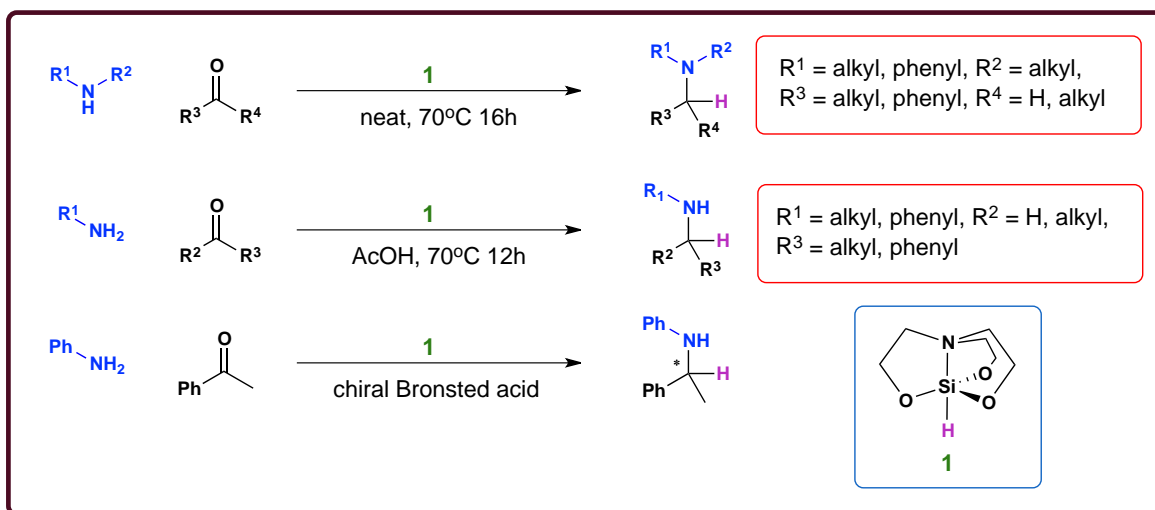
## DRA(MA) ON THE 'TRAIN: GREEN DIRECT REDUCTIVE AMINATIONS USING 1-HYDROSILATRNE

Vladislav Skrypai, Sami E. Varjosaari, Thomas M. Gilbert, Marc J. Adler\*

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA  
 vskrypai1@niu.edu, svarjosaari@niu.edu, tgilbert@niu.edu, mjadler@niu.edu

Direct reductive amination (DRA) is the most thought after method for synthesis of secondary and tertiary amines. Here we report a novel DRA method using 1-hydrosilatrane, both aldehydes and ketones react with primary and secondary amines with great functional group tolerance<sup>1</sup>. This method is safe, metal-free, and simple in operation, making it desirable for pharmaceutical and fine chemical applications. The reaction provides good to excellent yields both neat and with a minimal amount of solvent. All reactions were run under ambient conditions with no effort to exclude moisture or air from the reaction vessel. Furthermore, in the presence of a chiral Bronsted acid, the reaction of ketones and primary amine showed enantioselectivity.

<sup>1</sup> Vladislav Skrypai, Sami E. Varjosaari, Paolo Suating, Joseph J. M. Hurley, Ashley M. De Lio, Thomas M. Gilbert, Marc J. Adler *Adv. Synth. Catal.* **2017**, xx, xxx.



## P-30 PDMS/FLUOROSILICONE BLENDS

Camille Spigolis,\* Mathieu Doan, François Ganachaud\*

IMP@INSA, UMR5223, F-69621, Villeurbanne, France  
camille.spigolis@insa-lyon.fr, francois.ganachaud@insa-lyon.fr

Polydimethylsiloxane (PDMS) elastomers show outstanding resistances to high and low temperatures, but on the other hand they swell in a wide range of industrially used fluids and oil.<sup>1</sup> Fluorosilicones (FS) are, amongst other, resistant to fuels and oils, but they show substantially inferior thermal properties<sup>2</sup> and potentially produce HF during thermal degradation.<sup>3</sup> Hopefully, blending PDMS and FS would then be a convenient way to combine the pros of each polymer.<sup>4</sup>

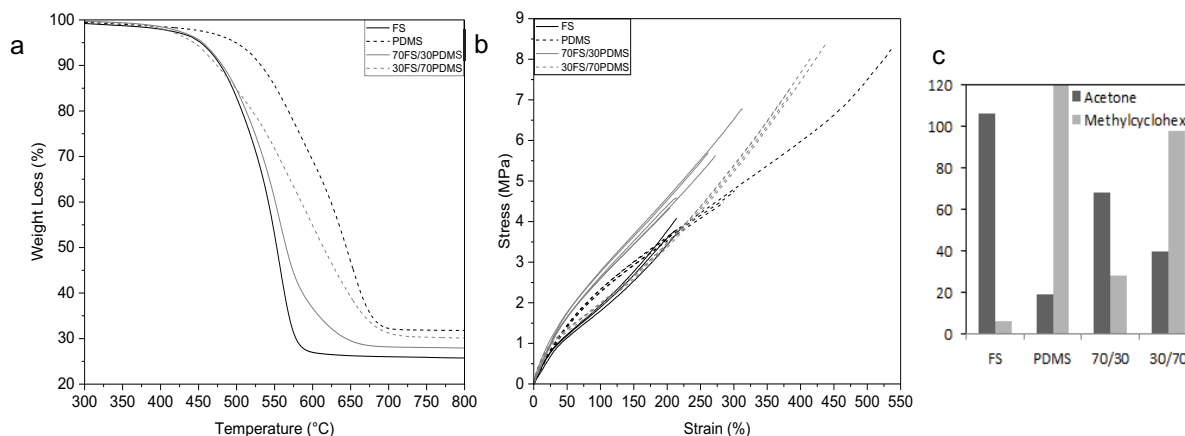
This work presents our study on the blending and crosslinking of PDMS/FS mixtures. Thermal and mechanical properties of the final elastomers were studied, as well as solvent resistance (**Figure 1**). Crosslinking, using different organic peroxides, showed to be a major parameter for achieving good mechanical properties. All these investigations suggested that the blend containing 30 parts of FS best fulfilled expectations in term of thermal stability, swelling and mechanical properties.

<sup>1</sup> D. K. Thomas, *Polymer* **1972**, 13, 479.

<sup>2</sup> B. Li, S. J. Chen, J. Zhang, *Journal of Applied Polymer Science* **2014**, 131

<sup>3</sup> G. J. Knight, W. W. Wright, *Thermochimica Acta* **1983**, 60, 187

<sup>4</sup> C. Bhuvanewari, R. Dhanasekaran, S. Chakravarthy, S. Kale, G. Gouda, *Progress in Rubber, Plastics and Recycling Technology* **2015**, 31, 207



**Figure 1:** a) Thermogravimetric analyses and b) mechanical properties, of FS (plain black), PDMS (black dash), and their blends, respectively 70/30 (plain grey) and 30/70 (grey dash). c) their swelling ratios in acetone (black) and in methylcyclohexane (grey).

## P-31 PHENYLSILANE OLIGOMERS FROM LITHIATION OF PHENYLSILYL ETHERS

Charles M. Stockdale, Yingjian Bo, Scott McN. Sieburth\*

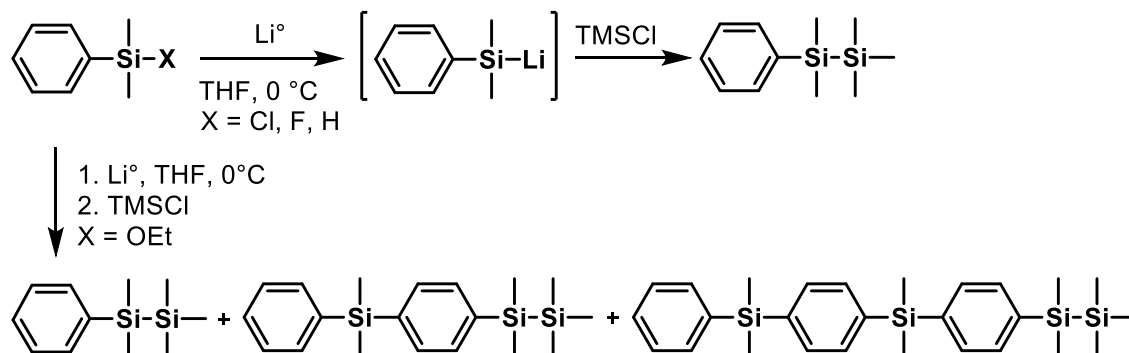
Temple University, Beury Hall, 1901 N. 13th St. Philadelphia, PA 19122, USA  
charles.stockdale@temple.edu, scott.sieburth@temple.edu

A surprising oligomerization of dialkylphenylsilyl ethers under standard lithiation conditions has been observed. Whereas phenyldimethylsilyl chloride,<sup>1</sup> fluoride,<sup>2</sup> and hydride<sup>3</sup> all yield the corresponding silyllithium reagent, the ethoxy derivative gives linear polyphenylsilanes. Efforts to optimize the formation of oligomers and to define the mechanism of this reaction will be presented.

<sup>1</sup> I. Fleming; R.S. Roberts; S.C. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1209-1214.

<sup>2</sup> Y. Bo, *Research Notes, Temple U.* **2011**.

<sup>3</sup> D. Hernandez; R. Mose; T. Skrydstrup, *Org. Lett.*, **2011**, *13*, 732-735.



**P-32****THERMAL ANNEALING OF GOLD THIN FILMS ON THE STRUCTURE AND SURFACE MORPHOLOGY USING RF MAGNETRON SPUTTERING**

Moniruzzaman Syed,<sup>a\*</sup> Caleb Glaser,<sup>b</sup> Muhtadyuzzaman Syed<sup>c</sup>

<sup>a</sup> Division of Natural and Mathematical Sciences, Lemoyne-Owen College, 807 Walker Ave, Memphis, TN 38126, USA

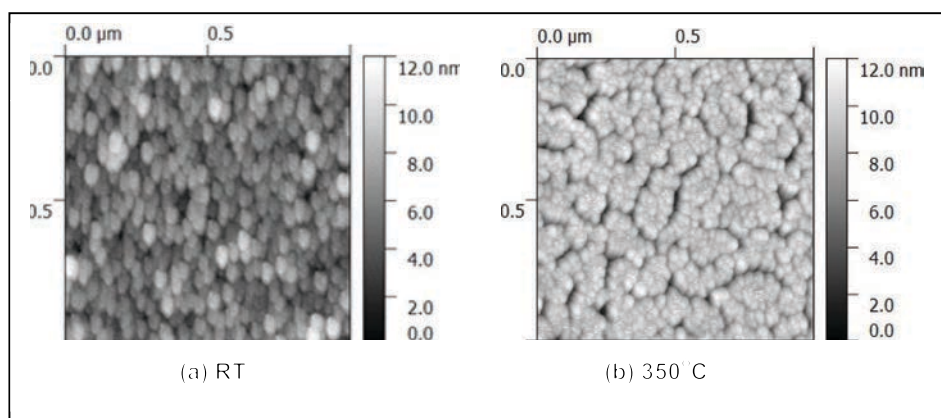
<sup>b</sup> Sandia National Laboratories, Albuquerque, NM, USA

<sup>c</sup> Department of Electrical and Computer Engineering, Purdue University, IN, USA

moniruzzaman\_syed@loc.edu

Gold (Au) thin films were deposited on SiO<sub>2</sub> substrates under argon (Ar) gas environment as a function of sputtering time [T<sub>s</sub>] using RF magnetron sputtering. These samples were annealed at 350°C under vacuum. The structural and surface morphological properties of both as-deposited and annealed films have been studied using an Atomic Force Microscope (AFM), X-ray diffraction (XRD) and Raman Scattering. The improvement of crystallinity was observed at 2 hours of annealing and degradation was found thereafter. In agreement with XRD and Raman measurements<sup>1</sup>, both crystallite size and crystalline volume fraction were found to be increased having maximum at 2 hours annealing and decreased afterward. This result can be explained by simple Kinetic Theory where sticking probabilities and surface coverage of Au atoms must be considered. Moreover, it can also be explained by the occurrence of two competing phenomena like roughening induced grain growth and smoothing induced inhibition of grain growth with increasing annealing time. Growth mechanisms are also discussed.

<sup>1</sup> J. Garnaes, F.E. Christensen, F. Besenbacher, E. Laegaggaard, I. Stensgard: Opt. Eng. 1999, 29, 666



**Figure 1:** AFM micro graphs (a) at room temperature and (b) at 350 °C

## P-33

## CONTROLLING THE JUNCTION SWITCH: ASYMMETRIC KETONE REDUCTIONS USING 1-HYDROSILATRANE

Sami E. Varjosaari, Vladislav Skrypai, Thomas M. Gilbert, Marc J. Adler\*

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, 60115, USA  
 svarjosaari@niu.edu, vskrypai1@niu.edu, tgilbert@niu.edu, mjadler@niu.edu

The reduction of prochiral ketones to chiral alcohols is a quintessential functional group manipulation in organic chemistry.<sup>1</sup> 1-Hydrosilatrane – a robust, inexpensive, easy to handle alkoxysilane derivative – has been shown to reduce carbonyls in the presence of Lewis base activators.<sup>2-3</sup> Therefore an appropriate chiral Lewis base could potentially induce enantioselectivity in prochiral ketones.<sup>4-6</sup> With this in mind, we have been able to obtain fair to excellent enantioselectivity using deprotonated chiral amino alcohols as activators. For example, acetophenone was reduced to (R)-phenylethanol with up to 99% yield and 85% e.e.

<sup>1</sup> Magano, J.; Dunetz, J.R. *Org. Process. Res. Dev.* **2012**, *16*, 1156-1184.

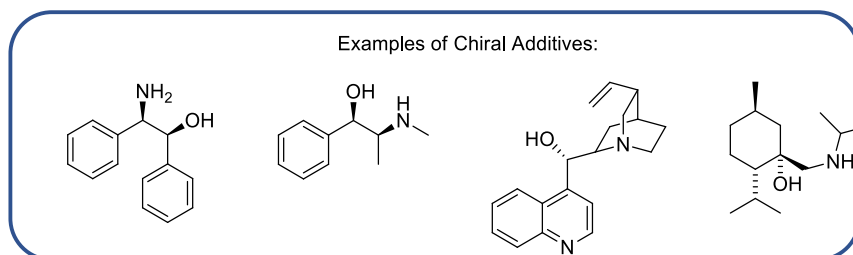
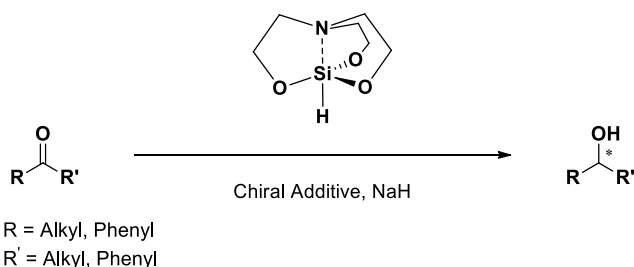
<sup>2</sup> Skrypai, V.; Hurley, J.M.; Adler, M.J. *Eur. J. Org. Chem.* **2016**, *12*, 2207-2211.

<sup>3</sup> Varjosaari, S.E.; Skrypai, V.; Suating, P.; Hurley, J.J.M.; Gilbert, T.M.; Adler, M.J. *Eur. J. Org. Chem.* **2017**, *2*, 229-232.

<sup>4</sup> Kohra, S; Hayashida, H.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 89-92.

<sup>5</sup> Schiffrers, R.; Kagan, H.B. *Synlett.* **1997**, 1175-1178.

<sup>6</sup> Gan, L.; Brook, M.A. *Can. J. Chem.* **2006**, *84*, 1416-1425.



**P-34**  
**INVESTIGATING THE MECHANISM OF ENANTIOSELECTIVE**  
**SILYLATION**

Sheryl L. Wiskur\*

*University of South Carolina, Department of Chemistry and Biochemistry, 631 Sumter St.,  
Columbia, SC 29208, USA  
wiskur@mailbox.sc.edu*

The kinetic resolution of secondary alcohols is an important transformation in asymmetric chemistry. While there are a number of great methods available, a majority of the work has focused on selective acylation with silylation-based kinetic resolutions only recently gaining interest. We are focused on promoting enantioselective silylation of racemic alcohols by employing chiral isothioureia catalysts and triphenylsilyl chlorides. Our methodology can be used to resolve secondary cyclic alcohols,  $\alpha$ -hydroxy carbonyl compounds, and 2-aryl cyclic alcohols. The mechanistic investigations of this methodology will be presented which includes kinetics, CD spectroscopy, and NMR experiments.



**P-35****BENZ- AND PYRIDO-ANNULATED SILYLENES AND THEIR ANALOGS: ELECTRONIC STRUCTURE, SELF-ASSEMBLY AND REACTIVITY**

Alexander V. Zabula,<sup>a\*</sup> Andrey Yu. Rogachev,<sup>b</sup> Jingbai Li,<sup>b</sup> Ilia A. Guzei,<sup>c</sup> Robert West,<sup>c</sup> Rinat R. Aysin,<sup>d</sup> Larissa A. Leites,<sup>d</sup> Sergey S. Bukalov<sup>d</sup>

<sup>a</sup> Department of Chemistry, University of Pennsylvania, 231 S 34st, Philadelphia, PA 19104, USA

<sup>b</sup> Illinois Institute of Technology, Chicago, IL 60616, USA

<sup>c</sup> University of Wisconsin, 1101 University Ave, Madison, WI 53726, USA

<sup>d</sup> Scientific and Technical Center on Raman Spectroscopy, INEOS RAS, 28 Vavilova str., Moscow 119991, Russia

zabula@sas.upenn.edu, andrey.rogachev@iit.edu

The stability, structure and reactivity of N-heterocyclic silylenes (NHSi's) and their analogues can be tuned by a careful choice of substituents at low-valent Group 14 element atom and overall cyclic backbones. In the present work, we report the molecular structures and unprecedented supramolecular self-assembly for the family of benz- and pyrido-annulated NHSi's and their analogs with Group 14 elements.<sup>1,2</sup> The degree of 10 $\pi$  electron aromaticity in the investigated compounds is elucidated based on optical (Raman, UV-vis) and computational data.<sup>3</sup> Unusual thermal transformation of pyridoannulated silylene and germylene resulted in the formation of the zwitter-ionic silene or germene products featuring tri-coordinated Group 14 element atoms.<sup>4</sup> The electronic structures of the resulting products are discussed based on computational studies.

<sup>1</sup> A. V. Zabula, A. Y. Rogachev, R. West, *Chem. Eur. J.* **2014**, *20*, 16652.

<sup>2</sup> R. R. Aysin, L. A. Leites, S. S. Bukalov, A. V. Zabula, R. West, *Inorg. Chem.* **2016**, *55*, 4698.

<sup>3</sup> R. R. Aysin, L. A. Leites, S. S. Bukalov, A. V. Zabula, *Dalton Trans.* **2017**, DOI:10.1039/C7DT00356K.

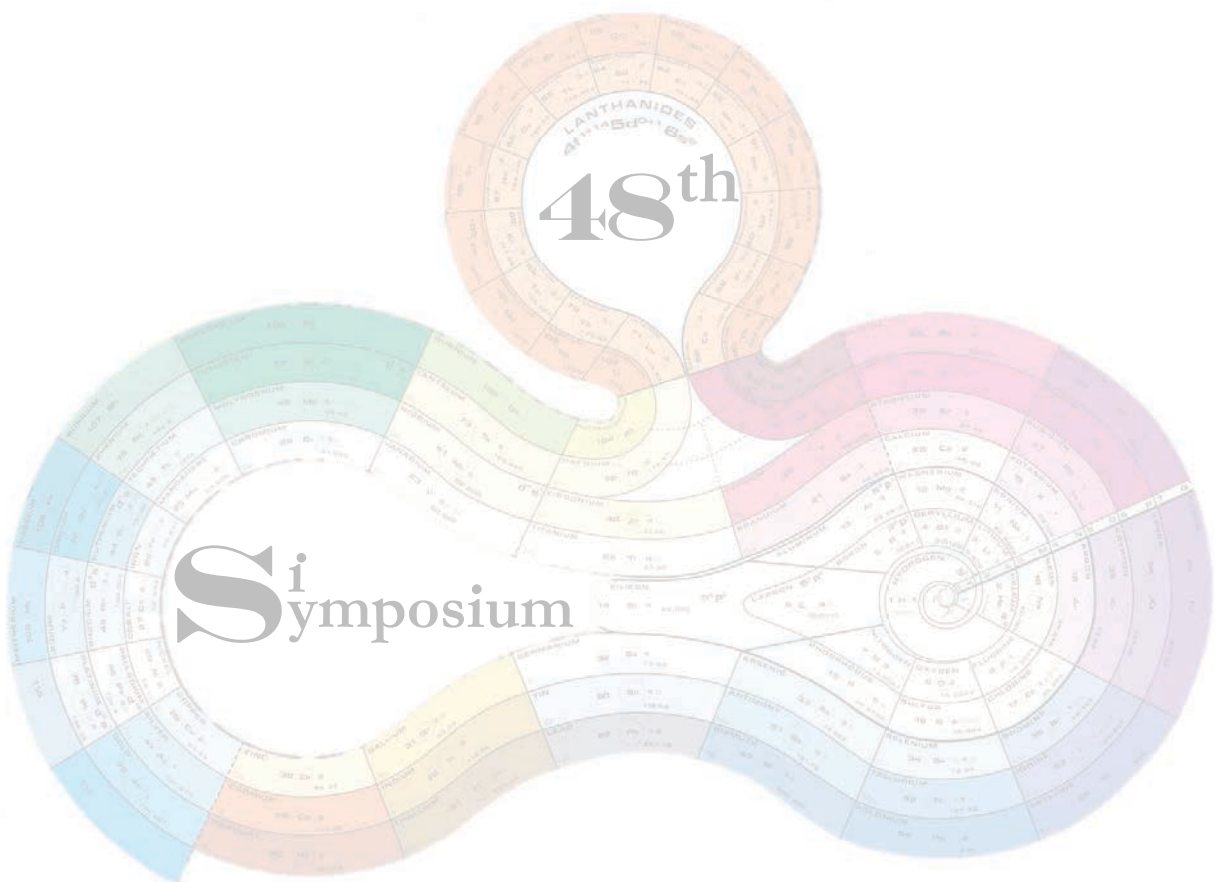
<sup>4</sup> A. V. Zabula, I. A. Guzei, R. West, J. Li, A. Y. Rogachev, *Angew. Chem. Int. Ed.* **2016**, *55*, 13465.



---

# Author Listing

---





<b>A</b>			P-1, P-3, P-9, P-12
Adler, Marc J.	SL-25, P-27, P-33		
Alston, Jeffrey R.	IL-2	Chen, Shawn	P-8
Ampomah, Natasha	P-1	Chen, Tong	SL-15
Anderson, Kenneth J.	SL-12, P-22	Chen, Yang	SL-18
Angeletakis, Christos	SL-19	Chinnam, Parameswara Rao	SL-10
Arkles, Barry	IL-4, SL-11, SL-23, P-17	Christopoulos, Viktor	SL-30, P-6
Armstrong, Brittany	P-2	Cinderella, Andrew P.	P-7
Artiga, Daniela	P-3, P-12	Crawford, Edward	IL-6
Asami, Kazunori	SL-6	Cui, Li	P-8
Auer, Dominik	P-5	Cummings, Michelle R.	SL-20
Aysin, Rinat R.	P-35	Cummins, Elizabeth	IL-10
<b>B</b>		<b>D</b>	
Baik, Mu-Hyun	P-27	Delebecq, Etienne	SL-17
Baines, Kim M.	SL-2	Derstine, Brenden P.	SL-26
Barth, Eva	SL-28	Diemoz, Kayla	SL-7
Bauer, Jonathan O.	SL-27, SL-28, P-4	Doan, Mathieu	P-30
Bharami, M.	SL-5	Driess, Matthias	IL-1
Bian, P.	PL-2	Duong, Hoan Q.	SL-24
Bilney, John	SL-19	<b>E</b>	
Bo, Yingjian	P-31	Egawa, Yasunobu	SL-6
Boudjouk, Philip	SL-12, P-22	Elias, Edwin	P-9
Bourque, Jeremy L.	SL-2	Ellison, Rylie J.	SL-13
Brick, Chad M.	SL-21	<b>F</b>	
Britt, R. David	P-2	Fauvre, Lucile	P-10
Brook, Michael A.	SL-15, SL-18, SL-32	Flagg, D. H.	PL-2
Bukalovd, Sergey S.	P-35	Fletcher, Steven E. S.	P-11
<b>C</b>		Fleurant-Jean, Ralph	P-12
Campos, Raymond	IL-2	Fleury, Etienne	P-10, P-21
Cervantes, J.	SL-16, P-14	Folster, Carlton P.	SL-29, P-13
Chauhan, Bhanu P. S.	SL-8,	Ford, Brian	IL-6
		Franz, Annaliese K.	SL-7, P-2, P-18
		Frohlich, Matthew	SL12
		Furgal, J.	SL-5

<b>G</b>			
Gallis, Spyros	IL-6	Ju, Ling	P-12 SL-9
Ganachaud, François	IL-7, SL-17, P-30, P-21, P-10	<b>K</b>	
Gaspar, Peter P.	SL-4	Kaloyeros, A. E.	P-17
Gilbert, Thomas M.	SL-25, P-27, P-30	Kampf, J.	SL-5
Glaser, Caleb	P-32	Kang, Jinyoung	IL-4
Goff, Jonathan	SL-11, SL-23	Kelly, Austin T.	P-18
Goforth, Andrea M.	SL-13	Khatri, Buddha B.	SL-26
Golz, Christopher	SL-28	Kieffer, J.	SL-5
González-Calderón, J.A.	SL-16	Kilina, Svetlana	P-22
González-García, G.	P-14	Kim, Dokyoung	IL-4
Goodson III, T.	SL-5	Kim, Taeho	IL-4
Green, Van V.	SL-31	Kim, B. J.	IL-4
Groy, Thomas L.	P-27	Klausen, Rebekka S.	SL-29, P-13
Guenther, Andrew J.	IL-2	Kloss, Marvin	P-5
Guillaussier, Adrien	IL-5	Kocherga, Margaret	P-19
Gutiérrez-Fuentes, J. A.	P-14	Korgel, Brian	IL-5
Guzei, Ilia A.	P-35	Krause, Sarah B.	P-20
<b>H</b>		Kulyk, Svitlana	SL-26
Haas, Michael	SL-22, SL-30, P-6, P-15	Kumar, Ramesh C.	IL-8
Haddad, Timothy S.	IL-2	<b>L</b>	
Hashemi, D.	SL-5	Laengert, Scott E.	SL-18
Huesing, Nicola	IL-3	Laine, Richard M.	SL-5
<b>I</b>		Lainer, Thomas	SL-30
Iacono, Scott T.	IL-2	Larribe, Gabriel	P-21
Inman Jr., William D.	SL-20	Leites, Larissa A.	P-35
<b>J</b>		Leiva, Juan	P-9
Jagannathan, Jake	SL-7	Lewicki, James P.	IL-9
Jeon, Junha	P-16	Lewis, Kenrick	IL-12
Jim, Cameron	P-8	Leybold, Mario	P-15
Johnson, Qiaxian R.	P-1, P-3, P-9,	Leyva-Ramírez, M. A.	P-14
		Li, Jingbai	P-35
		Liao, Mengchen	SL-32
		Livantsov, M. V.	P-23, P-24
		Livantsova, L. I.	P-23, P-24
		Lortie, Frédéric	SL-17
		Lovinger, Eric	SL-19
		<b>M</b>	
		Mabry, Joseph M.	IL-2
		Maddox, Annalese F.	SL-11

Marro, Eric A.	SL-29, P-13	Purkait, Tapas K.	SL-29, P-13, P-25
Mcatee, Jesse R.	P-20, P-26		
McCarthy, Thomas J.	PL-2		
McOnie, Sarah	SL-2		
Meléndez-Lira, M.	SL-16		
Meléndez-Zamudio, M.	SL-16		
Meléndrez, R.	SL-16		
Meleshonkova, N. N.	P-23, P-24		
Mendis, Shehani M.	P-13		
Min, Taewoo	SL-11		
Moghadam, M.	SL-5		
Moran, Kelly	P-1		
Morgan, Jennifer	SL-15		
Mukhopadhyay, Tufan K.	P-27		
<b>N</b>		<b>R</b>	
Nagai, Yuka	SL-6	Radebner, Judith	SL-22
Nikas, Vasileios	IL-6	Radlinger, Christine M.	SL-13
Novikova, O. P.	P-23, P-24	Rahman, Anis	SL-14
		Rahman, Aunik	SL-14
		Ramirez, Sean M.	IL-2
		Reid, William B.	P-26
		Rickard, Mark	P-8
		Robeyns, Constance	IL-7
			SL-17
		Rock, Christopher L.	P-27
		Rogachev, Andrey Yu.	SL-1, P-35
		Roll, M. F.	SL-5
<b>O</b>		<b>S</b>	
O'Neil, Gregory W.	IL-10	Sailor, Michael J.	IL-4
Okada, Jun	SL-21	Samedov, Kerim	SL-3
		Sanzone, Jillian R.	P-28
		Sato, Motoki	SL-21
		Sayler, Richard	P-2
		Schmedake, Thomas A.	P-19
		Schneider, Alyssa F.	SL-18, SL-32
		Schneider, Emily	IL-10
		Schwiderski, Ryan	SL-12
		Seim, Alexander	SL-4
		Senoo, Kazunobu	SL-21
		Shintaro, Yamada	P-8
		Shupe, Benjamin	P-2
		Sieburth, Scott McN.	SL-24, SL-26, P-11, P-31
			SL-25, P-29, P-33
		Skrypai, Vladislav	IL-7
		Spigolis, Camille	P-30
		Stockdale, Charles M.	P-31
		Strandwitz, Nicholas C.	SL-9
		Streb, Pedro Braun	P-5
<b>P</b>			
Pan, Youlin	IL-4, SL-11, P-17		
Pannell, Keith H.	P-14		
Pascault, Jean-Pierre	P-10		
Patel, Aarti	P-3		
Paul, LaBeaume	P-8		
Percival, Paul W.	SL-3		
Petrosyan, V. S.	P-23, P-24		
Pokhodnya, Konstantin	SL-12, P-22		
Portinha, Daniel	P-10		
Press, Eric M.	SL-29 P-13		
Prishchenko, A. A.	P-23, P-24		

Strohmann, Carsten	SL-27, SL-28, P-4, P-5	Wunder, Stephanie L.	P-28 SL-10
Stueger, Harald	SL-22, SL-30, P-6, P-15	<b>X</b>	
Surampudi, Sravan K.	SL-29	Xue, Genqiang	SL-31
Surti, Chandres	SL-19	<b>Y</b>	
Syed, Moniruzzaman	P-32	Yu, Yixuan	IL-5
Syed, Muhtadyuzzaman	P-32	<b>Z</b>	
<b>T</b>		Zabula, Alexander V.	SL-1, P-35
Tabassum, Natasha	IL-6	Zdilla, Michael	SL-10
Takeda, Nobuhiro	SL-6	Zibula, Lukas	SL-27
Tamaki, R.	SL-5		
Tashkandi, Nada Y.	SL-2		
Tilford, Susan H.	SL-23		
Trovitch, Ryan J.	P-27		
Tuteja, Anish	IL-2		
<b>U</b>			
Unno, Masafumi	SL-6		
<b>V</b>			
Van Vliet, Megan	SL-10		
Varjosaari, Sami E.	SL-25, P-29, P-33		
Veinot, Jonathan G. C.	P-25		
Villegas, A.	SL-16		
Vulovic, Bojan Z.	P-7		
<b>W</b>			
Wang, Joanna	IL-4		
Watson, Donald A.	IL-11, P-7, P-20, P-26		
Weber, Swen	P-4		
West, Robert	SL-3, P-35		
Wigman, Benjamin	P-2		
Wiskur, Sheryl L.	P-34		
Woerpel, Keith A.	PL-1,		