



50th Annual North American Silicon Symposium

May 13-15, 2019

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Scientific Schedule**Monday, May 13, 2019, Plenary Lecture**

5:30 PM Colin Nuckolls Silane Molecular Electronics

6:30 PM **OPENING RECEPTION****Tuesday, May 14, 2019**

9:00 AM Vladimir Gevorgyan Employment of Si-Tether Motif for C–H Functionalizations

9:40 AM Ryan Trovitch Design of Manganese Catalysts for Alkene Hydrosilylation

10:20 AM **COFFEE**10:40 AM Keith Pannell Triethylsiloxyethyl(dimethyl)amine, Et₃SiOCH₂NMe₂: A super aminomethyl transfer agent exhibiting Silick Chemistry.

11:00 AM Jongwook Choi, Kangsang Lee and Dimitris Katsoulis Rh-Catalyzed Intermolecular C-H Silylation Of Arenes And Heteroarenes With Various Silanes

11:20 AM Brandon Redden and Sheryl Wiskur Mechanistic insights into the silylation of secondary alcohols with isothiourea based catalysts.

11:40 AM Tian Zhang and Sheryl Wiskur Investigation of cation- π interactions in silylation-based kinetic resolutions12:00 PM **LUNCH - (on your own)**

1:30 PM	Lisa Rosenberg	Adventures in Si-H activation: Si-containing polymers and Lewis acid catalysts
2:10 PM	Liyun Yu and Anne Ladegaard Skov	Soft and flexible: Silicone elastomers for a variety of applications
2:50 PM	Barry Arkles, Youlin Pan and Jonathan Goff	Synthesis and Exploratory Deposition Studies of Isotetrasilane and Reactive Intermediates for Epitaxial Silicon
3:10 PM	COFFEE	
3:30 PM	Elke Fritz-Langhals and Richard Weidner	Low-valent Silicon Compounds as Catalysts for Industrial Organosilicon Chemistry
4:10 PM	Ichiro Imae, Nao Ueki and Yousuke Ooyama	Thermoelectric properties of conducting polymers doped with silicone-based polymer electrolyte
4:30 PM	Michael Yin Wong, Alyssa Schneider, Chen Yang and Michael A. Brook	Crosslinking via Si-H Functionality: A Catalyst-Free Route to Silicone Rubbers
4:50 PM	John Roberts, Vladimir Pushkarev, Jason Sturm and Dimi Katsoulis	A New Direct Process: Direct Synthesis Of Alkoxysilanes From Dimethyl Carbonate And Copper Silicides
5:30 PM	POSTER SESSION (2 hours)	

Wednesday, May 15, 2019

8:00 AM	James Cahoon	Synthesis of charge rectifying silicon nanostructures
8:40 AM	Frederique Cunin	Porous silicon, a biocompatible semiconductor for nanomedicine
9:20 AM	Rungthip Kunthom, Nobuhiro Takeda and Masafumi Unno	Novel Double-decker Cage Silsesquioxane: Synthesis, Characterization, Properties, and Application
9:40 AM	Yujia Liu, Masafumi Unno, Armelle Ouali and Nobuhiro Takeda	Design and Preparation of Innovative Functionalizable Silsesquioxanes as Building Blocks for New Nano-sized Supported Catalysts
10:00 AM	COFFEE	
10:20 AM	Annaliese Franz, Austin Kelly, Jacob Dalton and Kayla Diemoz	Advances in Enantioselective Methods for the Synthesis of Chiral Siloxanols and Mechanistic Studies for Catalysis
11:00 AM	Austin Kelly and Annaliese Franz	Rh-catalyzed Enantioselective Synthesis of Silicon Electrophiles to Access Chiral Siloxanes
11:20 AM	Mark B. Frampton, Andrea Blais, Zachary Raczynski and Paul M. Zelisko	Synthesis of Siloxane-Phospholipids and their Evaluation as Potential Drug Delivery Vehicles
11:40 AM	Marc Adler	Silatrane: A Versatile And User-Friendly Atom-Transfer Reagent
12:00 PM	LUNCH - (on your own)	

1:30 PM	Kim Baines, Nada Tashkandi, Bahar Farhadpour and Maissa Belcina	The Reaction Of Ditetrelenes With Organic Main Group Oxides
2:10 PM	Gregory Robinson and Yuzhong Wang	N-Heterocyclic Carbene Chemistry of Silicon: Recent Advances
2:50 PM	Janet Braddock-Wilking, Randy Winchester, Stephan Germann, Nigam Rath, Nick Viriyasiri and Rensheng Luo	Synthesis and Characterization of Luminescent 3,6-Disubstituted Silafluorenes and Germafluorenes
3:10 PM	COFFEE	
3:30 PM	Laura Turculet	Bis(phosphino)silyl Iron and Cobalt Pincer Complexes as Catalysts for the Reduction of Unsaturated Substrates
3:50 PM	Shelby Dickerson and Sheryl Wiskur	Exploration of Silicon Phthalocyanines as Viable Photocatalysts for Organic Transformations
4:10 PM	Margaret Kocherga, Michael Walter, and Thomas Schmedake	Hexacoordinate Silicon Complexes As Electron Transport Materials
4:30 PM	Charles Danehey and Angelika Sussman	The analysis of bis (3-triethoxysilylpropyl) tetrasulfide by utilizing NMR spectroscopy and SFC.
4:50 PM	Joe Xiaobing Zhou, Noel Chang, Jeanette Young and Xianghuai Wang	Selective Synthesis of 2,2,4,4-Tetrakisilylpentasilane
5:10 PM	Janis Matisons	Synthesis of POSS Photochromics & Their Properties
6:00 PM	SYMPOSIUM DINNER (Reservation required)	

Poster Session (Tuesday, 5:30-7:30 PM)

- | | | |
|-----|---|---|
| P1 | Andrey Prishchenko, Roman Alekseyev, Mikhail Livantsov, Olga Novikova, Ludmila Livantsova and Valery Petrosyan | Organosilicon-based synthesis of new methylenediphosphonic acids with azaheterocycles and amino acids moieties as perspective bioactive compounds |
| P2 | Andrey Prishchenko, Roman Alekseyev, Mikhail Livantsov, Olga Novikova, Ludmila Livantsova and Valery Petrosyan | Bis(trimethylsiloxy)phosphine as key synthon for synthesis of new aminomethylphosphinic acids with N-alkyl 4-hydroxypiperidines moieties |
| P3 | Paria Azadi-Namin and Paul M. Zelisko | Synthesis of Self-Healing and Recyclable Silicone Polymers Using the Diels-Alder Reaction as a Cross-Linker |
| P4 | Jorge Cervantes, Miguel Á. Meléndez-Zamudio, Ileana Bravo, Eulalia Ramírez-Oliva, Antonio Guerra-Contreras, Ramón Zárraga-Núñez and Gilberto Álvarez-Guzmán | Consolidant and Hydrophobic Stone Formulations Base on Glycol Alkoxysilanes and Chitosan |
| P5 | Antonio Guerra-Contreras, Miguel Ángel Meléndez-Zamudio and Jorge Cervantes | Synthesis of water-based functional organosilanes via the Piers-Rubinsztajn reaction |
| P6 | Miguel Melendez-Zamudio, Antonio Guerra-Contreras, Antonio Villegas and Jorge Cervantes | Aggregation induced effect (AIE) on gels based in siloxane amino co-polymer |
| P7 | Minji Jeong, Yeonjeong Lee, Younghun Kim, Hyeon Mo Cho and Moon Gun Choi | Neopentasilane for Liquid Phase Si Precursor to Metalloid Si |
| P8 | Chris Myers, Paul Spaltenstein and Gregory O'Neil | New (di)allylsilane-based carbon-carbon bond forming reactions |
| P9 | Nathanael Downes and Stephen Maldonado | Electrochemical Reactivity and Deposition Characteristics of Chlorosilanes in Nonaqueous Media |
| P10 | Michael Haaf, Jesse Hsu, Anthony DiBernardo and Omar Charaawi | Polymers of Intrinsic Microporosity with Azo and Silicone Functionalities |

Abstracts

Monday, 5:30 PM, Ballroom

Plenary - Silane Molecular Electronics

Colin P. Nuckolls*

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This presentation will provide an account of our recent efforts to uncover the fundamental charge transport properties of Si-Si and Ge-Ge single bonds and introduce useful functions into group 14 molecular wires. We utilize the tools of chemical synthesis and a scanning tunneling microscopy-based break-junction technique to study the mechanism of charge transport in these molecular systems. We evaluated the fundamental ability of silicon, germanium, and carbon molecular wires to transport charge by comparing conductances within families of well-defined structures, the members of which differ only in the number of Si (or Ge or C) atoms in the wire. We also studied their breakdown in electric fields. These fundamental studies have guided the design of new functional systems based on the Si- and Ge-based wires. For example, we exploited the principle of strain-induced Lewis acidity from reaction chemistry to design a single molecule switch that can be controllably switched between two conductive states by varying the distance between the tip and substrate electrodes. Furthermore, we demonstrate the first example of a stereoelectronic conductance switch, and we demonstrate that the switching relies crucially on the electronic delocalization in Si-Si and Ge-Ge wire backbones. Beyond making conductive materials from silanes and germanes, we have recently found that rigid, cage silanes are more insulating than vacuum. These studies illustrate the untapped potential in using Si- and Ge-based wires to design and control charge transport at the nanoscale and to allow quantum mechanics to be used as a tool to design ultra-miniaturized switches.

Tuesday, 9:00 AM

Employment of Si-Tether Motif for C–H Functionalizations

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NO ABSTRACT

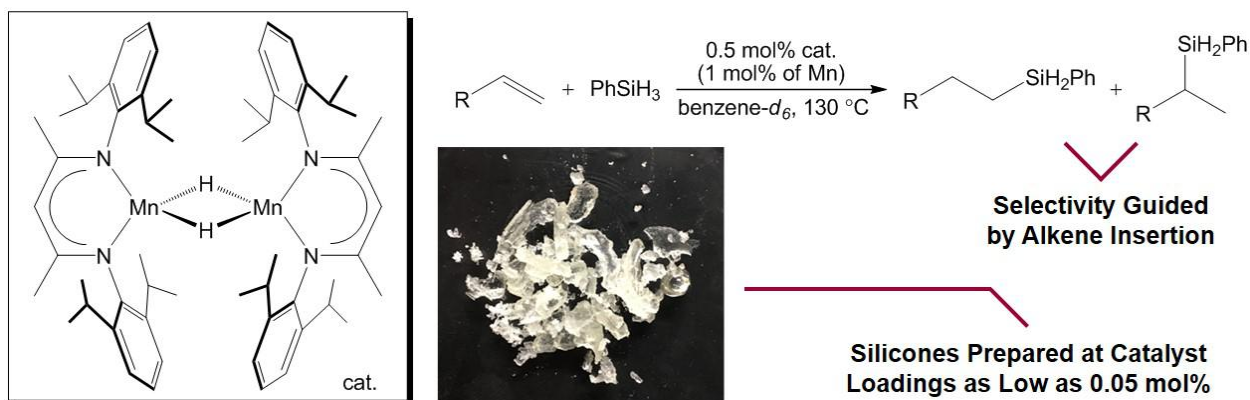
Tuesday, 9:40 AM

Design of Manganese Catalysts for Alkene Hydrosilylation

Ryan Trovitch*

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Hydrosilylation is relied upon for the large-scale production of silicone coatings, adhesives, and rubbers. The pursuit of sustainable, base metal replacements for common platinum hydrosilylation catalysts has intensified over the last decade due to the high cost and toxicity associated with precious metals. Research groups have largely focused on the development of iron, cobalt, and nickel catalysts for alkene hydrosilylation; however, manganese precatalysts for this application have remained overlooked. Efforts in our laboratory have focused on the utilization of ligand platforms that are capable of supporting substrate coordination and activation at highly-reactive, low-valent manganese centers. Several years ago, our approach allowed for the preparation of a formally zero-valent manganese complex, (Ph₂PPrPDI)Mn, which mediates carbonyl hydrosilylation with turnover frequencies of up to 4,900 min⁻¹ in the absence of solvent. Although this compound was not found to mediate alkene hydrosilylation, mechanistic insight has continued to guide our efforts to develop second-generation variants that do catalyze this transformation. We recently described the preparation of a beta-diketimate manganese hydride catalyst, [(2,6-iPr₂PhBDI)MnH]₂ (see Figure), which mediates alkene hydrosilylation at low catalyst loadings. Importantly, we have shown that [(2,6-iPr₂PhBDI)MnH]₂ is also capable of curing silicones in the presence of polymethylhydrosiloxane. Applications of this catalyst beyond alkene hydrosilylation will also be discussed if time permits.



Tuesday, 10:40 AM

Triethylsiloxymethyl(dimethyl)amine, Et₃SiOCH₂NMe₂: A super aminomethyl transfer agent exhibiting Silick Chemistry

Keith Pannell*

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We have reported that triethylsiloxymethyl-N-N-dimethylamine, Et₃SiOCH₂NMe₂ (**1**) is an excellent new Mannich reagent for amines, alcohols and thiols. When **1** is reacted with aniline, PhNH₂, the isolated product is 1,3,5-triphenyltriazine (**2**); (PhNCH₂)₃. This product was postulated to result from sequential aminomethylation of aniline, i.e. PhNHCH₂NMe₂ (**3**) → PhN(CH₂NMe₂)₂ (**4**); followed by elimination of (Me₂N)₂CH₂ to form an unstable imine, PhN=CH₂ (**5**). The imine finally trimerizes to product **2**. This is a complex process to propose, and no such intermediates were isolable. We have investigated the scope of this reaction with a series of anilines, ArNH₂, containing electron-donating (NMe₂, OMe, etc.) and electron-withdrawing (CF₃, NO₂, CN, etc.) substituents, and a sterically congested aniline, (Ar*₂NH₂) [Ar* = 2,6-bis(diphenylmethyl)-4-tert-butylphenyl]. By judicious choice of substituents we have now observed, isolated and structurally characterized examples of **3**, **4**, and **5** for the first time. We have also visited the reaction between **1** and ureas and uncovered new rearrangements as illustrated by the transformation observed from the reaction of **1** with 1,3-diphenylthiourea, PhNH(C=S)NHPh leading to PhNH(C=S)NMe₂. All will be revealed.

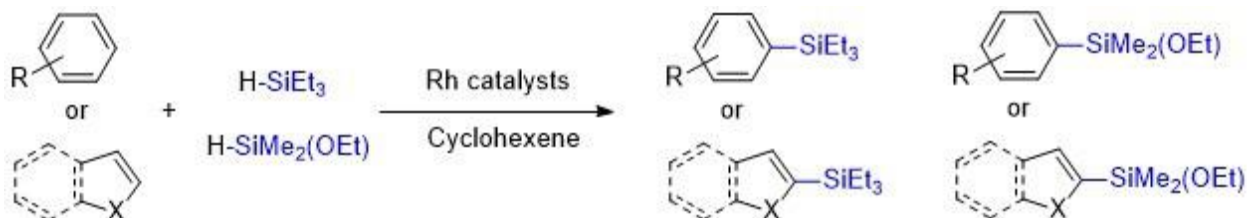
Tuesday, 11:00 AM

Rh-Catalyzed Intermolecular C-H Silylation Of Arenes And Heteroarenes With Various Silanes

Jongwook Choi,* Kangsang Lee and Dimitris Katsoulis

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Silicones containing phenyl groups are widely used in silicone business owing to their unique properties such as high thermal stability, high refractive index, and organic compatibility. However, utilization of silicones containing variously substituted aryl or heteroaryl groups is very limited despite the potential opportunities for new chemistries and benefits these substituents may provide. This is due to the lack of simple and efficient protocols to prepare substituted aryl- and heteroarylsilane intermediates. Herein, we disclose a methodology for the preparation of highly substituted arylsilane intermediates via the Rh-catalyzed C-H silylation of arenes and heteroarenes. More importantly, our synthetic protocol shows high efficiency in preparing industrially useful arylalkoxysilanes where low reactivity of the substrates and side-reactions have been difficult to overcome. In our presentation, we will discuss our methodology, the scope of the reactions and we will propose a reaction mechanism.



Tuesday, 11:20 AM

Mechanistic insights into the silylation of secondary alcohols with isothioureia based catalysts

Brandon Redden* and Sheryl Wiskur

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The silyl group is arguably one of the most common and useful protecting groups in organic chemistry. The Wiskur research group has extensively studied using triaryl silyl protecting groups in the presence of isothioureia based catalysts across various secondary alcohol substrate classes. My work has been to build on the methodology from a mechanistic standpoint using Donna Blackmond's reaction progress kinetic analysis. Experiments were conducted using an in situ react IR to determine the reaction order of each component of the reaction, as well as probing for any degradation of catalyst. A model of the reaction was then proposed based on my findings in conjunction with some previous work performed by other members of the group. The reaction order in triaryl silyl chlorides was found to be somewhere between one and two, meaning a second equivalent of silyl chloride must be involved in the reaction mechanism in some way. Additional experiments using non-coordinating additives (i.e. NaBARF) were conducted to determine how the components of the reaction work together to form the product. Our kinetic studies also prompted new studies of the bond formed between the isothioureia catalyst ((-)-benzotetramisole) and triphenyl silyl chloride with and without the presence of the NaBARF. All of the info gleaned from the various studies were brought together to paint an abstract picture of the overall silylation mechanism.

Tuesday, 11:40 AM

Investigation of cation- π interactions in silylation-based kinetic resolutions

Tian Zhang* and Sheryl Wiskur

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The silylation-based kinetic resolution developed by the Wiskur group has proven to be a selective approach to form enantiopure secondary alcohols. Cation- π interactions between a cationic isothioureia silylated catalyst and a π system on secondary alcohols were hypothesized to aid in controlling these reactions. Therefore, variations in steric and electronics on the substrate were explored to understand how they affected affect the cation- π interaction, as well as the selectivity of these kinetic resolutions. The study used derivatives of alkyl-2-hydroxycyclohexanecarboxylates and 2-arylcyclohexanols with various steric or electronic characteristics. Computational studies were also performed to support the involvement of cation- π interactions. The effect of sterics and electronics on selectivity and the linear free energy relationships obtained will be presented, along with preliminary computational results.

Tuesday, 1:30 PM

Adventures in Si-H activation: Si-containing polymers and Lewis acid catalysts

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This presentation will describe three projects that have grown from our efforts to harness catalytic Si-H activation chemistry in the synthesis of polysilanes. (i) Our focus on the post-polymerization modification of poly(phenylsilane), which can be prepared via the catalytic dehydrocoupling of phenylsilane, led to the discovery of high selectivity of the Lewis acid tris(pentafluorophenyl)borane for Si-H versus Si-Si bond activation in this polymer. This chemistry allows the introduction of a wide variety of functional groups; our exploration of the scope and limitations will be placed within the context of the generally accepted mechanisms for dehydrocoupling, dealkylative coupling, and hydrosilation reactions catalyzed by this electrophilic borane.[1,2] (ii) In a related project, we prepared a new, cationic metal phosphonium complex that is active for the catalytic hydrosilation of alkenes and ketones. We have demonstrated the ability of this unusual P(III)-based Lewis acid to activate silanes via an η -1 silane adduct that is directly analogous to that proposed for tris(pentafluorophenyl)borane.[3] (iii) Finally, returning to our exploration of the chemistry of poly(phenylsilane), we discovered that this linear polymer undergoes thermal redistribution to give a highly branched polysilyne material in good yield. Our characterization of this poly(phenylsilyne) and comparison of its properties with those of the original, Wurtz-coupled polysilynes reported by Bianconi and Weidman [4] will be described.

References:

- [1] P. T. K. Lee, L. Rosenberg, Dalton Trans. 2017, 46, 8818
- [2] P. T. K. Lee, M. K. Skjel, L. Rosenberg, Organometallics 2013, 32, 1575
- [3] W. E. Piers, A. J. V. Marwitz, L. G. Mercier, Inorg. Chem. 2011, 50, 12252
- [4] P. A. Bianconi, T. W. Weidman, J. Am. Chem. Soc. 1988, 110, 2342

Tuesday, 2:10 PM

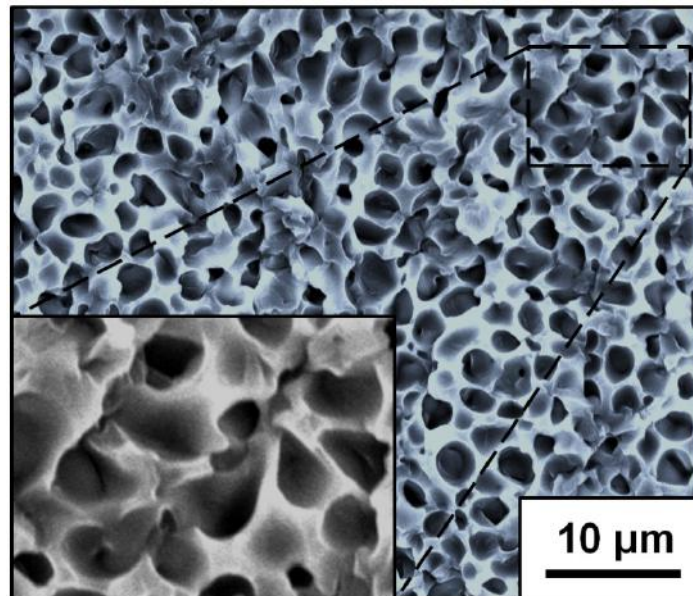
Soft and flexible: Silicone elastomers for a variety of applications

Liyun Yu and Anne Ladegaard Skov*

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Dielectric elastomers hold great promise as new transducer materials, mainly due to their inherent lightness and flexibility. These properties allow for constructing lightweight transducers but also for making completely novel transducers. However, the elastomers to realize these transducers have to fulfill a wide range of specifications and the ideal elastomer may not yet exist. Therefore, materials development is crucial to enable the full potential of dielectric elastomers. Silicone elastomers are currently the most promising elastomer candidates since they are very stable and usually survive more than 10 mio actuation cycles which is required for most industrial applications such as wave energy harvesting and actuators in cars. However, silicone elastomers possess low dielectric constant and for better energy density, this should be improved. Various approaches have been discussed in the recent review from our group. Among these approaches dipole grafting and inclusion of high dielectric liquids can be mentioned. An example of a high-permittivity silicone elastomer composite is shown in the figure, where a bicontinuous structure is formed from mixing in glycerol in silicone elastomer.

In this presentation, various applications will be discussed and the materials available for the given applications will be discussed with focus on the status of the materials and where the challenges lie.



Tuesday, 2:50 PM

Synthesis and Exploratory Deposition Studies of Isotetrasilane and Reactive Intermediates for Epitaxial Silicon

Barry Arkles,* Youlin Pan and Jonathan Goff

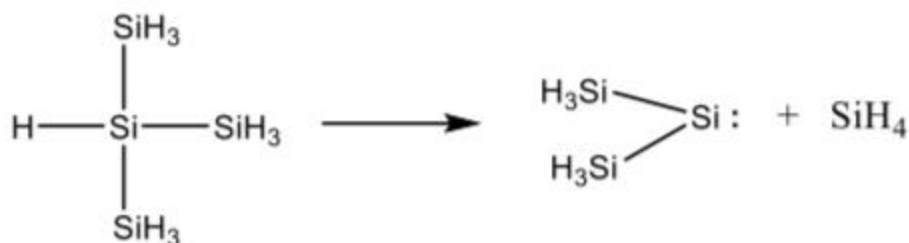
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A synthetic method for the production of isotetrasilane, a higher order perhydridosilane with the purity and volume necessary for use in the chemical vapor deposition (CVD) of epitaxial silicon (e-Si) thin films is presented. The chemical characteristics, thermodynamic properties and decomposition routes of isotetrasilane are compared with those of other perhydridosilanes. Preliminary findings are summarized for CVD of both e-Si and e-Si doped with germanium (Ge) and carbon (C) employing isotetrasilane as the source precursor at temperatures of 500-550°C. The results suggest that bis(trihydridosilyl)silylene is the actual deposition intermediate under conditions in which gas-phase depletion reactions are not observed.



Tuesday, 3:30 PM

Low-valent Silicon Compounds as Catalysts for Industrial Organosilicon Chemistry

Elke Fritz-Langhals* and Richard Weidner

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Silyliumylidene cations RSi^+ are of increasing interest in chemistry. Two vacant orbitals and a lone pair of electrons combine the characters of both strongly electrophilic silylium cations R_3Si^+ and nucleophilic silylenes $\text{R}_2\text{Si}:$. Whereas the reactivity of silylenes $\text{R}_2\text{Si}:$ and silylium cations has been investigated in detail within the past 20 years, the reactivity of silylium-ylidene cations RSi^+ , however, is still in its infancy. Jutzí's $\text{Cp}^*\text{Si}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (Cp^* = penta-methylcyclopentadienyl), however, represents a unique cationic silyliumylidene structure, because the cationic silicon center is only stabilized on one side by a Cp^* residue and therefore has free coordination sites. The catalytic potential of this extraordinary structure, however, was unknown.

We found that Cp^*Si^+ efficiently catalyzes reactions which are of technical relevance in industrial organosilicon chemistry. For example, it is a very efficient nonmetallic catalyst for the hydrosilylation of alkenes at low catalyst amounts of < 0.01 mole %, and for the Piers-Rubinsztajn reaction which is a versatile tool to make controlled silicone architectures.

Tuesday, 4:10 PM

Thermoelectric properties of conducting polymers doped with silicone-based polymer electrolyte

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Thermoelectric (TE) devices based on the Seebeck effect are able to harvest electricity from waste heat generated in households, chemical plants, or even human bodies by utilizing the diffusion of charge carriers induced by the temperature gradient. Until quite recently, a number of studies have been devoted to the development of TE devices based on inorganic materials such as Bi-Te, Co-Sb, Bi-Pb, Sn-Te alloys, and transition metal oxides. However, the inorganic TE materials are generally expensive, rare, heavy, brittle, poorly flexible, and relatively difficult to process, and thus impeding their widespread use. In addition, some inorganic TE materials are not suitable for the practical use because of their toxic nature. Compared to the inorganic TE materials, conducting polymers are recently attracting attentions as promising candidates for TE materials because of low environmental burden, low cost of fabrication, abundance of raw materials, flexibility, and solution processability. In order to develop flexible and free-standing thermoelectric materials, we report here the synthesis of novel conducting polymers doped with silicone-based polymer electrolyte.

Tuesday, 4:30 PM

Crosslinking via Si-H Functionality: A Catalyst-Free Route to Silicone Rubbers

Michael Yin Wong,* Alyssa Schneider,* Chen Yang* and Michael A. Brook*

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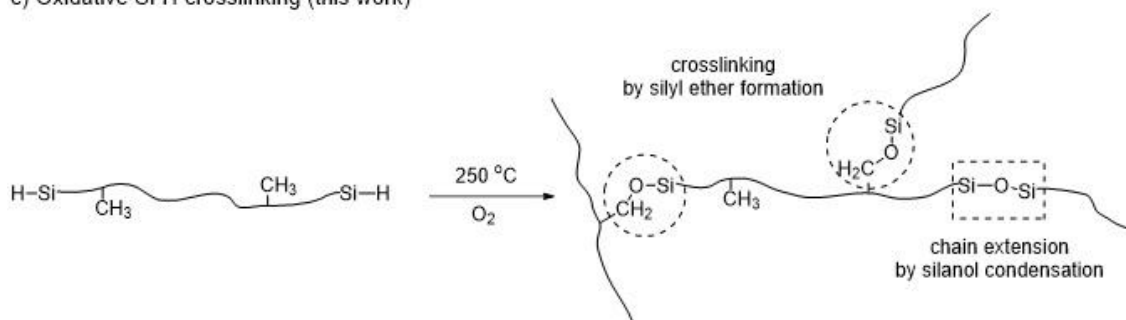
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Crosslinked silicone materials are important industrial products thanks to their many unique properties including low glass transition temperature (T_g), low surface energy, outstanding chemical and thermal stability as well as excellent biocompatibility.¹ Currently, the common methods to prepare silicone elastomers invariably require catalysts,² including platinum for hydrosilylation cure, tin for moisture or room temperature vulcanization (RTV) or catalytic organic peroxides. For reasons of cost, toxicity and/or need to remove residues,^{3,4} none of these processes are ideal.

The relatively weak Si-H bond is known to undergo oxidative cleavage by a variety of reagents. We were curious to better understand if its oxidative lability could be used as a cure technology in the absence of the catalysts noted above. We show that silicone elastomers may be prepared in a simple manner via oxidative curing SiH-containing polymers at 250 °C in the presence of air without any catalyst (Scheme 1); the elastomers prepared were bubble-free, transparent and colorless. The key merits of this method over traditional crosslinking approaches are that Si-H macromers are readily available at low cost. In addition, the hardnesses of the elastomers can be easily controlled both by curing time and total SiH concentration in the starting materials and the products do not show yellowing at 300 °C over 7 days; the optimal curing temperature was found to be 250 °C. The interaction between oxygen and the Si-H functionality were shown to play critical roles the oxidative curing process – both oxidative chain extension (Scheme 1) and radical insertion (Scheme 1) were shown to be operating.

c) Oxidative Si-H crosslinking (this work)



Scheme 1. Elastomer formation via thermal crosslinking of Si-H functionality.

References:

1. Longenberger, T.; Ryan, K.; Bender, W.; Krumpfer, A.; Krumpfer, J. J. Chem. Educ. 2017, 94, 1682-1690.
2. Wang, D.; Klein, J.; Mejía, E. Chem. Asian J., 2017, 12, 1180-1197.
3. Feng, L.; Zhou, L.; Feng, S. RSC Adv., 2016, 6, 111648-111656.
4. Métivier, T.; Beyou, E.; Cassagnau, P. Eur. Polym. J., 2018, 101, 37-45.

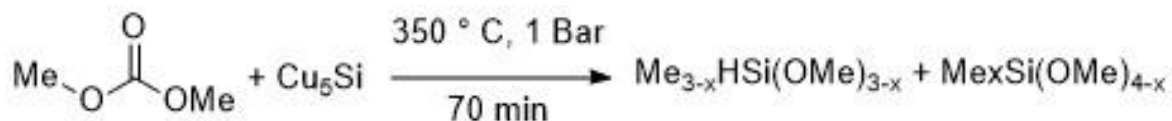
Tuesday, 4:50 PM

A New Direct Process: Direct Synthesis Of Alkoxysilanes From Dimethyl Carbonate And Copper Silicides

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The Rochow-Müller Direct Process reaction, the etching of silicon with methyl chloride in the presence of a copper catalyst to give chlorosilanes, is the foundation of the silicones industry. Practiced for over 70 years, it is highly optimized, and the products of this reaction serve as the building blocks for nearly all silicones. The related etching of silicon to afford alkoxysilanes, however, has never been fully realized. We report a silicon etch reaction where dimethyl carbonate is used to etch silicon (in the form of a silicide, Cu₅Si) to afford methyl methoxysilanes. Selectivities of up to 75 % of the desired Me₂Si(OMe)₂ were observed when using Cu₅Si made from metallurgical-grade silicon. When high-purity Cu₅Si was used, selectivity to Me₂Si(OMe)₂ dropped dramatically, prompting us to analyze the impurities in the metallurgical-grade silicide. By synthesizing a series of high-purity silicides doped with a single element, we determined that tin was a crucial promoter for methyl incorporation onto the silane and overall reaction rate. XPS and XANES analysis of the reaction in situ showed that tin segregates to the surface of the silicide at reaction temperatures and that an overlayer of graphitic carbon and silica forms on the silicide surface during the etch reaction. To our knowledge, this is the first example of a direct synthesis reaction affording alkoxysilanes with high methyl selectivity.



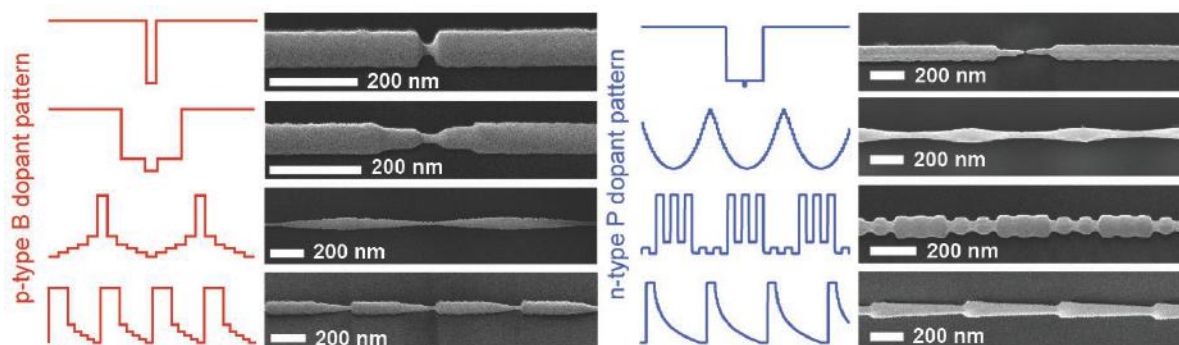
Wednesday, 8:00 AM

Synthesis of charge rectifying silicon nanostructures

James Cahoon*

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Silicon nanowires have been widely pursued as a technology for electronic, photonic, and renewable energy devices. Here, we describe a bottom-up method to modulate nanowire shape and composition along the growth axis with sub-10 nanometer spatial resolution. The rapid modulation of phosphorus or boron incorporation during vapor-liquid-solid (VLS) growth is used to encode a complex pattern of dopants. Subsequent solution processing creates high-resolution structures such as bow-ties, gratings, sawtooths, fractals, nanorods, sinusoids, and nanogaps. Several examples of complex morphology in degenerately-doped p-type and n-type silicon are shown in Figure 1.



This synthetic capability enables the creation of new, charge-rectifying nanostructures. First, we demonstrate a non-centrosymmetric nanowire that can rectify and ratchet the motion of ballistic electrons. By designing asymmetry on a length scale comparable to the mean free path of electrons, we create a geometric diode that funnels electrons in one direction and has a near-zero turn-on voltage. At GHz-THz frequencies, this structure ratchets electrons, enabling a new class of high-frequency diode. Second, we demonstrate the synthesis of p-i-n nanowire superlattices encoded with arbitrary numbers of junctions. Abrupt and degenerate doping levels ensure the creation of n-p tunnel junctions, enabling the realization of multijunction single-nanowire photovoltaic devices. Decuple-junction devices generate more than 2 V of photovoltage under 1-sun illumination. When functionalized with catalysts, these nanostructures can be used for single-particle water splitting in a particle suspension reactor that generates H₂ and O₂.

Wednesday, 8:40 AM

Porous silicon, a biocompatible semiconductor for nanomedicine

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The application of nanotechnologies into medicine promises to offer solutions when applied to health challenges such as cancer. Our research projects aim to develop biodegradable multifunctional anti-cancer materials based on mesoporous silicon-based nanostructures to be used for the local treatment of cancer. Porous silicon nanoparticles (pSiNP) are fully bioresorbable, and nontoxic in vivo, in addition they can be excited by near infrared (NIR) two photon excitation light offering possibilities for phototherapies, and for light triggered and focalized treatment.

The development of photoactive porous silicon nanovectors functionalized with organic ligands for applications in imaging, nucleic acids and drug delivery, as well as photo-activated therapies will be presented [1-4].

References:

[1] A. Chaix, K. Rajoua, V. Stonajovic, K. El Cheikh, E. Bouffard, A. Brocéro, M. Garcia, M. Maynadier, A. Morère, M. Gary-Bobo, F. Favier, J.O. Durand, and F. Cunin. *Chem Nano Mat.* 2018, 4, 343-34.

[2] A. Chaix, K. El Cheikh, E. Bouffard, M. Maynadier, D. Aggad, V. Stojanovic, N. Knezevic, M. Garcia, P. Maillard, A. Morère, M. Gary-Bobo, L. Raehm, S. Richeter, J. O. Durand and F Cunin, *J. Mater. Chem. B*, 2016, 4, 3639.

[3] E. Secret; M. Maynadier; A. Gallud; A. Chaix; E. Bouffard; M. Gary-Bobo; N. Marcotte; O. Mongin; K. El Cheikh; V. Hugues; M. Auffan; C. Frochot; A. Morère; P. Maillard; M. Blanchard-Desce; M.J. Sailor; M. Garcia; J.O. Durand; F. Cunin, *Adv. Mater.* 2014, 26(45), 7643.

[4] E. Secret, M. Maynadier, A. Gallud, M. Gary-Bobo, A. Chaix, E. Belamie, P. Maillard, M. J. Sailor, M. Garcia, J.O. Durand, F. Cunin, *Chem. Commun.*, 2013, 49(39), 4202.

Wednesday, 9:20 AM

Novel Double-decker Cage Silsesquioxane: Synthesis, Characterization, Properties, and Application

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One common kind of incompletely condensed silsesquioxane containing four reactive end groups is well known in the name of double-decker silsesquioxane (DDSQ). DDSQ is an organic-inorganic hybrid material possess high thermal stability, good mechanical properties, and softness, etc. resulting from inorganic core, covering with organic arms which are easily modified to the functional groups. There are many reports about easy synthetic pathway of sodium octaphenyltetracyclooctasilsesquioxanolate (DDSQ-ONa), which has been coupled with monosilanes (T_8D_2).¹ Interestingly, the study of compounds, which prepared by the capping reaction of DDSQ with disiloxane, trisiloxane, or polysiloxane have never been investigated into a new type of condensed polyhedral structures. The key for designing DDSQ bearing disiloxane or trisiloxane is the presence of lager-sized molecule and more organic functional groups on a DDSQ with remaining of high thermal stability.

Meanwhile, diglycidyl ether allyl bisphenol A (DGEABA) epoxy resin has attached much attention as coating, adhesive, and matrices for composites applications. Recently, closed- T_8D_2 DDSQ structure included epoxy resin was revealed to show higher thermal stability and to change surface properties from hydrophilic to hydrophobic.²

In this work, disiloxane- (T_8D_4) and trisiloxane- (T_8D_6) capped DDSQ were successfully synthesized and revealed as butterfly-shape silsesquioxane for the first time. All structures of products were characterized using ¹H NMR, ¹³C NMR, ²⁹Si NMR, MALDI-TOF MS, elemental analysis, and X-ray crystallography techniques. TG/DTA analysis showed high thermal stability properties of these compounds. Moreover, we have synthesized and studied the physical properties and thermal stability of epoxy polymer from open- T_8D_4 and closed- T_8D_4 DDSQ structures.

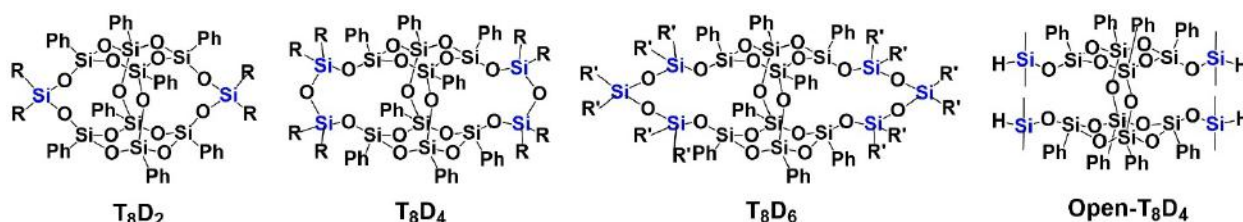


Figure The synthetic closed- T_8D_2 , T_8D_4 , and T_8D_6 structures (R = Me, i-Pr, Ph and R' = Me) and open- T_8D_4 structure

References

- (a) K. Mituła, J. Duszczyk, D. Brzakalski, B. Dudziec, M. Kubickia, B. Marciniak, *Chem. Commun.* 2017, 53, 10370-10373. (b) D. W. Lee, Y. Kawakami, *Polym. J.*, 2007, 39, 230-238.
- J. Cao, H. Fan, B.G. Li, S. Zhu, *Polymer*, 2017, 124, 157-167.

Wednesday, 9:40 AM

Design and Preparation of Innovative Functionalizable Silsesquioxanes as Building Blocks for New Nano-sized Supported Catalysts

Yujia Liu,* Masafumi Unno,* Armelle Ouali* and Nobuhiro Takeda*

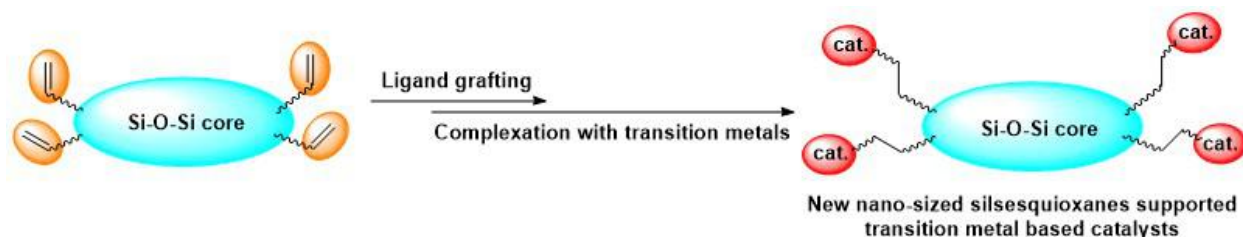
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In recent years, increasing demands have been observed on the development of materials with high function like thermal stability, low-k value, or high refractive index. Among the possible candidates of these materials, silsesquioxanes ($\text{RSiO}_3/2$ where R can be hydrogen, alkyl or aryl groups) with well-defined structures is one of the most promising compounds. Especially, the cubic polyhedral oligosilsesquioxanes (POSS) have been the most studied for various applications.[1] In the past decade, the group of POSS was extended by another class, the double-decker silsesquioxane (DDSQ) whose synthesis and properties have been studied.[2] By introducing reactive substituents, the resulting silsesquioxanes can potentially be used as nanometer-scale precursors and building blocks in electronic materials, medicinal chemistry and catalysis. Catalysis plays an important and essential role in today's chemical industry. Nanocatalysts have recently attracted much attention due to their high activity, selectivity, ease of separation and recovery.[3] Our work is focusing on the synthesis of high-ordered nano-sized double-decker siloxanes as building blocks for new supported nanocatalysts and exploitation of their catalytic activities. In this short talk, preparation of new double-decker siloxanes bearing tetra-vinyl and allyl functional groups will be presented and the functionalization reactions of these synthesized silsesquioxanes will be showed as well.[4]



[1] D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* 2010, 110, 2081-2173.

[2] B. Dudzic, B. Marciniak, *Current Org. Chem.* 2017, 21, 2794-2813.

[3] (a) S. B. Singh, P. K. Tandon, *J. Energy Chem. Eng.* 2014, 2, 106-115; (b) For multivalent/synergistic effects between neighboring catalytic sites: A.-M. Caminade, A. Ouali, R. Laurent, C.-O. Turrin, J.-P. Majoral, *Chem. Soc. Rev.* 2015, 44, 3890-3899.

[4] Y. Liu, N. Takeda, A. Ouali, M. Unno, paper submitted.

Wednesday, 10:20 AM

Advances in Enantioselective Methods for the Synthesis of Chiral Siloxanols and Mechanistic Studies for Catalysis

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Enantioenriched siloxanes and silanols that have a chiral silicon center provide new opportunities for applications as catalysts, ligands and materials. The development of enantioselective methods for the selective synthesis of chiral siloxanols and disiloxanediols remains a challenge, and the synthesis and continued study of these silanols provides fundamental insight for their applications. In particular, the incorporation of silanol groups into organic scaffolds provides the opportunity to develop new activating groups for small molecule catalysts, chelating ligands and supramolecular synthons. This presentation will discuss the challenges and opportunities for two enantioselective methods to access chiral siloxanols. The effect of structure and reaction conditions on enantioselectivity will be presented. In parallel, we have designed and synthesized various organosilicon molecules incorporating silanol and siloxanol groups to study their catalytic activity, molecular recognition, hydrogen-bonding and metal-binding properties. Structural studies and various NMR binding studies provide molecular insights into H-bonding and metal binding properties that are relevant for catalyst activity, ligand design, and supramolecular assembly. Kinetics, NMR binding studies, and structural studies will also be presented for mechanistic and molecular insights for catalyst activity and design.

Wednesday, 11:00 AM

Rh-catalyzed Enantioselective Synthesis of Silicon Electrophiles to Access Chiral Siloxanes

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The efficient and selective access to chiral-at-silicon compounds is an exciting challenge to synthetic chemists. Specifically, the synthesis of enantioenriched siloxanes and silyl ethers remains highly under-represented in current literature. The development of methods for the selective synthesis of enantioenriched siloxanols, disiloxanediols, and hydride-bearing siloxanes will be presented. A rhodium-catalyzed enantioselective alcoholysis allows access to enantioenriched electrophilic silicon centers that can be transformed using amino nucleophiles to produce enantioenriched hydride-bearing silylamines. The scope of reactivity of the silylamine will be described along with the stereochemical outcomes of these reactions. This presentation will also discuss the procedural challenges in the analysis and isolation of silylamines and the inherent thermodynamic challenges of overcoming the strength of the Si-O bond to allow for the conversion to the Si-N bond.



Wednesday, 11:20 AM

Synthesis of Siloxane-Phospholipids and their Evaluation as Potential Drug Delivery Vehicles

Mark B. Frampton, Andrea Blais, Zachary Raczywolski and Paul M. Zelisko*

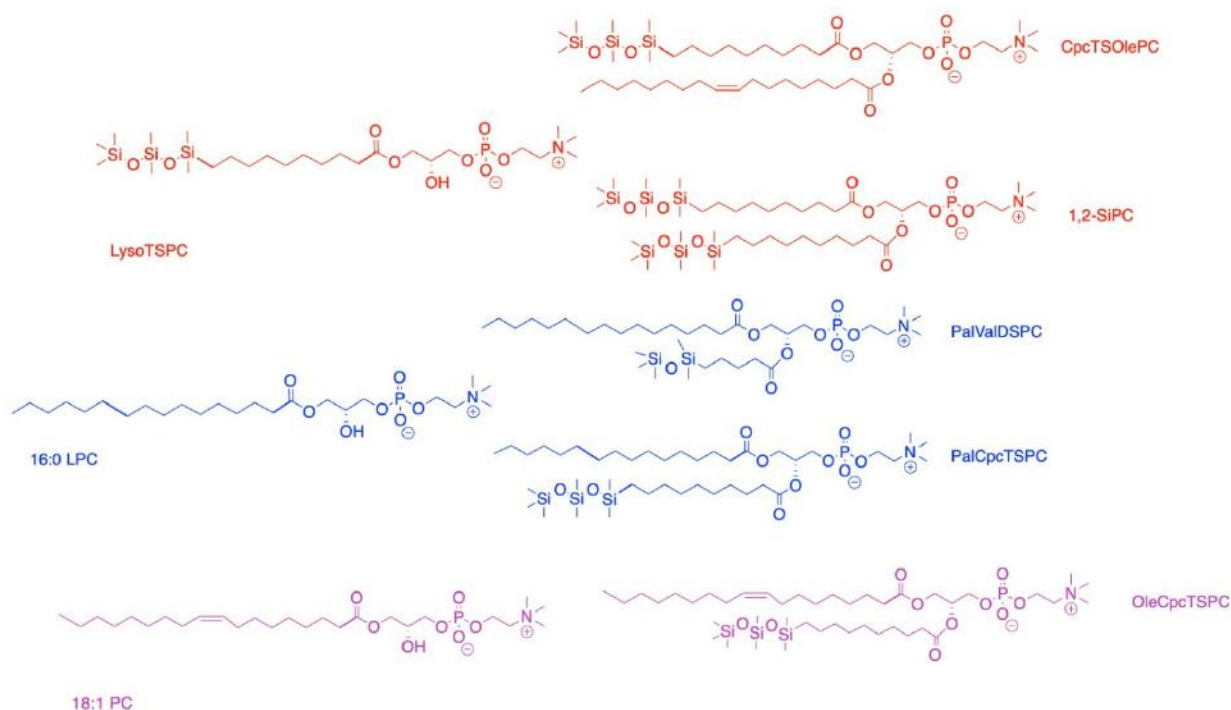
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Liposomes based on phospholipid species have the potential to deliver biologically active material, especially DNA and proteins on the cellular level. However, the utility of liposomes is hampered by the multiple extrusion and/or sonication cycles required to achieve unilamellar vesicles that are ~100 nm in diameter; the encapsulation process can result in significant loss of the material to be delivered. Siloxane-phospholipids (SiPCs) modelled after 1-palmitoyl-2-oleoyl-sn-glycero-5-phosphocholine (POPC) have been shown to spontaneously self-assemble into unilamellar vesicles that are on average between 100-120 nm in diameter. A second-generation chemoenzymatic synthesis for siloxane-phospholipids has been developed permitting access to a library of SiPCs. The unique physical properties of these SiPCs, their capacity to form liposomes, and their potential for delivery applications at three different physiological pH values will be discussed.



Wednesday, 11:40 AM

Silatrane: A Versatile And User-Friendly Atom-Transfer Reagent

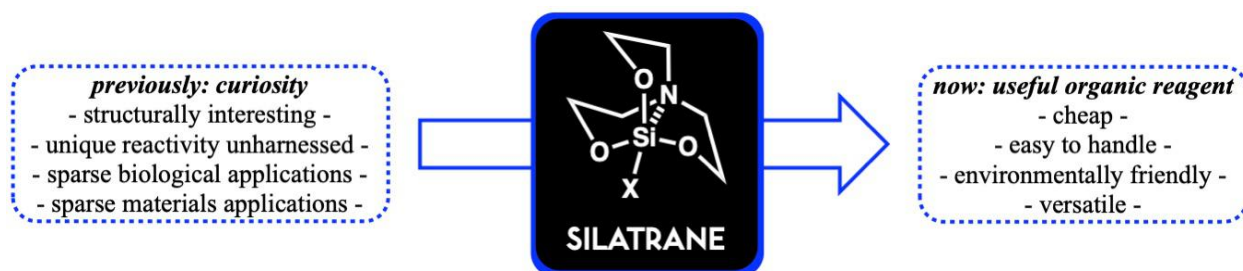
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Organosilanes are useful in synthetic organic chemistry as hydride- and carbon-transferring reagents. They are attractive as reagents for organic synthesis because 1) molecular silicon is naturally abundant and thus inexpensive, 2) silicon-containing precursors to reagents are readily available in a variety of functional forms, and 3) organosilanes and byproducts are generally non-toxic and can be easy to handle. However, one is always faced with a choice between two types of unideal organosilane atom-transfer reagents: milder ones such as trialkylsilanes, which require forceful activation, or more reactive ones such as trialkoxy- or trihalosilanes, which are difficult and/or hazardous to handle. We have recently demonstrated hydrosilatrane as a hydride-transferring reagent that elegantly toes the line between functional activity and deleterious reactivity; it is able to do this because its stable caged structure masks its inherent reactivity. In our lab we have shown that this versatile reagent is useful for a number of important chemical transformations, and we continue to showcase its utility and versatility in ongoing projects. This talk will highlight published work and describe ongoing efforts in the lab to establish silatranes as powerful tools for organic synthesis.



Wednesday, 1:30 PM

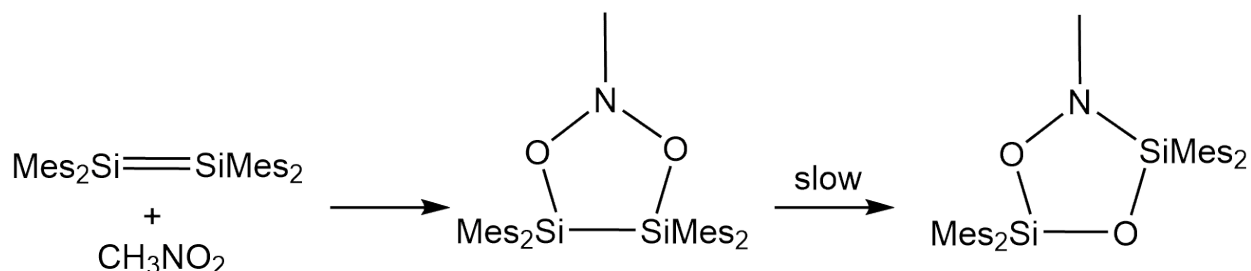
The Reaction Of Ditetrelenes With Organic Main Group Oxides

Kim Baines,* Nada Tashkandi, Bahar Farhadpour and Maissa Belcina

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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 detailed 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 ditetrelenes are guided by our interest in the fundamental addition chemistry of ditetrelenes and our hypothesis that the chemistry of molecular disilenes and digermenes can provide some important insights into the organic functionalization of Si- and Ge(100) 2 x 1 reconstructed surfaces. In this lecture, the addition of a variety of functional groups to disilenes and digermenes will be presented and compared to the analogous surface chemistry. The focus will be on the addition of organic main group oxides to the ditetrelenes.



Wednesday, 2:10 PM

N-Heterocyclic Carbene Chemistry of Silicon: Recent Advances

Gregory Robinson* and Yuzhong Wang

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This laboratory has long been interested in the synthesis and structure of unusual molecules. These efforts resulted in experimental realization of metalloaromaticity (the concept that metallic rings may also display traditional aromatic behavior) and novel compounds containing multiple bonding between main group elements. Recent efforts concerning the utilization of N-heterocyclic carbene ligands (L:) with highly reactive main group compounds has afforded carbene-stabilized examples of diborene (H-B=B-H), diphosphorus (P₂), and disilicon (Si₂). This presentation will prominently feature both the critical role of N-heterocyclic carbenes and interesting aspects concerning the synthesis, structure, and reactivity of carbene-based silicon molecules.

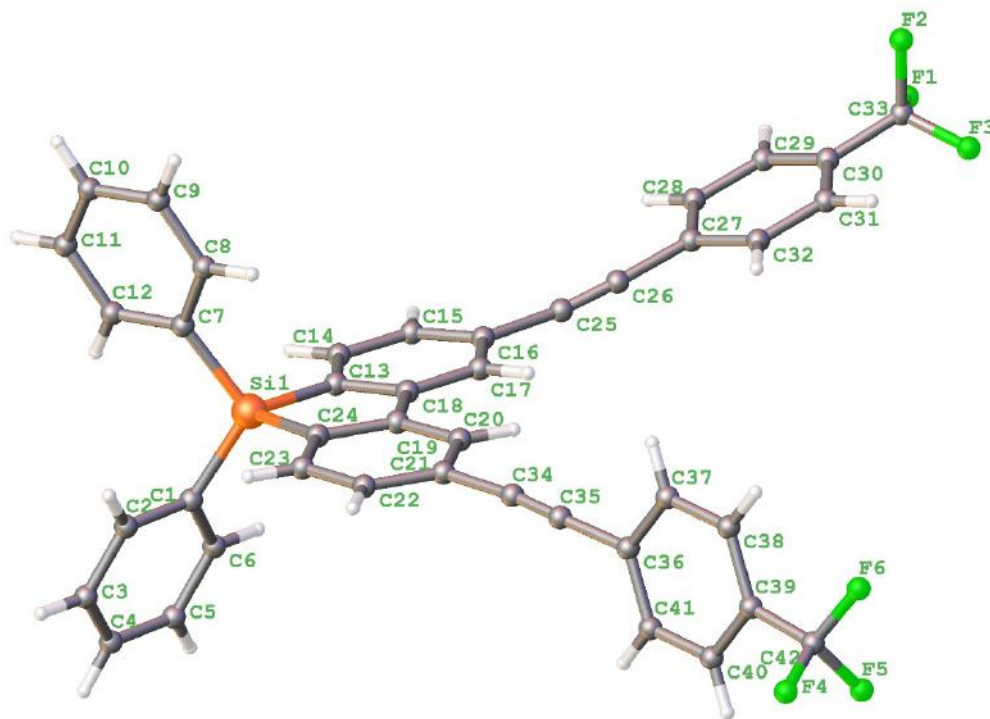
Wednesday, 2:50 PM

Synthesis and Characterization of Luminescent 3,6-Disubstituted Silafluorenes and Germafluorenes

Janet Braddock-Wilking,* Randy Winchester, Stephan Germann, Nigam Rath, Nick Viriyasiri and Rensheng Luo

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Luminescent Group 14 metalloles and related compounds have attracted significant attention over the last several decades due to their unique properties and potential applications in chemical and biological sensing and as components in OLED devices and solar cells. A series of luminescent 3,6-bis[alkynyl(aryl)]-9,9-diphenylgermafluorenes and silafluorenes have been synthesized using a palladium-catalyzed Sonogashira coupling reaction to incorporate different aryl(alkynyl)-groups at the 3,6-positions on the metallafluorene ring. The molecular structures for several of the derivatives have been confirmed by X-ray crystallography. Results from the synthesis and characterization of these luminescent metallafluorenes will be presented.



Wednesday, 3:30 PM

Bis(phosphino)silyl Iron and Cobalt Pincer Complexes as Catalysts for the Reduction of Unsaturated Substrates

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This presentation will detail recent developments in our group pertaining to the synthesis and characterization of low-coordinate Fe and Co complexes featuring bis(phosphino)silyl (PSiP) ligation,[1] including complexes that display high activity in the reduction of unsaturated substrates such as alkenes. Emphasis will be placed on the characterization of hydrido species of this type, which are likely to be of catalytic relevance in such reductions. Furthermore, the intermediacy of η^2 -(Si-H) bonded complexes will be examined, including the possible involvement of such species in enabling unique modes of catalytically useful metal-ligand cooperative behavior.

[1] (a) L. J. Murphy, M. J. Ferguson, R. McDonald, M. D. Lumsden, L. Turculet, *Organometallics* 2018, 37, 4814–4826; (b) L. J. Murphy, A. J. Ruddy, R. McDonald, M. J. Ferguson, L. Turculet, *Eur. J. Inorg. Chem.* 2018, 4481-4493.

Wednesday, 3:50 PM

Exploration of Silicon Phthalocyanines as Viable Photocatalysts for Organic Transformations

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Photocatalysis has increasingly become a major focus as a sustainable pathway for chemical reactions with visible light photocatalysts performing a large range of reactions such as redox reactions, cyclization reactions, and energy transfer reactions. Silicon phthalocyanines (SiPcs) have been largely ignored as photosensitizers in photocatalytic reactions, despite their low energy excitation, long triplet lifetimes, and their ability to form singlet oxygen. By incorporating alkyl, aryl, and silicon protecting groups as axial ligands on the silicon center, three SiPcs have been generated by the Wiskur research group with the goal of developing three novel photocatalysts for organic synthesis. Using cyclic voltammetry and Stern Volmer quenching studies, we have shown SiPcs are capable of acting as electron donors or acceptors with appropriate substrates, including Hünig's base, maleic anhydride, and benzoquinone, with varying redox potentials. We have also successfully used a SiPc catalyst in a reductive quenching reaction where Hünig's base served as a sacrificial electron donor in the reaction. In addition to being redox-active, our preliminary data also shows SiPcs are capable of performing energy transfer reactions, by performing a reaction that utilizes singlet oxygen as a reactant under visible light conditions. This reaction, in combination with cyclic voltammetry studies, has also served as a model to understand how axial substitution on the silicon center seems to influence the photostability of these species. These results, as well as the photophysical and electrochemical experiments for each SiPc, will be presented.

Wednesday, 4:10 PM

Hexacoordinate Silicon Complexes As Electron Transport Materials

Margaret Kocherga, Michael Walter, and Thomas Schmedake*

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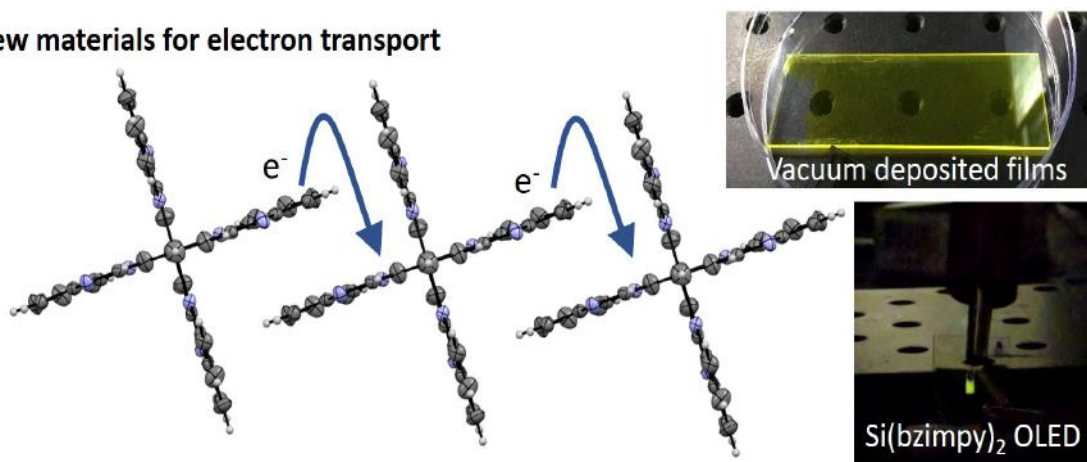
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Hexacoordinate silicon complexes based on dianionic pincer ligands are attractive candidates for applications in organic electronics, such as, organic light emitting diodes, photovoltaics and spin valves. The wide variety of available pincer ligands provides tailorability of the electronic properties, and the hexacoordinate silicon center enforces a rigid planar environment to minimize rotational relaxation modes. Thin films of a variety of new silicon complexes have been grown using thermal vacuum deposition. Electron mobilities of the $\text{Si}(\text{pincer})_2$ complexes have been measured and demonstrate that $\text{Si}(\text{pincer})_2$ complexes are efficient electron transport layers with electron mobilities comparable to or better than of widely employed Alq_3 .

New materials for electron transport



Wednesday, 4:30 PM

The analysis of bis (3-triethoxysilylpropyl) tetrasulfide by utilizing NMR spectroscopy and SFC

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The presentation will center on a problem critical to the Tire Business. When tire makers introduced a silica filler in conjunction with a silane coupling agent as a means of reducing rolling resistance in the tire tread it became important for Momentive to do a complete characterization to specifically determine the sulfur distribution in bis(3-triethoxysilylpropyl)tetrasulfide, $[(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2)_2\text{S}_4$]. The combination of ^1H and ^{13}C NMR results showed the distribution of sulfur species ($\text{S}_2\text{...S}_7$) in the nominal tetrasulfide silane. The chemical shift region in ^{13}C NMR spectrum for methylene carbon bonded to sulfide ($-\text{CH}_2\text{S}-$) was deconvoluted and the results compared with the peak areas from supercritical fluid chromatography (SFC) data. The NMR and chromatographic data were in good agreement.

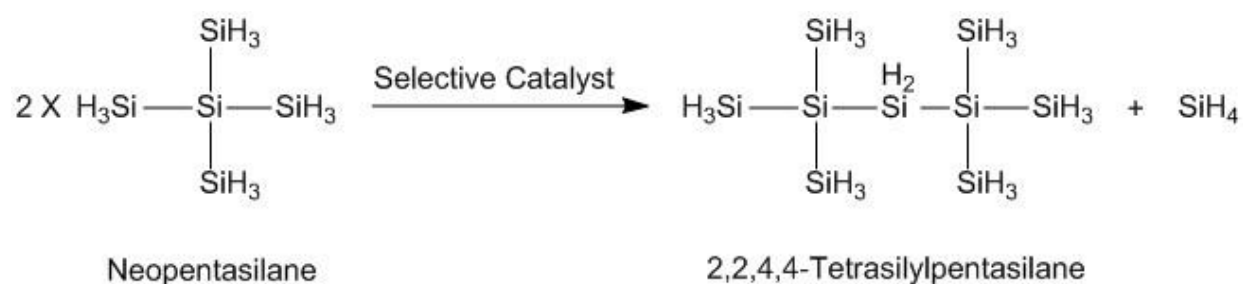
Wednesday, 4:50 PM

Selective Synthesis of 2,2,4,4-Tetrasilylpentasilane

Joe Xiaobing Zhou,* Noel Chang, Jeanette Young and Xianghuai Wang

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Containing over 90wt% silicon, perhydro higher silanes, $\text{Si}_n\text{H}_{2n+2}$ or cyclo- Si_nH_{2n} ($n \geq 3$), are useful precursors towards Si-based semiconductors or dielectrics. However, synthesis of these molecules in a high purity and in a cost-effective way is difficult. Only a short list of perhydro higher silanes, including trisilane (TS), isotetrasilane (ITS), neopentasilane (NPS), cyclopentasilane (CPS) and cyclohexasilane (CHS), have been made pure and evaluated for applications. In the research on branched higher silanes derived from hexachlorodisilane (HCDS; an industrial feedstock), we found a selective method to synthesize a new structural isomer of perhydro nonasilane, 2,2,4,4-tetrasilylpentasilane (BNS). This species can be formed from neopentasilane at over 90% selectivity in the presence of a selective catalyst. We have optimized the catalyst systems and reaction conditions to make 99% BNS, characterized the molecular structure with GC-MS and NMR (^1H and ^{29}Si), and studied the stability, reactivity and chemical bonding features of the molecule.



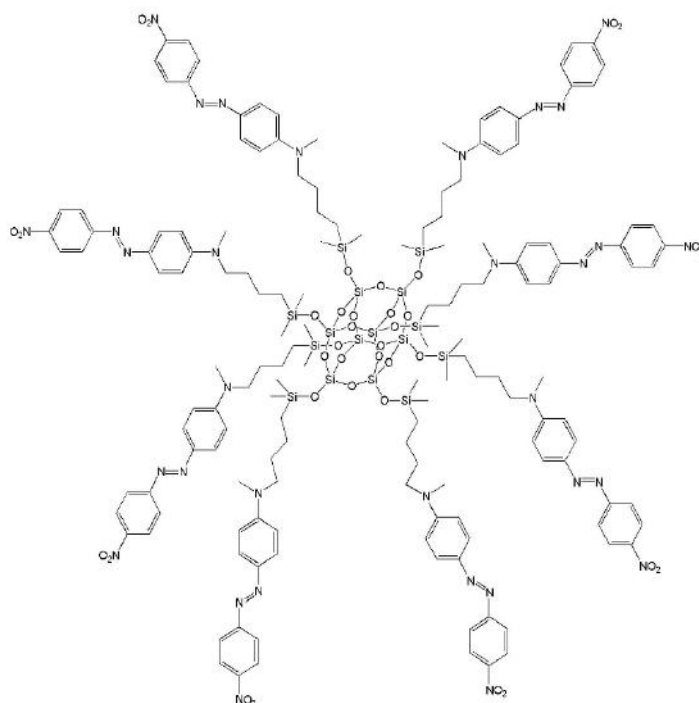
Wednesday, 5:10 PM

Synthesis of POSS Photochromics & Their Properties

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POSS core molecules have a considerable amount of free volume around the core. Photochromic switching can benefit from access to such free volume. The integration of such functionalized POSS nanoparticles into polymer coating and resins then provides useful photochromic materials that can not only toughen the product but also are able to switch rapidly between the two photochromic light/dark states. The design, synthesis, characterization and thermal analysis of novel Octa-Azobenzene POSS photochromic Supermolecules will be presented. These supermolecules needed to be synthesized via a divergent route, using hydrosilylation to generate high yielding diazonium salt chemistry, that was then used to produce a variety of azobenzene “arms” with different peripheral functional groups. An aliphatic spacer component was introduced into the organic arms extending from the POSS core molecule, resulting in some liquid crystalline properties. With nitro groups on the periphery, the azobenzene groups are electron donor/acceptors and therefore suitable for use in electro-optic materials. In addition, the terminal carboxylic acid functionality offers access to star-like crosslinking materials as well as thermoset nanocomposite materials.



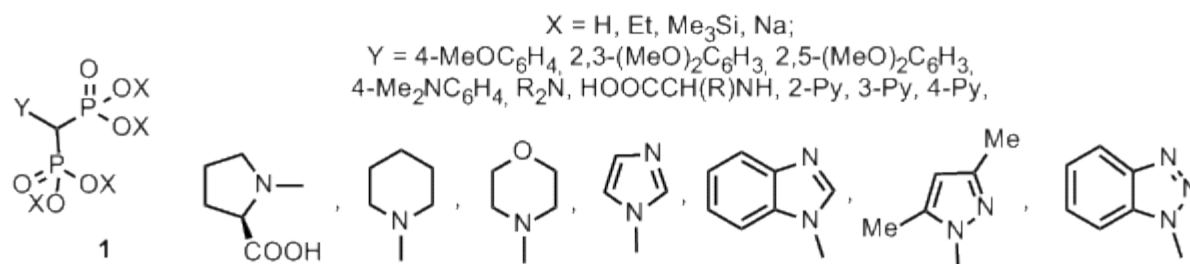
Poster Abstracts

P1 - Organosilicon-based synthesis of new methylenediphosphonic acids with azaheterocycles and amino acids moieties as perspective bioactive compounds

Andrey Prishchenko,* Roman Alekseyev, Mikhail Livantsov, Olga Novikova, Ludmila Livantsova, Valery Petrosyan

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Functionalized methylenediphosphonic acids and their derivatives with aromatic and heterocyclic moieties 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 [1]. Organosilicon-mediated synthesis of functionalized organophosphorus acids and their derivatives was used recently by us as convenient method of creating of P-C bonds. We have synthesized the new functionalized methylenediphosphonic acids and their derivatives **1** including aromatic, azaheterocyclic, and amino acids moieties via addition of tris(trimethylsilyl) phosphite to corresponding formamides in the presence of effective catalyst – trimethylsilyl triflate under mild conditions [2,3]. Also 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.



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 supported by the Russian Foundation for Basic Research (grant № 17-03-00169).

References

- [1] Kolodiazhnyi O.I. Russ. Chem. Rev., 2006, 75, 227.
- [2] Prishchenko, A.A.; Alekseyev, R.S.; Livantsov, M.V.; Novikova, O.P.; Livantsova, L.I.; Petrosyan, V.S. J. Organomet. Chem., 2018, 867, 149.
- [3] Prishchenko, A.A.; Alekseyev, R.S.; Livantsov, M.V.; Novikova, O.P.; Livantsova, L.I.; Petrosyan, V.S. J. Organomet. Chem., 2018, 871, 36.

P2 - Bis(trimethylsiloxy)phosphine as key synthon for synthesis of new aminomethylphosphonic acids with N-alkyl 4-hydroxypiperidines moieties

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The synthesis of new compounds containing several bioactive groups around the organoelement moieties currently is a modern trend of bioorganic chemistry. Functionalized phosphonic acids and their derivatives with two bioactive groups are of special interest because these groups are connected by phosphoryl scaffold via two stable non-hydrolysable P-C bonds. Functionalized phosphonic and phosphonic acids as well as their derivatives are the important organophosphorus biomimetics of natural amino (hydroxyl) substituted carboxylic acids, and some of them are found in living systems. Many of these substances exhibit properties as antibacterial, antiviral and antitumor agents, antibiotics, enzyme inhibitors, plant growth regulators. Functionalized hydroxymethylphosphonic acids and corresponding phosphonopeptides compete with the carboxyl containing analogues for the active sites of the enzymes and cell receptors, and also they inhibit the enzymes involved in the metabolism of carboxylic acids, thus affecting various biological processes in the cell [1]. We have proposed the convenient synthesis of new aminomethylphosphonic acids and their derivatives containing N-alkyl 4-hydroxypiperidines moieties. So the addition of bis(trimethylsiloxy)phosphine to N-alkyl 4-piperidones proceeds under mild conditions to give PH-phosphinates **1** as key compounds for preparation of trimethylsilyl esters **2** of above acids via interaction with various aminals. The further treatment of trimethylsilyl esters **2** with the methanol resulted in the corresponding acids **3**.



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References

- [1] Kukhar, V.P., Hudson, H.R. Aminophosphonic and Aminophosphonic Acids. Chemistry and Biological Activity. New York: Wiley, 2000, 634 p.
[2] Prishchenko, A.A.; Alekseyev, R.S.; Livantsov, M.V.; Novikova, O.P.; Livantsova, L.I.; Petrosyan, V.S. Inorg. Chim. Acta, 2019, 484, 319.

P3 - Synthesis of Self-Healing and Recyclable Silicone Polymers Using the Diels-Alder Reaction as a Cross-Linker

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The strong and flexible nature of elastomers have led to them being used numerous applications in various industries, products, and technologies. Silicone elastomers, in comparison to other materials, have been shown to have high tensile strengths, tear resistance, and in some cases fire resistance.

We are exploring the cross-linking of silicone polymers using the Diels-Alder (DA) reaction in an effort to make silicone elastomers recyclable and self-healing. Siloxane polymers possessing a furan moiety as the diene have been synthesized, and cross-linked using the DA reaction with N,N'-(1,3-phenylene)dimaleimide as the dienophile to yield silicone elastomers with a slight golden color and various thicknesses. These elastomers could be deformed and would recover their original shape. The physical properties of these elastomers, along with their capacity for self-healing and potential for recyclability will be discussed.



P4 - Consolidant and Hydrophobic Stone Formulations Base on Glycol Alkoxysilanes and Chitosan

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Stone consolidants have been widely used in order to protect historical monuments. Consolidants and hydrophobic formulations based on alkoxysilanes have been an alternative mostly using tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) and alkylalkoxysilanes as precursors¹, silanes that are not soluble enough in water so it is necessary to add an organic solvent. In the search of other silicon derivatives with potential use in this field, it is suggested to use tetrakis(2-hydroxyethyl)silane or orthosilicate (THEOS) and tris(2-hydroxyethyl)methyl silane (MTHEOS) as water soluble precursors². Additionally, it has been reported THEOS is compatible with different natural polysaccharides and the same behavior is expected for MTHEOS³. The approach is to use both glycol modified alkoxysilanes to obtain hybrid consolidants and hydrophobic formulations-chitosan (as polysaccharide) with the following main goals: the use of water soluble silanes in stone conservation based on both silicate and calcareous composition⁴. In the case of calcareous building stones is well known the non-compatibility with alkoxysilanes based formulations¹ and it is expected to solve it by using chitosan. The glycol modified alkoxysilanes were obtained by the most reported esterification of TEOS or MTEOS with ethylene glycol² but also by the Piers-Rubinsztajn (PR) reaction as a new alternative⁵. The glycol derivatives can be synthesized at moderated reaction conditions using the PR. Some examples of applications of the hybrid consolidant and hydrophobic formulations will be presented. The surface modification of different substrates, mainly building stones from historical and archeological sites from the Guanajuato city and state was studied. The authors wish to acknowledge CONACYT-México (Project 284510), supported by the Fondo Sectorial de Investigación para la Educación and the University of Guanajuato (Guanajuato-México).

References

- (1) Wheeler, G. Alkoxysilanes and the consolidation of stone. The Getty Conservation Institute. Los Angeles, Cal. EUA. (2005).
- (2) Mehrotra, R.C. and Narain, R. P. Indian J. Chem. 5, 444 (1967).
- (3) Shchipunov, Y.A., Yu, T., Karpenko, Y., and Krekoten, A.V. Composite Interfaces, Vol. 11, No. 8-9, pp. 587–607 (2005)
- (4) Cervantes, J., Meléndez-Zamudio Miguel A., Bravo, I., Ramírez-Oliva, E., Guerra-Contreras, A., Zárraga-Núñez, A., and Álvarez-Guzmán, G. Manuscript in preparation (2019).
- (5) Blackwell, J.M., Foster, K.L., Beck, V.H. and Piers, W.E. J. Org. Chem., 64, 13, 4887-4892 (1999)

P5 - Synthesis of water-based functional organosilanes via the Piers-Rubinsztajn reaction

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Organosilanes serve as bridges between inorganic or organic substrates (such as minerals, fillers, metals and cellulose) and organic/polymeric matrices (such as rubber, thermoplastics or thermosets) and, hence, can dramatically improve adhesion between them [1]. Any application where organosilanes are involved requires the silane molecule to undergo hydrolysis and condensation reactions. The hydrolysis reaction can be catalyzed using either an acid or a base. Mechanisms of acid- and base catalyzed hydrolysis of organosilanes have been extensively studied since their discovery [2]. Because organosilanes hydrolyze before reacting with each other or with the hydroxyl groups present at a substrate surface, it is important to understand the rates of both hydrolysis and condensation which are influenced by changing pH levels. This is true whether the reaction is catalyzed by acid or base. However, the optimum pH for hydrolysis is not the same for condensation [3]. In this regard, we propose a very interesting alternative method for the synthesis of several functional silanes with precise and well-defined structures through the Piers-Rubinsztajn reaction (PR). The PR reaction catalyzed by tris(pentafluoro)phenylborane (B(C₆F₅)₃) allows the interaction of a silane with a wide variety of functional groups such as alcohols, aldehydes, ketones, carboxylic acids, esters, amides and arylphenyl ethers [4] thus avoiding any undesired acidic/basic reaction condition as occurs with the sol-gel process. The water-based organosilanes were obtained by PR reaction between alkoxy silanes or hydrosilanes with ethylene glycol and then structurally characterized. The results were compared with those by the most reported route, esterification. The functional organosilanes may be applied to the formulation of water-based for stone consolidants in order to protect historical monuments.

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References

- [1] F. de Buyl, *Int. J. Adhesives and Adhesion*, 21(5), 411-422 (2001).
- [2] F.D. Osterholtz, E.R. Pohl, *J. Adhesion Sci. Technol.*, 6(1), 127-149 (1992).
- [3] T. Materne, F. de Buyl and G.L. Witucki. *Dow Corning Corporation*, (2012).
- [4] J. M. Blackwell, K. L. Foster, V. H. Beck, and W. E. Piers, *J. Org. Chem.*, 64, 13, 4887-4892, (1999).

P6 - Aggregation induced effect (AIE) on gels based in siloxane amino co-polymer

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Fluorescence is an unexpected phenomenon when we talk about silicone gels and elastomers. Generally, these types of materials develop great mechanical and thermal properties that arise due to the combination of the chemical properties both of the siloxane bond and the corresponding to the alkoxy silanes used as crosslinkers. In fact, crosslinkers are the molecules that allow the gels and elastomers to get interesting properties as high thermal stability, resistance to oxidation and ionizing rays, good dielectric properties, biocompatibility and high hydrophobicity. On the other hand, fluorescence emission, can be developed using fluorophores as crosslinkers, for example Rossi N. et al.¹, using the hydrosilylation reaction synthesize a crosslinker based on the prop-3-enyloxymethylpyrene obtaining emission at 390 nm. In the present work, during the search of a suitable matrix for a PDMS/PANI composite², gels and elastomers were designed to improve interactions between the PDMS matrix and PANI using poly(dimethyl-co-(3-aminopropylmethyl)siloxane) and dicarboxylic acids as crosslinkers. Unexpectedly, interaction between the co-polymer and the dicarboxylic acid was observed, generating gels with coloration, moldable with low mechanical properties. These materials were obtained due to electrostatic interaction and hydrogen bonding³ between the carboxylic acids and the co-polymer amino groups. To improve the mechanical properties of the materials, a RTV system was added to the gels obtaining hypothetical interpenetrated system that behaves as an elastomer. The materials were characterized by ATR/IR⁴ and fluorescence emission spectroscopy. The elastomers emit at 452 nm and 502 nm suggesting that the fluorescence emission observed is because of an aggregation induced effect (AIE) specifically to a restriction of the intramolecular motion (RIM)⁵, occasioned by the electrostatic interaction between the dicarboxylic acids and the co-polymer. The authors wish to thank: CONACYT-México (Project number: 284510), supported by the Fondo Sectorial de Investigación para la Educación and University of Guanajuato for financial support.

(1) Rossi, N. A. A.; Duplock, E. J.; Meegan, J.; Roberts, D. R. T.; Murphy, J. J.; Patel, M.; Holder, S. J. J. *Mater. Chem.* 2009, 19 (41), 7674–7686.

(2) Meléndez-Zamudio, M.; Villegas, A.; González-Calderón, J. A.; Meléndez, R.; Meléndez-Lira, M.; Cervantes, J. J. *Inorg. Organomet. Polym. Mater.* 2017, 27 (3), 622–632.

(3) Zhong, D.-C.; Liao, L.-Q.; Wang, K.-J.; Liu, H.-J.; Luo, X.-Z. *Soft Matter* 2015, 11 (32), 6386–6392.

(4) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *J. Mol. Struct.* 2002, 608 (2–3), 123–133.

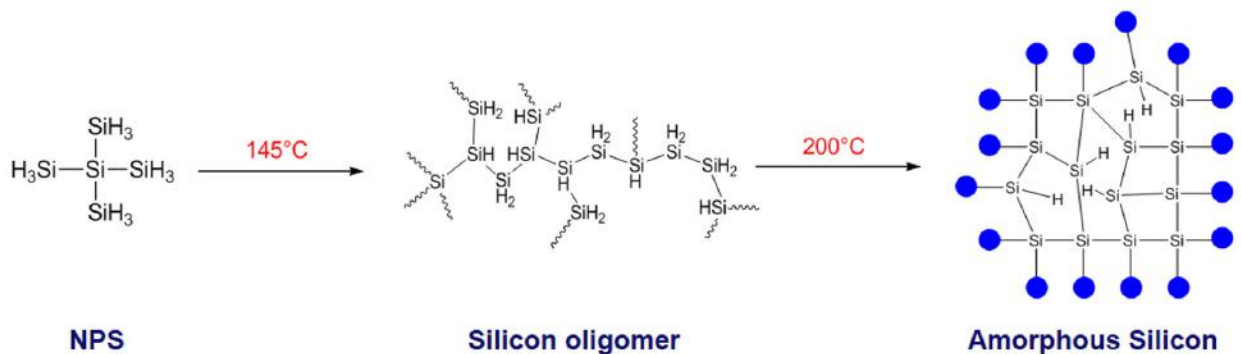
(5) Wang, H.; Zhao, E.; Lam, J. W. Y.; Tang, B. Z. *Mater. Today* 2015, 18 (7), 365–377.

P7 - Neopentasilane for Liquid Phase Si Precursor to Metalloid SiMinji Jeong, Yeonjeong Lee, Younghun Kim, Hyeon Mo Cho and Moon Gun Choi*

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As a size of a semiconductor changes from microscale to nanoscale, a development of new semiconductors is actively growing. Nowadays, the 3D NAND technology is being researched as future semiconductor, and development of organic soluble silicon metalloid precursors has attracted a lot of interest. Specifically, organic soluble liquid silicon precursors are able to be applied to a lot of field such as 3D printing, anode material of secondary battery and semiconductor fields, because of its capability to form various forms of amorphous silicon.

In the present study, pyrophoric liquid neopentasilane(NPS) was synthesized in two sequential reactions. At first, $\text{Si}(\text{SiCl}_3)_4$ was synthesized by a reaction of perchlorodisilane (Si_2Cl_6) and 1,4-diazabicyclo[2,2,2]octane (DABCO). Then, neopentasilane (NPS) was synthesized through an immediate reduction by diisobutylaluminum hydride (DIBAL). Then, the oligomerization of NPS was occurred at 145°C and the additional thermal process led a production of crystalline silicon. The precursor was converted to silicon metalloid at 200°C and a supplementary heating at 400°C led a disappearance of Si-H bond which was analyzed by IR spectroscopy. The thin film of silicon was formed by spin coating on the silicon wafer and baking processes. These were analyzed by IR spectra and SEM images. In this presentation, we will provide the synthesis of liquid phase silicon precursor and a transformation of the precursor to metalloid silicon.



P8 - New (di)allylsilane-based carbon-carbon bond forming reactions

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Several new transformations involving both allyl- and diallylsilanes that result in the formation of new carbon-carbon bonds will be presented. Examples include chemoselective carbonyl additions, rearrangements, and olefin metathesis. The products from these reactions represent useful intermediates for the synthesis of natural products and their derivatives.

P9 - Electrochemical Reactivity and Deposition Characteristics of Chlorosilanes in Nonaqueous Media

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The efficacy of several electrolytes for Si electrodeposition in propylene carbonate has been investigated using voltammetric techniques and scanning electron microscopy. The motivation is to develop a process to produce crystalline Si electrochemically at comparatively low temperatures. Three parameters have been studied: the size of the chlorosilanes, the concentration of chlorosilanes, and the identity of the background salt. The most common precursor for Si electrodeposition, SiCl₄, is inadequate for crystalline Si electrodeposition due to its low boiling point, high vapor pressure, and severe chemical instability. Cyclic voltammetry experiments show qualitatively that larger chlorosilanes are similarly active but without the high vapor pressure and low boiling point complications. Several chlorosilanes are reduced at similar potentials and with an apparently similar mechanism as SiCl₄, indicating a related/equivalent active species. A combination of chronoamperometric methods and scanning electron microscopy, showed the chlorosilane concentration directly affected the efficiency for and the rate of Si electrodeposition. Finally, the identity of the background salts affected the stability of the employed chlorosilanes. Chloride salts showed a strong propensity for chlorosilane decomposition above temperature. Perchlorate salts facilitated silica formation under reduction potentials. Tetraphenylborate salts showed metastability but the highest faradaic efficiencies. Preliminary evidence further suggest that tetraalkylammonium salts inhibited electrodeposition rates as compared to Na salts. These cumulative results show that for the electrodeposition of silicon thin films, the specific composition of the electrolyte solution is important and that the possibility for high efficiency, high rate electrodeposition of crystalline Si exists.

P10 - Polymers of Intrinsic Microporosity with Azo and Silicone Functionalities

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A relatively new class of 2D linear polymers, known as polymers of intrinsic microporosity (PIMs), derive their porous characteristics from backbone rigidity, rather than a cross-linked 3-D network of covalent bonds. A PIM is typically comprised of inflexible spiro monomers that create regular twists in the backbone, imparting permanent porosity in the bulk material. Unlike insoluble network solids, PIMs typically exhibit solubility in organic solvents, which allows for easier purification, characterization and structural modification of these 2D polymers. In the interest of broadening the scope and potential applications of PIMs, two new PIM structures will be described, including a PIM built from monomers containing a photo-switchable azo group, as well as a PIM featuring silicone functionalities in its backbone. The synthesis, characterization, and properties of these novel PIM structures will be discussed.