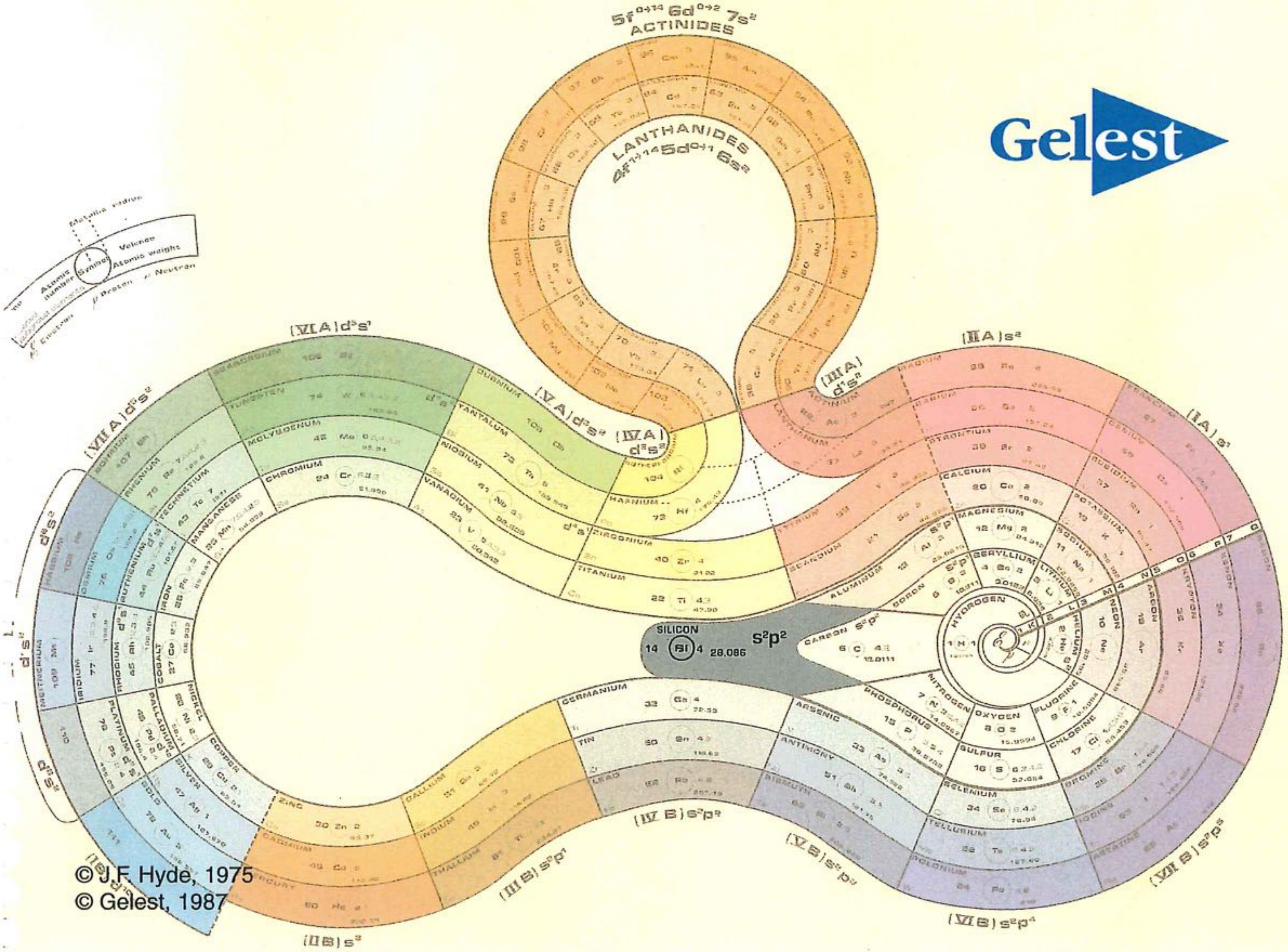
SILICON SYMPOSIUM

MAY 20-22, 2004

UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PA

Co-hosted by **Gelest Inc.** &
The University of Pennsylvania
Department of Chemistry

Gelest



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37TH SILICON SYMPOSIUM

UNIVERSITY OF PENNSYLVANIA
MAY 20-22, 2004

CO-HOSTED BY:

GELEST, INC.

THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA

ORGANIZERS

DONALD BERRY, PENN

BARRY ARKLES, GELEST

JERRY LARSON, GELEST

38TH SILICON SYMPOSIUM

MAY, 2005
PROFESSOR JOSEF MICHL
BOULDER, CO – UNIVERSITY OF COLORADO

9TH INTERNATIONAL SILICON SYMPOSIUM

JULY 31 – AUGUST 4, 2005

PROFESSOR REINHOLD TACKE
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WÜRZBURG, GERMANY

37TH SILICON SYMPOSIUM

SPONSORS

THE COMPANIES AND ORGANIZATIONS LISTED BELOW HAVE CONTRIBUTED GENEROUSLY TO THE SUPPORT OF THE 37TH SILICON SYMPOSIUM BOTH IN KIND AND THROUGH FINANCIAL CONTRIBUTIONS. THIS HAS ALLOWED FOR THE OFFERING OF SIX LOW-COST, HIGH-QUALITY TUTORIAL SESSIONS, AND LOW COST REGISTRATIONS AND ACCOMMODATIONS FOR STUDENTS AND POSTDOCTORAL RESEARCH ASSOCIATES. THE AIM OF BRINGING MORE OF THE YOUNGER GENERATION AND USERS OF SILICON CHEMISTRY TO THE MEETING HAS BEEN GREATLY AIDED BY THE STRONG SUPPORT PROVIDED.

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37TH SILICON SYMPOSIUM

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ACKNOWLEDGEMENTS

The success of the Silicon Symposium has not been a result of the work of the three organizers, but rather that of a team of talented and hard working individuals. The people listed below have contributed their talents, ideas, time and energy to the various functions necessary for a successful scientific meeting. The organizers wish to express their sincere thanks to this group of individuals who have helped to insure the success of the symposium.

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PAST, PRESENT AND FUTURE SILICON SYMPOSIA

Date	Kipping Awardee	Site	Host
April 1967	M. Kumada	University of Pennsylvania	A. MacDiarmid
April 1968	U. Wannagat	University of Wisconsin	R. West
April 1969	R. Benkeser	Marshall, Minnesota	E. Carberry
May 1970	R. West	SUNY Albany	J. Zuckerman
March 1971	A. MacDiarmid	Carnegie Mellon University	C. Van Dyke
April 1972	D. Seyferth	University of Maryland	J. Bellama
April 1973	A. Brook	North Texas State University	P. Jones
March 1974	H. Schmidbauer	University of Missouri, St. Louis	J. Corey
April 1975	H. Bock	Case Western Reserve University	M. Kenney
April 1976	M. Lappert	University of Windsor	J. Drake
March 1977		Kansas City, Missouri	J. Connolly
March 1978	H. Sakurai	Iowa State University	T. Barton
March 1979		University of Michigan	M. Curtis
March 1980	E. Ebsworth	Texas Christian University	R. Neilson
March 1981		Duke University	R. Wells
June 1982	T. Barton	Dow Corning, Midland, MI	C. Frye
June 1983		North Dakota State University	P. Boudjouk
April 1984	R. Corriu	General Electric, Schenectady, NY	R. Shade
April 1985		Louisiana State University	F. Cartledge
April 1986	P. Gaspar	Union Carbide, Tarrytown, NY	B. Kanner
June 1987		St. Louis, MO, with VIII International	P. Gaspar. J. Corey, E. Corey
June 1988	R. Calas	University of Montreal	J. Harrod
April 1989		Petrarch Systems, Philadelphia, PA	B. Arkles
April 1990	J. Speier	Dow Corning, Midland, MI	T. Lane
April 1991		University of Texas, El Paso	K. Pannell
April 1992	N. Wiberg	University of Southern California	W. Weber
March 1993		Univ of Indiana -Purdue Univ / Indianapolis	M. Zeldin
March 1994	R. Walsh	General Electric, Schenectady, NY	J. Rich, J. Crivello
March 1995		PCR, Inc., Gainesville, FL	PDR, Inc., U. Florida
March 1996	W. Ando	Northwestern University	J. Lambert
May 1997		University of Western Ontario	K. Baines, M. Brook
May 1998	J. Lambert	Tulane University	M. Fink, K. Birdwhistell
March 1999		Sigma-Aldrich, Milwaukee, WI	C. Recatto, M. Steinmetz
April 2000	P. Jutzi	Dow Corning, Midland, MI	W. Schulz
May 2001		Crompton, Whiteplains, NY	K. Lewis
August 2002	K. Tamao	Guanajuato, MX, with IX International	J. Cervantes
May 2003		University of Akron	C. Tessier, W. Youngs
May 2004	J. Mark	University of Pennsylvania and Gelest	D. Berrry, B. Arkles, J. Larson
May 2005		University of Colorado	J. Michl

Colin Eaborn

15 March 1923 – 22 February 2004

The death of Colin Eaborn is a significant loss to the organosilicon community in general and a great personal loss to the many individuals who knew him as a friend, colleague, collaborator, and mentor. Many of the new generation of silicon chemists will not have met Colin personally but will have been aware of his work and influence through his prodigious research output and through his 32 year regional editorship (until the end of 1995) of the Journal of Organometallic Chemistry (through which many authors have been grateful for his thorough editing and helpful advice on the writing of good chemical English). Colin had not been active at conferences since about 1988 but had, since then, remained highly productive, publishing over 150 papers in his "retirement".

Colin spent his early years in Wales and received his BSc and PhD degrees from the University College of North Wales, Bangor in 1944 and 1947 respectively. He started his first independent research in 1947 as an assistant lecturer at the (then) University College Leicester in 1947 where he was promoted to a Lectureship in 1950 and Readership in 1954. In 1962 he became one of the four founding science professors at the newly formed University of Sussex where he was to spend the next twelve years as head of chemistry building up the School of Chemistry and Molecular Sciences as a vibrant, internationally recognised centre of chemical teaching and research. He was active not only in chemical research but played a significant role in establishing the new University of Sussex acting as Dean to the School and as Pro-Vice-Chancellor of the University as well as being on numerous national and international committees concerning teaching and collaboration [1].

The degree of success achieved can be appreciated by the fact that by the late 1970s the Unit of Nitrogen Fixation, led by Professor Joseph Chatt, was attached to the School and there was a large highly active group of academic faculty, including seven Fellows of the Royal Society, two of whom were Nobel Laureates. Colin was awarded the F. S. Kipping Award in 1964, was the honoured guest at the XIX Organosilicon Symposium in Baton Rouge, 1985, and received many other awards throughout the years [1] including election to Fellowship of the Royal Society in 1970.

Colin's research has ranged over much of group 14 chemistry but concentrated on the organometallic compounds of silicon. He published over 550 papers from 1949-2004 starting with “Organosilicon compounds. I. Formation of alkyliodosilanes” published in the *Journal of the Chemical Society*. His early papers elucidated the nature of many of the steric and electronic effects in organosilicon chemistry that today are part of the bedrock of basic silicon chemistry. His interest in the steric effects of substituents at silicon was a thread which ran through much of his research and can be traced from a paper in 1952 to his recent work on compounds containing the $(Me_3Si)_3C$ group. One of his most enduring contributions was the publication in 1960 of his book “Organosilicon Compounds” which was the silicon chemist’s “Bible” for several decades and which remains a treasured volume on many shelves. Apart from his early work on the preparation and interconversion of various functional groups at silicon he published a long series of papers on the cleavage of Si-C, Ge-C and Sn-C bonds, reactions that have found increasing use in modern organic chemistry [2]. He also made major contributions to the chemistry of chiral silicon compounds, the mechanisms of aromatic substitutions, the chemistry of silyl, germyl and stannyl mercurials and the chemistry of compounds containing Si-Pt, Ge-Pt or Sn-Pt bonds. Since about 1977 Colin’s research output was dominated by investigations into the chemistry of compounds containing the $(Me_3Si)_3C$ (“trisyl”, Tsi) group both on a silicon atom [3] and on many other elements in the periodic table [4]. The considerable steric hindrance provided by this bulky group and groups like it enabled many novel structures to be determined and much new mechanistic chemistry to be uncovered. The use of these trisilylmethyl substituents has now been adopted by many other research groups who have found that such groups are particularly good at stabilising novel functional groups and coordination geometries.

Colin is survived by Joyce, his wife and companion of 50 years. He will rightly be remembered for many academic contributions to chemical research and teaching but to those who knew him he will also be remembered for his great kindness, unfailing courtesy, charm and wit. In summary, he will be remembered as a chemist and a gentleman.

Alan R. Bassindale and Paul D. Lickiss
March 2004

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1. For a more detailed list, see M. F. Lappert’s Introduction to volume 341 of *J. Organomet. Chem.*, 1988, a volume published to celebrate Colin’s 65th birthday and his contributions to organometallic chemistry.
2. For details of this work see Colin’s own review in *J. Organomet. Chem.*, 1975, **100**, pp. 43-57.
3. For a review see C. Eaborn, *J. Chem. Soc., Dalton Trans.*, 2001, pp. 3397-3406.
4. For a review see C. Eaborn and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2001, pp. 1541-1552.

Thursday - May 20, 2004	
5:00 - 7:00	Registration and Mixer - Inn at Penn (3600 Sansom St.)

Friday - May 21, 2004						
7:30	Coffee / Registration					
8:30	Opening Remarks (Room 102)					
8:45	Plenary 1 - James Mark					
	Session A (Lynch Room)		Session B (Room 102)		Session C (Room B-13)	
10:00	IL-1	Nuzzo	IL-2	Tilley		
10:30	A-1	Krempner	B-1	Braddock-Wilking		
10:50	Break					
11:10	A-2	Unno	B-2	Kira		
11:30	A-3	Abe	B-3	Fink		
11:50	A-4	Kawakami	B-4	Gavenonis		
12:10	A-5	Defriend	B-5	Brutchey		
12:30	Lunch					
2:00	IL-3	Yilgör	IL-4	Rosenberg	IL-5	Jung
2:30	A-6	Boucher	B-6	Pannell	C-1	Rubinsztajn
2:50	A-7	Aubert	B-7	Peng	C-2	Driess
3:10	Break					
3:40	A-8	Gunji	B-8	Imae	C-3	Marciniec
4:00	A-9	Cyr	B-9	Yu	C-4	Sakurai
4:30	Plenary 2 - Michael Sailor (Room 102)					
5:45 - 6:30	Board Buses					
6:15	Cocktails / National Constitution Center and Museum					
7:45	Banquet					
9:15	"A Visit with Madame Curie"					

SATURDAY - MAY 22, 2004

	SESSION A (LYNCH ROOM)		SESSION B (ROOM 102)		SESSION C (ROOM B-13)	
8:00	COFFEE					
8:30	PLENARY 3 - JAMES LEIGHTON (ROOM 102)					
9:40	IL-6	WIESNER	IL-7	STROHMANN	IL-8	WEST
10:10	A-10	TANABE	B-10	DAIß	C-5	OTTOSSON
10:30	BREAK					
10:50	A-11	ROSSI	B-11	CLARK	C-6	JOUIKOV
11:10	A-12	ZHANG	B-12	MARTEL	C-7	SEKIGUCHI
11:30	A-13	LEWIS	B-13	BANASZAK-HOLL	C-8	MICHL
11:50	A-14	WANG	B-14	ZHANG	C-9	KOST
12:10	LUNCH					
2:00	IL-9	IISKOLA	IL-10	LIN	IL-11	WALSH
2:30	A-15	CHAUHAN	B-15	BRANDSTADT	C-10	LEIGH
2:50	A-16	SEKI	B-16	SAHOO	C-11	GLATTHAAR
3:10	BREAK					
3:40	A-17	MEDINA	B-17	LAMBERT	C-12	BECERRA
4:00	A-18	GLEASON	B-18	KENNEY	C-13	BAINES
4:20	A-19	WEINSTEIN	B-19	GRISWOLD	C-14	HILL
4:40 - 7:00	POSTER SESSION / REFRESHMENTS					

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

FRIDAY, MAY 21, 2004

Morning

7:30-8:30	COFFEE	

Combined Session (Room 102)

8:30-8:45	Opening Remarks and Future Meetings	
8:45-9:45	PL-1	**J. E. Mark** *Some Interesting Things about the Polysiloxanes*

Session A - Morning (Lynch Room)

K. Lewis, chair

10:00-10:30	IL-1	**R. G. Nuzzo** *Micro, Nano, Macro: Silicon, Silicones, and Soft-Lithography Off Road on the Road Map*
10:30-10:50	A-1	**C. Krempner**, U. Jaeger-Fiedler, H. Reinke, K. Weichert *Novel Polysilanols – Synthesis, Structure and Coordination Chemistry*
10:50-11:10		COFFEE BREAK
11:10-11:30	A-2	**M. Unno**, Y. Kishimoto, H. Matsumoto *Trihydroxycyclotrisiloxanes*
11:30-11:50	A-3	**Y. Abe**, Y. Kadota, K. Arimitsu, T. Gunji *Syntheses of Ladder Oligosilsesquioxanes*
11:50-12:10	A-4	**Y. Kawakami** *Stereoregular Silicon-Containing Polymers*
12:10-12:30	A-5	**K. A. DeFriend**, D. A. Loy, K. V. Salazar, K. V. Wilson, Jr. *Silylation of Low-Density Silica and Bridged Polysilsesquioxane Aerogels*
12:30-2:00		Lunch Break

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

FRIDAY, MAY 21, 2004

Session A - Afternoon (Lynch Room)

J. Kennan, chair

2:00-2:30	IL-3	**I. Yilgör**, E. Yilgör *New Generation of Silicone-Urea Elastomers: New Synthetic Methods, Novel Backbone Architectures and Designed Properties*
2:30-2:50	A-6	**M. A. Boucher**, D. E. Katsoulis, M. E. Kenney *New Organosilicon Sheet Polymers*
2:50-3:10	A-7	**M. A. Aubert**, M. B. Abrams, R. T. Boaron, M. Hull, D. Kobeda, D. Mountz, R. Siebenlist, G. S. Silverman, S. A. Swan, K. Tseng *Developmental and Synthetic Challenges in Triorganosilyl-Based Marine Antifoulant Coatings – High Throughput Approaches*
3:10-3:40		COFFEE BREAK
3:40-4:00	A-8	**T. Gunji**, Y. Sakai, K. Arimitsu, Y. Abe, R. West *Preparation of C_{60}-Polysiloxane Hybrid Materials*
4:00-4:20	A-9	**P. W. Cyr**, E. H. Sargent, I. Manners *Photocontrol of Polyferrocenylsilanes*

Combined Session (Room 102)

D. Berry, chair

4:30-5:30	PL-2	**M. J. Sailor** *Smart Dust: Photonic Crystals Derived from Nanocrystalline Porous Si and Their Applications in Sensors and Medicine*
5:45 - 6:30		Board Buses
6:15-7:45		Cocktails / National Constitution Center and Museum
7:45		Banquet
9:15		A Living History of Marie Curie

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

FRIDAY, MAY 21, 2004

Morning

7:30-8:30	COFFEE	

Combined Session (Room 102)

8:30-8:45	Opening Remarks and Future Meetings	
8:45-9:45	PL-1	**J. E. Mark** *Some Interesting Things about the Polysiloxanes*

Session B - Morning (Lynch Room)

K. Pannell, Chair

10:00-10:30	IL-2	**T. D. Tilley** *Participation of Ligand Alpha-Substituents in Bond Activations and Catalytic Transformations Involving Silicon*
10:30-10:50	B-1	**J. Braddock-Wilking**, J. Y. Corey, K. Trankler, L. French, K. K. Dill, N. P. Rath *Pt-Si Monomers, Dimers, and Trimers*
10:50-11:10		COFFEE BREAK
11:10-11:30	B-2	**M. Kira**, Y. Sekiguchi, T. Iwamoto, C. Kabuto *Synthesis and Structure of 14-electron Disilene-Palladium Complex*
11:30-11:50	B-3	**M. J. Fink**, J. T. Mague, R. C. Boyle *Activation of Si-H and Si-Si Bonds by Palladium Bisphosphine Complexes: Evidence for Long-Lived s-Complexes*
11:50-12:10	B-4	**J. Gavenonis**, T. D. Tilley *Synthesis and Reactivity of Tris(imido) Rhenium Complexes Containing Rhenium-Main Group Element Bonds. Silicon-Carbon Bond Activation of* $PhSiH_3$ *by Silyl Complexes*
12:10-12:30	B-5	**R. L. Brutchey**, T. D. Tilley *Design and Synthesis of Heterogeneous Catalysts and Catalyst Supports Derived from Metal Siloxide Molecular Precursors*
12:30-2:00		LUNCH BREAK

FRIDAY, MAY 21, 2004

Session B - Afternoon (Room 102)

M. Fink, chair

2:00-2:30	IL-4	**L. Rosenberg** *Catalytic Si-H Activation in the Synthesis and Modification of Oligosilanes*
2:30-2:50	B-6	H. K. Sharma, P. Apodaca, F. Cervantes-Lee, **K. H. Pannell** *Carbosila-, Carbogerma-, and Related Transition Metallocycles and Their Ring Opened Polymers*
2:50-3:10	B-7	**W. Peng**, J. Koe *Composition-Driven Chiral Selection in Optically Active Polyalkylarylsilane Aggregates*
3:10-3:40		COFFEE BREAK
3:40-4:00	B-8	**I. Imae**, Y. Kawakami *Synthesis and Properties of Phenyl-Substituted Oligosilanes with Well-Defined Structures*
4:00-4:20	B-9	**X.-H. (Bruce) Yu**, Z.-L. (Ben) Xue *γ-Hydrogen Abstraction by Silyl Ligands: Preparation of Metallacyclic Complexes and Kinetic Studies of the Reactions*

Combined Session (Room 102)

D. Berry, chair

4:30-5:30	PL-2	**M. J. Sailor** *Smart Dust: Photonic Crystals Derived from Nanocrystalline Porous Si and Their Applications in Sensors and Medicine*
5:45 - 6:30		Board Buses
6:15-7:45		Cocktails / National Constitution Center and Museum
7:45		Banquet
9:15		A Living History of Marie Curie

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

FRIDAY, MAY 21, 2004

Session C - Afternoon (Room B-13)

A. Bassindale, chair

2:00-2:30	IL-5	**I. N. Jung** *Dehydrogenative Double Silylation of Acetylenes with Bis- and Tris(dichlorosilyl)methanes*
2:30-2:50	C-1	**S. Rubinsztajn**, J. A. Cella *New Condensation Process Leading to the Formation of Siloxane Bonds*
2:50-3:10	C-2	**M. Driess**, N. Dona, K. Merz *Intramolecular Electron-Transfer in Hypervalent Silicon-Complexes and Related Systems*
3:10-3:40		COFFEE BREAK
3:40-4:00	C-3	**B. Marciniec** *Stereo- and Regio-Selective Synthesis of Compounds with Vinylsilicon Functionality via Ruthenium-Catalyzed Silylative Coupling – Recent Advances*
4:00-4:20	C-4	**H. Sakurai**, S. Onai, T. Sanji *Organosilicon and Organometallic Way to Efficient Dechlorination of Polychlorinated Arenes*

Combined Session (Room 102)

D. Berry, chair

4:30-5:30	PL-2	**M. J. Sailor** *Smart Dust: Photonic Crystals Derived from Nanocrystalline Porous Si and Their Applications in Sensors and Medicine*
5:45 - 6:30		Board Buses
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37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

SATURDAY, MAY 22, 2004

Morning

8:00-8:30	COFFEE	

Combined Session (Room 102)

J. Larson, chair

8:30-9:30	PL-3	**J. L. Leighton** *Strained Silacycles: A Powerful Platform for Asymmetric Reaction Design*

Session A - Morning (Lynch Room)

B. Arkles, chair

9:40-10:10	IL-6	**U. Wiesner** *Polymer Approaches to Silicon Based Nanostructured Hybrid Materials*
10:10-10:30	A-10	**M. Tanabe**, S. C. Bourke, I. Manners *Photochemically-Induced Ring-Opening Polymerization of Sila[1]ferrocenophanes*
10:30-10:50		COFFEE BREAK
10:50-11:10	A-11	**N. A. A. Rossi**, Z. Zhang, R. West *Liquid Siloxane Copolymers for Application in High Energy Density Lithium Batteries*
11:10-11:30	A-12	**Z. Zhang**, L. J. Lyons, K. Amine, R. West *Novel Network-Type Polymer Electrolytes Based on Oligoethyleneoxy-Functionalized Cyclopentasiloxanes for Use in Lithium Polymer Batteries*
11:30-11:50	A-13	**K. M. Lewis** *Impact of Blowing Agents on Silicone Surfactant Selection for the Stabilization of Rigid Polyurethane (PUR) and Polyisocyanurate (PIR) Foams*
11:50-12:10	A-14	**X. Wang**, Y. Yuan, I. Cabasso *Novel Hydrogen Electrode on the Electrosynthesis of High Yield Silane Oligomers*
12:10-2:00		LUNCH BREAK

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

Saturday, MAY 22, 2004

Session A - Afternoon (Lynch Room)

N. Shephard, chair

2:00-2:30	IL-9	**E. Liskola** *Molecular Control of Interface Chemistry by Atomic Layer Deposition (ALD): A Case Study on Novel Gas-Solid Interactions of Aminoalkoxysilanes with Silica*
2:30-2:50	A-15	**B.P.S. Chauhan** Pt-Silicones Reservoirs And Their Applications In Hydrosilylation Catalysis
2:50-3:10	A-16	S. Tsukuda, **S. Seki**, S. Tagawa, M. Sugimoto, K. Jimbo, A. Kohyama *Cross-Linked Silicon-Based Polymer Nanowire Formation by High Energy Charged Particles*
3:10-3:40	COFFEE BREAK	
3:40-4:00	A-17	**I. Medina**, J. T. Mague, M. J. Fink *Silylated Bimetallic Compounds as Single-Source Precursors to Binary and Ternary Metal Chalcogenide Materials*
4:00-4:20	A-18	H. G. P. Lewis, S. Murthy, S. O'Shaughnessy, M. C. Kwan, **K. K. Gleason** *Hot Filament Chemical Vapor Deposition of Organosilicon and Fluorocarbon-Organosilicon Thin Films*
4:20-4:40	A-19	**B. Weinstein** *Acrylic Thermosets: A Green Chemistry Alternative to Formaldehyde-Based Resins*
4:40-7:00		POSTER SESSION

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

SATURDAY, MAY 22, 2004

Morning

8:00-8:30	COFFEE	

Combined Session (Room 102)

J. Larson, chair

8:30-9:30	PL-3	**J. L. Leighton** *Strained Silacycles: A Powerful Platform for Asymmetric Reaction Design*

Session B - Morning (Room 102)

P. Hudrlik, chair

9:40-10:10	IL-7	**C. Strohmann**, D. Auer, M. Bindl, J. Hörnig, V. C. Frab, D. Schildbach *About the Stereochemistry of Lithiated Silanes*
10:10-10:30	B-10	**J. O. Daiß**, W. Bains, G. A. Showell, J. Warneck, R. Tacke *Synthesis and Pharmacological Characterization of Sila-Venlafaxine, a Silicon Analogue of the Antidepressant Venlafaxine*
10:30-10:50		COFFEE BREAK
10:50-11:10	B-11	**C. T. Clark**, K. A. Scheidt *Copper-Catalyzed Disilylation of Electron-Deficient Alkenes Utilizing a Lewis Base-Activation Strategy*
11:10-11:30	B-12	**A. Martel**, T. Guliashvili, A. Fischer, P. Akselsson *2-Silenolates: Heavy Enolates with a Potential in Stereoselective Synthesis*
11:30-11:50	B-13	R. H. Walker, **M. M. Banaszak Holl** *C-H-Activation of Alkanes, Ethers, and Amines Using a Mixed Silylene/Aryl Halide Reagent*
11:50-12:10	B-14	P. F. Hudrlik, **L. Zhang**, W. Arasho, J. Cho, A. M. Hudrlik *Synthesis of Calix[4]arenes Containing a Disiloxane Bridge as Potential Anionic Receptors*
12:10-2:00		LUNCH BREAK

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

Saturday, MAY 22, 2004

Session B - Afternoon (Room 102)

S. Sieburth, chair

2:00-2:30	IL-10	**V. S.-Y. Lin** *Gatekeeping Effect: Synthesis of Multi-functionalized Mesoporous Silica Nanosphere Materials as Biosensors, Selective Catalysts, and Stimuli-Responsive Controlled Release Delivery Carriers*
2:30-2:50	B-15	A. R. Bassindale, **K. F. Brandstadt**, T. H. Lane, P. G. Taylor *Siloxane Biocatalysts*
2:50-3:10	B-16	**B. Sahoo**, K. F. Brandstadt, T. H. Lane, R. A. Gross *Biocatalytic Reactions to Form Organosilicon Carbohydrate Macromers*
3:10-3:40	COFFEE BREAK	
3:40-4:00	B-17	**J. B. Lambert**, G. Lu, V. Kolb *Silicate Complexes of Sugars in Aqueous Solution*
4:00-4:20	B-18	M. Guo, **M. E. Kenney** *The Organosilicon Drug Pc 4 and Its Fluoro Analogue*
4:20-4:40	B-19	P. Lehmann, **R. Griswold** *Silylated Polyurethane (SPUR^{SM}) Sealants: Property Tailoring*
4:40-7:00	POSTER SESSION	

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

SATURDAY, MAY 22, 2004

Morning

8:00-8:30	COFFEE	

Combined Session (Room 102)

J. Larson, chair

8:30-9:30	PL-3	**J. L. Leighton** *Strained Silacycles: A Powerful Platform for Asymmetric Reaction Design*

Session C - Morning (Room B-13)

J. Shibley, chair

9:40-10:10	IL-8	**R. West**, D. F. Moser, N. J. Hill, M. P. Egorov, B. Tumanskii *The Radical Chemistry of Stable Silylenes*
10:10-10:30	C-5	**H. Ottosson**, T. Guliashvili, A. Martel, I. El-Sayed *Zwitterionic Silenes from Oligosilylamides: Their Formation and Trapping Reactions*
10:30-10:50		COFFEE BREAK
10:50-11:10	C-6	**V. Jouikov**, R. Keyrouz *Electrogeneration of Silanones(?): New Synthetic Route to Functionalized Siloxanes*
11:10-11:30	C-7	**A. Sekiguchi**, R. Kinjo, M. Ichinohe, M. Toyoshima *Stable Disilyne with a Silicon-Silicon Triple Bond,* $\mathit{Dis_2{}^iPrSi\text{-}SiSi\text{-}Si^iPrDis_2}$*: A New Entry for the Multiple Bond Chemistry*
11:30-11:50	C-8	**J. Michl**, D. W. Rooklin, A. Bande, M. Peters, T. Schepers *What Does It Take to Suppress Sigma Delocalization in an Oligosilane?*
11:50-12:10	C-9	B. Gostevskii, A. Sivaramakrishna, I. Kalikhman, **D. Kost** *Reactivity of Siliconium-Ion Complexes: C-C Bond Formation Through Inter-Chelate Rearrangement*
12:10-2:00		LUNCH BREAK

37TH SILICON SYMPOSIUM PROGRAM
LECTURE PRESENTATIONS

Saturday, MAY 22, 2004

Session C - Afternoon (Room B-13)

R. West, chair

2:00-2:30	IL-11	R. Becerra, S. E. Boganov, M. P. Egorov, V. I. Faustov, I. V. Krylova, O. M. Nefedov, V. M. Promyslov, **R. Walsh** *What We Have Learned About the Stabilities of Silirane (Germirane) and Silirene (Germirene) Through Gas-Phase Kinetic and Quantum Chemical Studies of the Reactions of* SiH_2 *(*GeH_2*) with Ethylene and Acetylene*
2:30-2:50	C-10	**W. J. Leigh**, T. R. Owens, Y. Apeloig, D. Bravo-Zhivotovskii *Protonation of the Silicon-Carbon Double Bond. A Kinetic Study of the Addition of Alcohols and Acids to a Stabilized Silene in Solution*
2:50-3:10	C-11	G. Maier, **J. Glatthaar** *The Direct Reaction of Silicon with Methanol: A Matrix Spectroscopist's View*
3:10-3:40		COFFEE BREAK
3:40-4:00	C-12	**R. Becerra**, M. J. Almond, N. Goldberg, R. Walsh, J. P.Cannady, J. S. Ogden *Experimental and Theoretical Studies of the Gas-Phase Reactions of* $SiH_2 + H_2O$ *(*D_2O*) and* $SiH_2 + HCl$*. Kinetic and Quantum Chemical Studies*
4:00-4:20	C-13	**K. M. Baines**, S. E. Gottschling, K. K. Milnes *Alkyne Cycloaddition Reactions of Disilenes: The Real Story*
4:20-4:40	C-14	**N. J. Hill**, R. West *Recent Developments in Stable Silylene Chemistry*
4:40-7:00		POSTER SESSION

POSTER PRESENTATIONS

SATURDAY, MAY 22, 2004

4:40-7:00 POSTER SESSION (refreshments served)

P-1 **N. Niamsiri**, D. F. Schmidt, D. Shah, T. A. Wilson, E. P. Giannelis, C. A. Batt
Hybrid Organic-Inorganic Polymeric Nanocomposites for Biosensor Applications

P-2 **J. Ebenhoch**, H. Oswaldbauer
Silicone Nanospheres for Polymer and Coating Applications

P-3 **J. Zou**, S. Kauzlarich
Synthesis and Size-Control of Si Nanoparticles Prepared by a Solution Route

P-4 K. A. Pettigrew, P. P. Power, **S. A. Kauzlarich**
Solution Synthesis and Characterization of Si & Si/Ge Nanoparticles

P-5 **K. Weissenbach**, R. Conn
Silylated Surfaces: Some New Insights

P-6 **J. Clapper**, L. G. Sneddon
Syntheses and Structural Studies of 10-Vertex Siladicarboranes and the First Silamonocarboranes

P-7 **X. Wei**, P. J. Carroll, L. G. Sneddon
Design, Synthesis and Ceramic Conversions of Molecular and Polymeric Single Source Precursors to Si-B-C and Si-B-N-C Composite Materials

P-8 **M. Driess**, G. Mera
Synthesis of Novel Unsaturated Si-Rich Polycarbosilanes and Their Conversion to Electrical Conductive Films

P-9 **N. Goldberg**, J. S. Ogden, M. J. Almond, R. Walsh, J. Lee, J. P. Cannady, R. Becerra
High Temperature Reactions of Si_2Cl_6 with Oxides of Nitrogen

P-10 R. Becerra, **J. P. Cannady**, R. Walsh, Does Silylene React with "Unreactive" *Molecules? Experimental and Theoretical Studies of the Gas-Phase Reactions of SiH2 with CO, CO_2, and N_2*

P-11 W. Peng, **J. Koe**
Synthesis of Poly(ethynylsilane)s

P-12 **L. French**, J. Braddock-Wilking, J. Corey, V. Speedie, M. Rutherford, N. P. Rath
Pt-Si Dimers Prepared from Silicon Heterocycles

P-13 P. Sengupta, H. Zhang, C. Rim, **D. Y. Son**
Bis(pyridiyl) Ligands Based on Organosilicon Linkers – Complex Formation with Late Transition Metals

P-14 B. Arkles, **Y. Pan**, G. L. Larson
Volatile Azasilanes: Novel Coupling Agents for Nanotechnology

POSTER PRESENTATIONS

P-15 **K. K. Milnes**, K. M. Baines
Alkyne Containing Mechanistic Probes: Development and Application

P-16 **T. Guliashvili**, A. Martel, A. Eklöf, H. Ottosson
A Computational Study on the Thermolytic Formation of Silenes Influenced by Reversed Si=C Bond Polarity

P-17 **B. Tumanskii**, P. Pine, N. J. Hill, R. West, Y. Apeloig
Radical Reactions of a Stable N-Heterocyclic Silylene: EPR Study and DFT Calculation

P-18 **Y. Kon**, K. Sakamoto, C. Kabuto, M. Kira
X-Ray and Theoretical Studies of Silacyclobutadiene Cobalt Complexes

P-19 **I. S. Toulokhonova**, R. West
Reaction of 1,1-Dilithiosiloles with 2,3-Dimethylbuta-1,3-diene

P-20 **A. Naka**, R. West
Mechanistic Interpretation for Reaction of a Stable Silylene with Chloroform

P-21 **J. Glatthaar**
1-Silaallene, a Key Intermediate in the Isomerization of Vinylsilylene into Silylacetylene

P-22 **T. Eliseeva**, W. Lewis, M. Panzer, M. Espe, C. A. Tessier, W. Youngs
Synthesis and NMR Characterization of Bis-Imidazole Complexes of Silanes

P-23 M. Caudillo, R. Zárraga, **J. Cervantes**
Oligosiloxanes of the Type Q_2M_6 *from the Trimethylsilylation Reaction of Complex Silicates*

P-24 E. N. Ofitserov, **J. A. Ubaskina**, E. G. Fetuhina, O. A. Kroncheva
About the Nature of Siliceous Rock Silica

P-25 **J. M. Shorb**, M. E. Silver, B. P. Krueger
Modeling the Behavior of Siloxane Polymers as Emulsifiers Using Molecular Dynamics Simulations

P-26 Th. Frey, **L. Rösch**, Ch. Ruedinger, J. Weis
Application of Microstructured Heaters for the Thermolysis of Carbamatosilanes

P-27 **V. Stanjek**, H. Sommer, R. Weidner
Silane Crosslinking High Performance Spray Foams

P-28 Th. Frey, **L. Rösch**, Th. Kammel, J. Weis
Continuous Production of Isocyanatosilanes Using Heterogeneous Catalysts

P-29 Th. Frey, **L.. Rösch**, Ch. Ruedinger, J. Weis
Thermolysis of Carbamatosilanes in the Microwave Field

P-30 **X. Chang**, M. C. Kung, H. H. Kung
Stepwise Synthesis of Siloxane Chains

POSTER PRESENTATIONS

P-31 **C. Angeletakis**, C. Luu
A New Dental Impression Material with Reduced Sulfur Sensitivity

P-32 **Z. Zhang**, L. J. Lyons, K. Amine, R. West
Synthesis and Ionic Conductivity of Short-Chain Siloxanes with Oligoethyleneoxy Combs

P-33 **D. M. Ballweg**, R. C. Miller, K. A. Scheidt
Synthesis of a-Silyl Amines Through the Addition of Silyl Anions to Imines

P-34 **J. A. Muchnij**, R. E. Maleczka, Jr.
Chemoselective Conjugate Reduction of a,b-Unsaturated Carbonyl Compounds with Polymethylhydrosilane

P-35 **R. J. Rahaim**, Jr., R. E. Maleczka, Jr.
A Versatile and Mild Reducing Method of Activated Alkenes and Alkynes, Halides, Nitro Groups, and Benzylic Oxygens via a Combination of Palladium Acetate, Poly(methylhydrosiloxane), and Aqueous KF

P-36 R. J. Fox, C. Sfouggatakis, **M. A. Foley**, A. B. Smith III
Evolution of Multicomponent Linchpin Couplings. Reaction of 2-Lithio-2-Silyl-1,3-Dithianes

P-37 **M. O. Duffey**, A. B. Smith III
Bifunctional Molecular Linchpins: A Three-Component Coupling Protocol Employing 2-Bromoallyltrimethylsilane

P-38 M. Sanganee, **J. D. Sellars**, P. G. Steel, D. K. Whelligan
Silenes: Novel Reagents for Organic Synthesis

P-39 **M. Penka**, S. Dragota, R. Bertermann, C. Burschka, R. Tacke
Spirocyclic Zwitterionic l^5Si-Silicates with Two Bidentate Ligands Derived from α-Amino Acids: Synthesis, Structure, and Stereodynamics

P-40 T. Heinrich, **B. Müller**, R. Bertermann, C. Burschka, A. Hamacher, M. U. *Kassack, B. Theis, R. Tacke*
Synthesis and Pharmacological Characterization of Sila-Haloperidol, A Silicon Analogue of the Dopamine (D2) Receptor Anatagonist Haloperidol

P-41 **O. Seiler**, C. Burschka, S. Metz, M. Penka, R. Tacke
Synthesis and Structural Characterization of Novel Neutral Higher-Coordinate Silicon Compounds with Mono- Bi-, Tri-, and Tetradentate Ligands Containing O- and N-Donor Atoms

P-42 **G. Liu**, S. McN. Sieburth
Alpha-Trialkylsilyl Amino Acids: Preparations and Applications

P-43 **M. Purushotham**, W. D. Arasho, S. McN. Sieburth
Silanediol-Based Inhibitors of the Metalloprotease Anthrax Lethal Factor

POSTER PRESENTATIONS

P-44 **S. Sen**, M. Purushotham, S. McN. Sieburth
Efficient and Enantioselective Synthesis of Silanediol Protease Inhibitors

P-45 P. F. Hudrlik, **D. Dai**, A. M. Hudrlik
Reactions of Dilithiobutadienes with Monochlorosilanes: Observation of Facile Loss of Organic Groups from Silicon

P-46 P. F. Hudrlik, **D. Dai**, A. M. Hudrlik
Reactions of Silafluorene Dianions with Mono- and Difunctional Alkylating Agents

P-47 P. F. Hudrlik, A. M. Hudrlik, **W. D. Arasho**
Methods for the Synthesis of Upper Rim Silylated Calix[4]arenes Using Halogen-Metal Exchange and the Wurtz-Fittig Reaction

P-48 **R. H. Walker**, M. M. Banaszak Holl
C-H Activation of Amines, Alkanes and Ethers with a Silylene/Aryl Iodide Reagent

P-49 **L. Pavelka**, K. Baines, I. Fleming
Probing the Mechanism of the Brook Rearrangement

P-50 **M. Shazim**, J. Yang, L. Varga, R. Stephani
Reactivity of Tris(trimethylsilylphosphite (TMSP): Cleavage of a-Lactams (Aziridinones)

P-51 **K. Hassall**, S. Lobachevsky, J. M. White
Synthesis and Structural Characterization of b-Silylated Carbenium Ions

P-52 **K. Lassen**, M. Sangi, M. P. Haaf
Stille Reactions Catalyzed by a Silylene-Palladium Complex

P-53 **S. I. M. Paris**, F. Lemke, E. Hey-Hawkins

Catalytic Hydrosilylation Employing Ruthenium Complexes Containing Air-Stable Primary and Secondary Phosphines

P-54 N. M. Yardy, S. I. M. Paris, **F. Lemke**
Ruthenium Catalyzed Hydrosilylation: Substituent and Concentration Effects on the Hydrosilylation of Phenylacetylenes

P-55 **Y. Zhang, Y. Jin**
Novel Process to Produce Organosilanes

P-56 **L. A. Morton**, Xianghua Yu, Z. (Ben) Xue
Kinetic and Thermodynamic Studies of an Unusual PMe_3*-Induced a-H Migration – The Interconversion* $(Me_3SiCH_2)_3WCSiMe_3(PMe_3)$ *with* $(Me_3SiCH_2)_2W(-CHSIMe_3)_2(PMe_3)$

P-57 **Y. Huo**, D. H. Berry
Synthesis and Characterization of Screw Sense Helical Polygermanes Bearing Remote Chiral Groups

POSTER PRESENTATIONS

P-58 **H. Yoo,** P. J. Carroll, D. H. Berry
Synthesis and Structure of Ruthenium-Silylene Complexes: Two-Step Activation of N-Heterocyclic Silanes

P-59 **M. Gallagher, N. Wieder,** P. J. Carroll, D. H. Berry
Reactivity of Organosilanes with Low Valent Ruthenium Complexes Bearing Tridentate Pyridyl Ligands

P-60 B. P. S. Chauhan, **A. Vela**
Biological Templates for Patterning of Novel Metal Nanoparticles

P-61 **M. Chauhan,** R. Pantano, J. S. Rathore, B. P. S. Chauhan
Silicon Based Templates for Synthesis and Stabilization of Nanosized Novel Metal Particles

P-62 B. P. S. Chauhan, **R. Sardar,** P. Sharma
Poly(methylhydrosiloxane) Directed Synthesis of Self-Assembled Nanosized Silver Necklaces

P-63 B. P. S. Chauhan, J. Rathore, T. Bandoo
Highly Chemoselective Hydrogenation Catalysts Based on "Silicones-Pd" Nanoconjugates

P-64 B. P. S. Chauhan, J. S. Rathore, **A. Sarkar,** N. Galloxhani
Nanocluster Catalyzed Macromolecular Grafting via Hydrosilylation Reactions

P-65 **S. Seki,** Y. Koizumi, T. Kawaguchi, H. Habara, S. Tagawa
Transient Spectroscopy of Radical Cations of a Variety of Substituted Polysilanes

LECTURE

ABSTRACTS

SOME INTERESTING THINGS ABOUT THE POLYSILOXANES

J. E. Mark, Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH 45221-0172.

Poly(dimethylsiloxane) [–$Si(CH_3)_2O$–] is by far the most studied of the polysiloxanes, and it's known to exhibit some intriguing physical properties, in particular very high permeability to gases. Simulations are underway in an attempt to understand some of these peculiarities. In addition, other symmetrically-substituted polysiloxanes exhibit mesophases that are not understood at all. In the case of cross-linked polysiloxanes, there have been many important developments, including (i) elastomers undergoing strain-induced crystallization through control of chain stiffness or stereochemical structure, (ii) model elastomers (including dangling-chain networks), (iii) possible thermoplastic elastomers, (iv) bimodal network chain-length distributions, (v) cross linking in solution or in a state of deformation, and (vi) gel collapse. Interesting elastomeric composites include those with (i) in-situ generated ceramic-like particles, (ii) ellipsoidal fillers, (iii) clay-like layered fillers, (iv) polyhedral oligomeric silsesquioxane (POSS) particles, (v) porous fillers, (vi) controlled particle-elastomer interfaces, and (vii) elastomeric domains generated within ceramic phases. Also of interest are some new techniques that have been used to characterize polysiloxane networks.

SMART DUST: PHOTONIC CRYSTALS DERIVED FROM NANOCRYSTALLINE POROUS SI AND THEIR APPLICATIONS IN SENSORS AND MEDICINE

Michael J. Sailor, Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla CA 92093-0358

The synthesis of nanostructured porous silicon films and particles that possess the properties of photonic crystals will be described. The chemistry and materials science that allows the use of these materials in remote chemical sensing, medical implant, and high throughput screening applications will be described. With appropriate modification of the electrochemical preparation conditions, multilayered structures can be generated that behave as 1-D photonic crystals. These structures can be encoded and used as remote sensors for chemicals. For example, small particles of nanoencoded microporous Si are used to detect volatile organic compounds in the environment. The intensity and wavelength of reflected light is determined in part by the refractive index of the porous nanostructure, which can be modified by adsorption of vapors within the porous matrix. High throughput screening, biosensing, and in-vivo drug delivery applications of these encoded particles will also be discussed.

Strained Silacycles: A Powerful Platform for Asymmetric and Tandem Reaction Design

James L. Leighton

Department of Chemistry, Columbia University, New York, NY 10027

When constrained in a five-membered ring with 1,2-diols, aminoalcohols and diamines, silicon exhibits significant Lewis acidity leading to unusual reactivity patterns. For example, uncatalyzed aldol and allylation reactions based on this concept have been demonstrated in which no external Lewis acid catalyst/promoter is required. Various strategies for exploiting this phenomenon will be described. Asymmetric allylation and crotylation of aldehydes and related processes such as a new asymmetric allylation of *N*-acyl hydrazones have been achieved. Finally, when strategically coupled with reactions that produce functionalized aldehydes directly, this type of Lewis acidity has been shown to be uniquely amenable to the development of tandem reactions that allow the synthesis of polyketide frgaments containing up to four stereocenters in a single step.

Micro, Nano, Macro: Silicon, Silicones, and Soft-Lithography Off Road on the Road Map.

Ralph G. Nuzzo
Frederick Seitz Materials Research Laboratory
Department of Chemistry
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

The emergence of new forms and applications of electronics presents both opportunities and challenges for developing new approaches to materials patterning. This talk will explore these issues in the context of recent advances made in Soft-Lithography: methods that allow the removal of design rule constraints for devices that are intrinsic to patterning protocols based on photolithography. New forms of materials for applications in electronics, processes for integrating them in complex functional arrays, and the development of a new model for fabrication based on both bottom-up and top-down approaches to large area patterning will be discussed.

Participation of Ligand Alpha-Substituents in Bond Activations and Catalytic Transformations involving Silicon

T. Don Tilley
University of California, Berkeley
and
Lawrence Berkeley National Laboratory

Transition metal compounds are widely employed as reagents and catalysts for chemical conversions. The great utility of metal complexes in this regard derives from their ability to activate small molecule substrates toward a variety of different transformations. These activations are associated with a small number of fundamental steps, such as binding, oxidative addition and insertion. A lesser-known fundamental process involves the migration of a substituent from a donor atom to the metal. This type of 1,2-shift, which can take a complex of the general form $L_nM\text{-}Si(R)X_m$ to a more reactive $L_n(R)M{=}SiX_m$ structure, represents a potentially important step in substrate activation and catalysis. Such migrations may be coupled with oxidative addition to provide the direct conversion of a free silane to a silyene complex. This chemistry may be incorporated into the design of new catalysts. Alpha-substituents have been found to play key roles in other types of transformations. For example, alpha-agostic interactions have been observed to activate a Hf-Si bond toward new sigma-bond metathesis processes. Carbon-hydrogen activations of this kind have been incorporated into new catalytic cycles for the conversion of inert hydrocarbons such as methane. In related systems involving tin, alpha-eliminations of a different type are relevant to the mechanism of the metal-catalyzed dehydropolymerization of secondary stannanes to polystannanes.

NEW GENERATION OF SILICONE-UREA ELASTOMERS: NEW SYNTHETIC METHODS, NOVEL BACKBONE ARCHITECTURES AND DESIGNED PROPERTIES

Iskender Yilgor and Emel Yilgor
Chemistry Department, Koc University, Sariyer 34450, Istanbul, Turkey

Silicone-urea segmented copolymers with novel backbone architectures, such as segmented, hyperbranched copolymers, and copolymers with a gradient polyether interphase, were prepared. Isopropanol was employed as the reaction solvent which allowed the preparation of high molecular weight siloxane-urea copolymers with urea hard segment contents ranging from 10 to over 40% by weight. Thermal, mechanical and morphological characterization of polymers demonstrated the formation of microphase separated systems with unique combination of properties. It has been demonstrated that by proper design of the copolymer backbone, properties such as modulus, ultimate tensile strength, water absorption and refractive index can independently be controlled in these novel silicone-urea copolymer systems.

CATALYTIC SI-H ACTIVATION IN THE SYNTHESIS AND MODIFICATION OF OLIGOSILANES

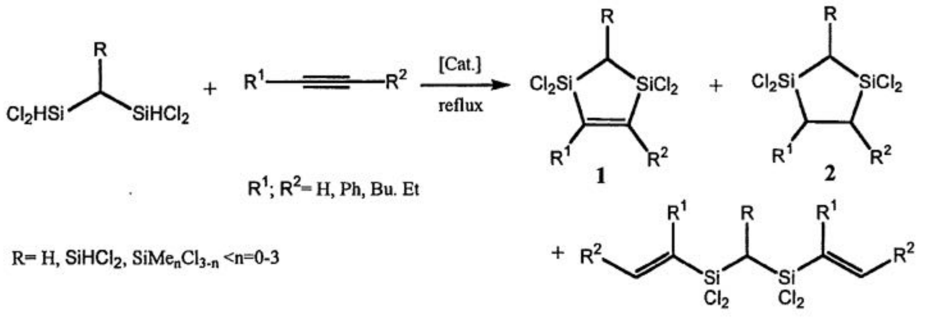
Daniel J. Harrison, Catrin E. Hughes, Danielle N. Kobus, Lisa Rosenberg
Department of Chemistry, University of Victoria, P.O.Box 3065, Victoria, BC, Canada, V8W 3V6

Our interest in probing the relationship of chain conformation to electronic and optical properties of polysilanes has led us to explore new routes to functionalized oligosilanes and methods for their structural modification. We have been using Wilkinson's catalyst, $(Ph_3P)_3RhCl$, in the synthetic scale preparation of Si-H functionalized di- and trisilanes via dehydrogenative coupling of secondary silanes. We have found that chemoselectivity in these reactions is extremely sensitive to the rate of hydrogen gas removal, a feature not observed in the analogous dehydrocoupling reactions catalyzed by Group 4 metallocenes. The Rh-catalyzed dehydrocoupling of primary alkyl silanes also shows a sensitivity to $H_2(g)$ concentrations, which may allow us to control chain length distributions in the product oligomers. Our recent studies have focused on optimizing these reactions to provide useful quantities of Si-H functionalized oligomers, and on establishing key intermediates in this Rh(I)-mediated catalysis. We have also begun to study the reactivity of Si-H bonds in our product oligosilanes, and in polyphenylsilane (prepared by dehydrocoupling of phenylsilane using Zr-based catalysts). Preliminary results suggest that Lewis acid-catalyzed hydrosilation (of aldehydes, ketones or thioketones) or heterodehydrocoupling (with thiols) may allow substitution at Si in these catenated chains, without compromising the Si-Si bonds.

DEHYDROGENATIVE DOUBLE SILYLATION OF ACETYLENES WITH BIS- AND TRIS(DICHLOROSILYL)METHANES*

Son Thanh Phan, Weon Cheol Lim, Joon Soo Han, Bok Ryul Yoo, and **Il Nam Jung**
Organosilicon Chemistry Laboratory, Korea Institute of Science and Technology,
PO Box 131, Cheongryang, Seoul 130- 650, South Korea

The dehydrogenative double silylation reactions of acetylenes with bis- and tris(dichlorosilyl)methanes [1] in the presence of tetrakis(triphenylphosphine)palladium catalyst afford 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes in fair to excellent yields [2]. However, the same reactions using platinum catalysts gave the double hydrosilylation products of 1,3-disilacyclopentanes as the major products. The details of the efficient and high yield synthesis of 1,3-disilacyclopent-4-enes, **1** and 1,3-disilacyclopentanes, **2** will be discussed. The absorption and emission spectra of 1,3-disilacyclopent-4-ene derivatives will be also mentioned.



[1] Yoo, B. R.; Jung, I. N. *Adv. organometal. Chem.* **2004,** *50*, 145.
[2] Phan, T. S.; Lim, W. C.; Han, J. S.; Yoo, B. R.; Jung, I. N. *Organometallics* **2004**, *23*, 169.

- We would like to thank Dow Corning Corporation for the financial support.

POLYMER APPROACHES TO SILICON BASED NANOSTRUCTURED HYBRID MATERIALS

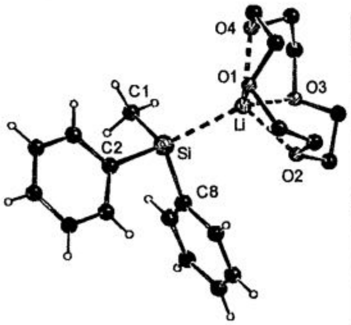
Ulrich Wiesner
Department for Material Science and Engineering, Cornell University,
329 Bard Hall, Ithaca, NY 14853
Phone: (607) 255 3487; Fax: (607) 255 2365
e-mail: ubw1@cornell.edu

The study of polymer based self-assembly ("bottom-up") approaches to multifunctional polymer-inorganic hybrid materials is an exciting emerging research area interfacing solid state and soft materials and offering enormous scientific and technological promise. By choice of the appropriate synthetic polymers as well as silicon based ceramic precursors unprecedented morphology control down to the nanoscale is obtained. Tailoring of the polymer–inorganic interface is of key importance. The structures generated on the nanoscale are a result of a fine balance of competing interactions, a typical feature of complex biological systems. The potential for new multifunctional materials lies in the versatility of the polymer chemistry as well as that of the silicon chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructued hybrid materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. In all cases cooperative self-assembly of organic and inorganic species is induced through amphiphilic macromolecules. Besides amorphous and crystalline oxide materials novel systems toward high temperature SiCN and SiC structures are introduced. Examples will include the preparation of mesoporous materials and superparamagnetic mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis, solid hybrid polymer electrolytes for battery applications, the synthesis of nanoparticles with controlled shape, size, and composition for applications in the life sciences, as well as thin film materials with potential applications in microelectronics and nanobiotechnology.

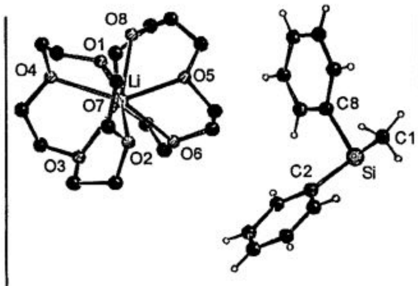
ABOUT THE STEREOCHEMISTRY OF LITHIATED SILANES

C. Strohmann, D. Auer, M. Bindl, J. Hörnig, V. C. Fraaß, D. Schildbach
Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany
E-mail: mail@carsten-strohmann.de

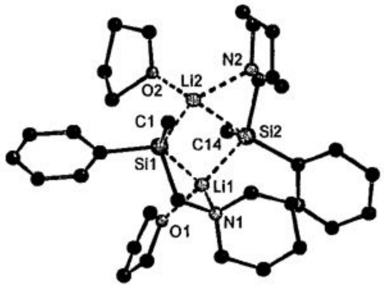
The crystal structures of lithiated silanes – obtained in the presence of coordinating solvents – are dominated by monomeric molecular structures with an Si-Li distance of around 2.65 Å. By the addition of intermolecularly coordinating 12-crown-4, the detachment of the lithium center can be achieved, while an intramolecularly coordinating aminomethyl ligand gives rise to a dimeric molecular structure.



$Ph_2MeSiLi\cdot$12-crown-4

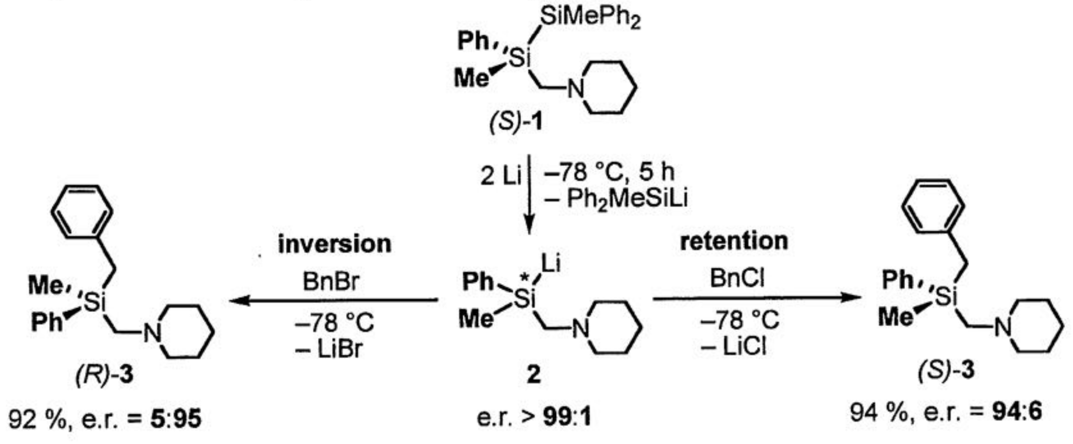


$[Ph_2MeSi]\ [Li\cdot(12\text{-crown-}4)_2]$



$[PhMeSi(Li)CH_2NC_5H_{10})\cdot THF]_2$

These structural aspects of lithiated silanes will be discussed together with the phenomena observed in subsequent reactions and in combination with quantum-chemical studies. If e. g. highly enantiomerically enriched silyllithium compound 2[1,2] is reacted with benzyl halides, an enantiodivergent transformation, controlled by the applied benzyl halide, is observed resulting in the inversion (benzyl bromide) or the retention of configuration (benzyl chloride) at the stereogenic silicon center [based on disilane *(S)*-**1**].[2]



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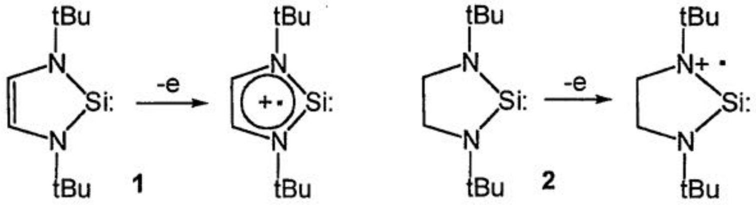
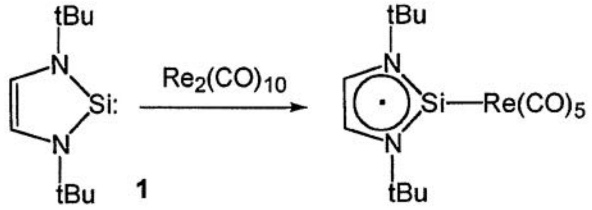
THE RADICAL CHEMISTRY OF STABLE SILYLENES

Robert West,* Daniel F. Moser,* Nicholas J. Hill,* Mikhail P. Egorov,[‡] and Boris Tumanskii[§] *Organosilicon Research Center, University of Wisconsin, 1101 University Ave., Madison, WI 53706 USA; [‡]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia; [§]Department of Chemistry, Technion, Haifa, Israel.

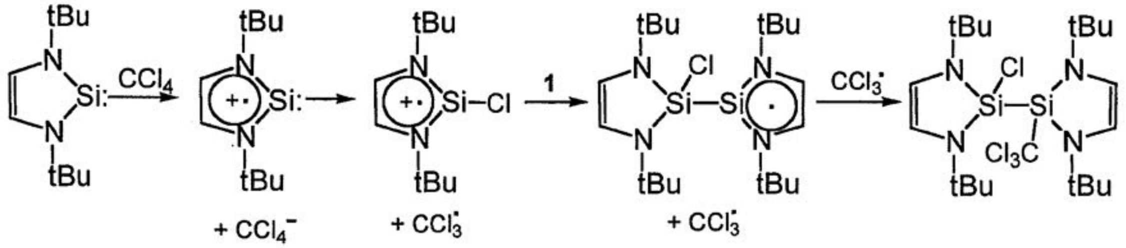
Stable silylenes **1** and **2** can be oxidized electrochemically to cation-radicals. Epr spectra of the radicals show that the unpaired electron in the cation-radical of **2** is localized on one nitrogen atom, whereas in that for **1** it is delocalized over the ring, consistent with the aromatic structure for **1**:



Silylene **1** reacts with free radicals, or radical-generating molecules, to give neutral radicals. An example is shown below for $Re_2(CO)_{10}$. In these radicals also, the unpaired electron is delocalized over the aromatic silylene ring:



Both **1** and **2** undergo an anomalous reaction with halocarbons to give disilanes. These reactions are now believed to take place through single electron transfer and a silylene radical:



Molecular Control of Interface Chemistry by Atomic Layer Deposition (ALD), A Case Study on Novel Gas-solid Interactions of Aminoalkoxysilanes with Silica

Eero Iiskola, Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, P.O.B. 6100, FIN-02015, Espoo, Finland

email: eero.iiskola@hut.fi

Abstract

A recent development in thin film deposition from volative precursors involves Atomic Layer Deposition (ALD), a chemical technique based on gas-solid reactions. ALD is a surface-controlled layer-by-layer deposition process involving alternating, self-limiting surface reactions to achieve controlled and conformal atomic/molecular-level deposition[1-4] on planar/porous substrates. ALD is a novel revolutionary tool in the area of nanotechnology[5].

The self-limiting reaction sequence (i.e., the ALD reaction cycle) does not typically result in monolayer deposition per cycle. Depending upon the size of the reactant and the attached ligands, saturation exposure and reaction of the precursor is most often submonolayer, and thus the resulting deposition layer produced per cycle is typically submonolayer. Hence, multiple cycles are commonly required to deposit a single monolayer.

In the silylation chemistry, the ALD method gives a very reproducible product in one reaction step and, at the same time, eliminates many of the tedious operations that are involved in the alternative "wet" methods[6-8], where the steps are controlled hydrolysis of alkoxysilanes, solvent removal/recovery, and washing procedures.

In our case study, ALD technique is used to manufacture high-density and conformal aminofunctional molecular layers on a high-surface area silica[9]. The precursors are aminoalkoxysilanes (e.g., $H_2N(CH_2)_3Si(OEt)_3$, $H_2N(CH_2)_3SiMe(OEt)_2$, $H_2N(CH_2)_3SiMe_2OMe$, $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$) that can be evaporated without decomposition in vacuum. In the ALD reaction cycle alkoxysilanes provide strong covalent bonding via siloxane groups with the silica surface.

The effect of the reaction/hydrolysis temperature, precursor molecule and the number of ALD reaction/hydrolysis cycles on the surface composition of materials are envisaged by elemental analysis, DRIFT and the solid state ^{13}C and ^{29}Si spectroscopy. It is hoped that the basic scientific understanding of interface phenomena between inorganic and organic materials would create a solid foundation in this new branch of ALD processing.

Gatekeeping Effect: Synthesis of Multi-functionalized Mesoporous Silica Nanosphere Materials as Biosensors, Selective Catalysts, and Stimuli-Responsive Controlled Release Delivery Carriers

Victor S.-Y. Lin

Assistant Professor, Department of Chemistry, Ames, Iowa State University, Iowa 50011-3111, phone: 515-294-3135, fax: 515-294-0105, e-mail: vsylin@iastate.edu

We have recently synthesized a series of multi-functionalized, MCM-41 type mesoporous silica nanosphere (MSN) materials.[1-5] The mesopore surface of these materials was derivatized with fluorescence sensor groups that could recognize and react with amino acid-based neurotransmitters. The exterior surface of the MSN materials was covalently coated with polylactides or polypeptides. By utilizing the polylactide or polypeptide layer as a *gatekeeper* to regulate the rates of diffusion of several structurally similar neurotransmitters, such as dopamine, tyrosine, and glutamic acid, into the sensor mesopores, a highly selective fluorescence biosensor that could distinguish dopamine from glutamic acid under physiological condition was synthesized. The *in vitro* biocompatibility with neurons, astrocytes, and stem cells was also investigated. This type of MSN materials were also designed as a stimuli-responsive controlled release delivery system.[3] Several pharmaceutical drugs and neurotransmitters were encapsulated inside the mesopores of MSN by capping the openings of the mesopores with various *chemically removable caps*, such as surface-derivatized cadmium sulfide (CdS) nanocrystals and cell membrane permeable dendrimers, e.g. polyamidoamine (PAMAM) dendrimer, to block the molecules of interest from leaching out. We studied the stimuli-responsive release profiles of several drug/neurotransmitter-loaded MSN systems by using various non-cytotoxic chemicals as *release triggers*. The biocompatibility and delivery efficiency of the MSN system with various neural cells *in vitro* were investigated. In addition, utilization of these gatekeeper-functionalized MSN materials as selective catalysts will be demonstrated. This research is supported by NSF (CHE-0239570) and DOE-office of BES (W-7405-Eng-82).

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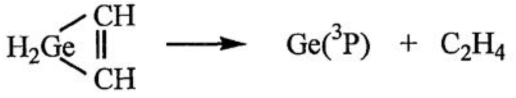
WHAT WE HAVE LEARNED ABOUT THE STABILITIES OF SILIRANE (GERMIRANE) AND SILIRENE (GERMIRENE) THROUGH GAS-PHASE KINETIC AND QUANTUM CHEMICAL STUDIES OF THE REACTIONS OF SIH_2 (GEH_2) WITH ETHYLENE AND ACETYLENE.

by **Rosa Becerra,** *Instituto de Quimica-Fisica 'Rocasolano', C.S.I.C., Madrid, Spain,* **Sergey E. Boganov, Mikhail P. Egorov, Valery I. Faustov, Irina V. Krylova, Oleg M. Nefedov, Vladimir M. Promyslov** *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russian Federation,* and **Robin Walsh**, *School of Chemistry, University of Reading, Whiteknights, Reading, UK.*

The addition of silylene, SiH_2, and germylene, GeH_2 to ethylene and acetylene results in the initial formation of 3-membered ring heterocycles (silirane, silirene, germirane and germirene) just as methylene forms cyclopropane and cyclopropene in the analogous additions. This study will review the findings of gas-phase laser flash photolysis investigations of these systems (including isotopic variants). The studies are all supported by *potential energy surface* calculations not only of the addition process, but also of possible further rearrangements of the heterocycles themselves.

The findings include:

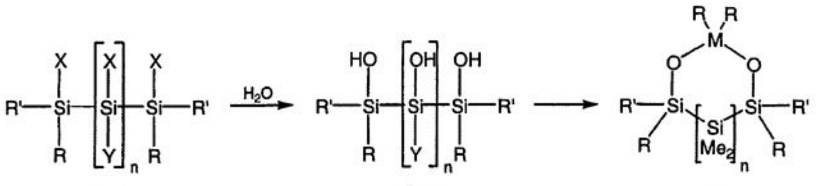
- That, whereas methylene reacts to produce chemically activated rings which isomerise further, the heavy methylenes form the rings in third body assisted association reactions.
- That the heterocycle rings are labile such that they can undergo rapid reversible interconversions with their ring opened alkyl (or alkenyl) heavy carbene isomers (eg silirane to ethylsilylene) under addition conditions.
- Unique amongst this set of heterocycles, germirene has a low energy decomposition pathway:



Novel Polysilanols – Synthesis, Structure And Coordination Chemistry

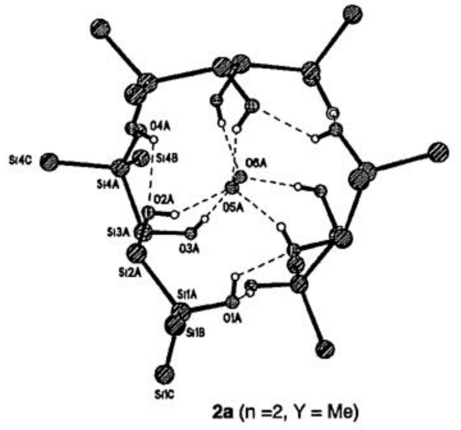
__C. Krempner__, U. Jaeger-Fiedler, H. Reinke, K. Weichert
Dept. of Chemistry, University of Rostock, Einsteinstr. 3a, D-18051, Rostock, Germany

Oligosilanes, molecules with a long backbone of silicon atoms, have been shown to display unusual optoelectronic properties. In context with studies concerning the influence of OR groups (R = H, alkyl, acetyl, silyl) on the electronic properties of the silicon chain, polysilanols **2a-c** have been prepared by careful hydrolysis of well defined precursor compounds such as chloro and acetoxysilanes **1a-c** and their molecular structures have been determined. The molecular structure of tetraol **2a** (scheme) reveals an unusual supramolecular self-assembly of three molecules of **2a** with two molecules of water interacting with each other by effective hydrogen bonds.

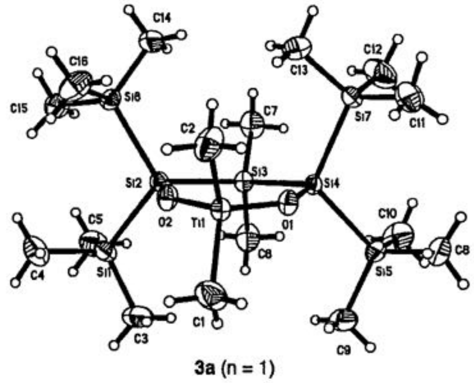


1a-c **2a-c** **3a**

a R = R' = SiMe$_3$, n = 0-2
b R = R' = t.-Bu, n = 0-2
b R = Si(SiMe$_3$)$_3$, R' = Me, n = 0
X = OAc^f, OTf, Cl, Me
Y = OAc^f, OTf, Cl, Me, SiMe$_3$



2a (n =2, Y = Me)



3a (n = 1)

With the aim of exploring the coordination chemistry of this novel class of polysilanol ligands, tridentate and bidentate metalsiloxides (M = Ti, Zr, Ln, Al) have been synthesized and structurally characterized. Their molecular structures and reaction behavior towards organometallic reagents and small organic molecules will be discussed.

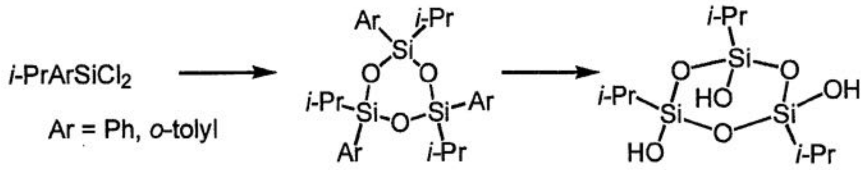
TRIHYDROXYCYCLOTRISILOXANES

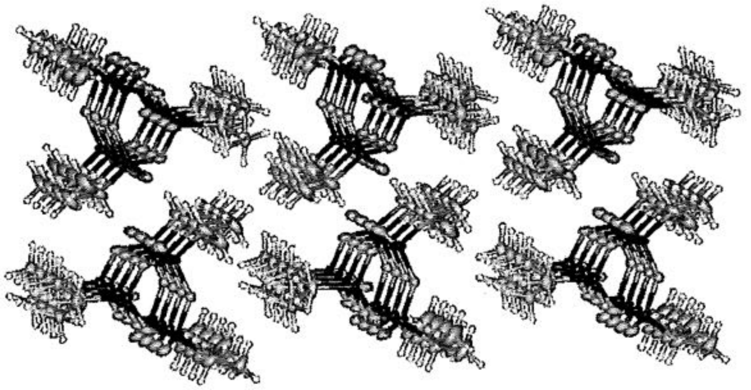
Masafumi Unno, Yukiko Kishimoto, and Hideyuki Matsumoto
Department of Nano-Material Systems, Graduate School of Engineering,
Gunma University, Kiryu, Gunma 376-8515, Japan

Cyclotrisiloxanetriol bearing isopropyl group was prepared by novel dearylchlorination method as the first example of those with small alkyl groups.

Several reports have appeared regarding the preparation of trihydroxycyclotrisiloxanes, however, all compounds demand bulky groups or host molecule, which prohibited further transformation of this intriguing compounds. We have demonstrated the versatility of cyclic silanol, [*i*-PrSi(OH)O]$_4$ as precursors of various siloxanes or supramolecular aggregates.[1] These preceding results prompted us to develop a convenient method for the synthesis of its smaller homologue, 1,3,5-trihydroxycyclotrisiloxane [*i*-PrSi(OH)O]$_3$.

Our tactics towards the synthesis of trihydroxycyclotrisiloxanes includes following two steps as shown in the Scheme. Chlorodearylation and following hydrolysis of cyclotrisiloxanes afforded only *cis,trans*-cyclotrisiloxanetriol selectively regardless of the conformation of starting compounds. The structure of [*i*-PrSi(OH)O]$_3$ was determined crystallographically, and supramolecular form in the crystal was revealed.





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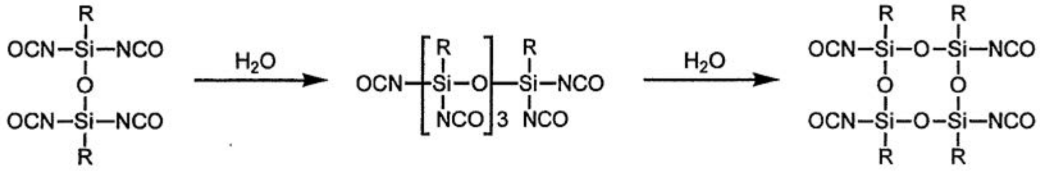
1. a) M. Unno, K. Takada, and H. Matsumoto, *Chem. Lett.*, **1998**, 489; b) M. Unno, A. Suto, K. Takada, and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 215.; c) M. Unno, A. Suto, and H. Matsumoto, *J. Am. Chem. Soc.*, 2002, **124**, 1574; d) M. Unno, K. Takada, and H. Matsumoto, *Chem. Lett.*, **2000**, 242.

Syntheses of Ladder Oligosilsesquioxanes

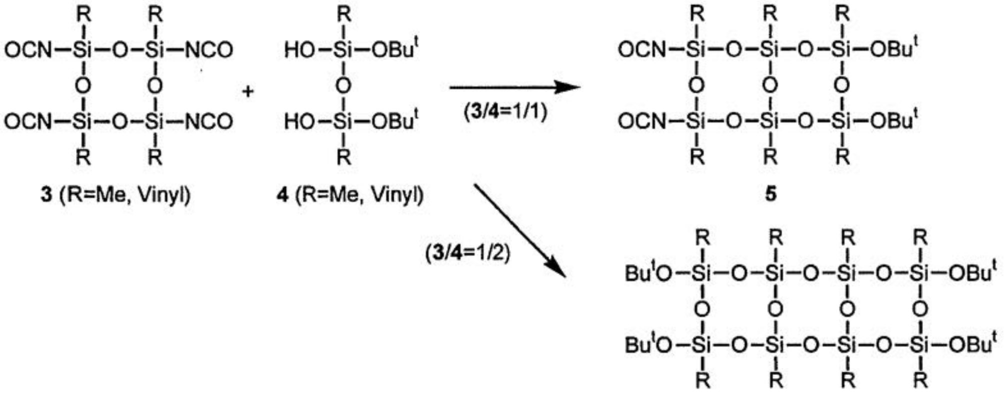
Yoshimoto Abe, Yumi Kadota, Koji Arimitsu, And Takahiro Gunji
Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510 Japan

Ladder-type silsesquioxanes have been noted as mysterious compounds because of their difficulty in synthesis, isolation and characterization. A typical synthetic strategy for phenylpolysilsesquioxane is the hydrolysis of trichloro(phenyl)silane followed by condensation in the presence of potassium hydroxide. However, phenylpolysilsesquioxane thus formed is thought to be an "incomplete" ladder silsesquioxane. The ladder polysilsesquioxane will be prepared by a careful synthesis based on specific chemical reactions to construct siloxane skeleton. In this paper, therefore, the preparation of oligosilsesquioxanes will be reported by a selective condensation reactions of disiloxanes as precursors for ladder-type polysilsesquioxanes.

Cyclic tetraisocyanatotetrasiloxanes (**3**) were prepared by two step reactions by the hydrolysis of 1,1,3,3-tetraisocyanatodisiloxanes (**1**). The hydrolysis of **1** in vapor phase yielded 1,1,3,5,7,7-hexaisocyanatotetrasiloxanes. The hydrolysis of **2** was proceeded to isolate **3** by distillation.



1 (R=Me, Vinyl) **2** **3**



3 (R=Me, Vinyl) **4** (R=Me, Vinyl) **5** **6**

A bicyclic compound (**5**) was prepared by condensation reaction of **3** with an equal molar amount of 1,3-di-*t*-butoxydisiloxane-1,3-diols (**4**). This reaction was specific and quantitative to provide **5**. Similarly, the reaction of **3** with **4** in the molar ratio of **3**/**4**=2/1 in the presence of triethylamine provided a tricyclic compound (**6**).

STEREOREGULAR SILICON-CONTAINING POLYMERS

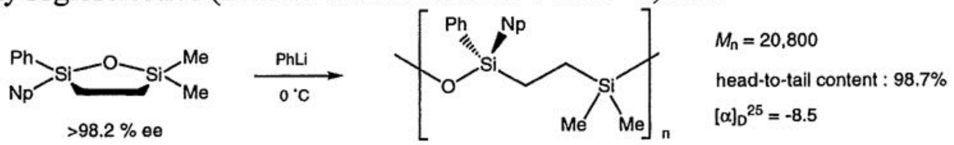
Yusuke KAWAKAMI

Asahidai 1-1, Tatsunokuchi_Ishikawa 9231292_Japan

Stereoregularity of chiral silicon centers of silicon-containing polymers were regulated for poly(carbosilane)s, poly(carbosiloxane)s and polysiloxanes by the use of optically active silicon compounds.

Polyaddition by hydrosilylation of an optically active allylphenylmethylsilane gave isotactic poly[(phenylmethylsilylene)trimethylene]. Ring-opening polymerization (ROP) of 1-methyl-1-(1-naphthyl)-2,3benzosilacyclobute-2-en gave optically pure, almost completely isotactic polymers via regiospecific and stereospecific ROP.

ROP of an optically pure (*S*)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane by phenyllithium gave almost optically pure and highly isotactic poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] ($[\alpha]_D^{25}$ = -8.5, M_n = 20,800 (calculated from ^{29}Si NMR), M_n/M_w = 1.1 (by SEC)) by highly regioselective (head-to-tail content 98.7 % at 0 °C) ROP



Catalytic dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with compounds having labile hydrogen afforded silphenylene-containing polycarbosiloxanes, poly(silyl ether)s, poly(silyl ester)s and polycarbosilazanes of controlled structure. Dehydrocoupling polymerization of optically active pure (*S,S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol with 1,3-dihydro-1,3-dimethyl-1,3-diphenyldisiloxane [(*R,R*) : (*S,R*) : (*S,S*) = 84 : 16 : 0] at 60 °C in the presence of [RhCl(cod)$_2$] (5.0 mol%) and triethylamine (1.0 equivalent) gave poly(methylphenylsiloxane). Assignment of the triad signals of the resulting poly(methylphenylsiloxane) by ^{1}H NMR of methyl protons (I = 0.04, H = 0.09, and S = 0.14 ppm) was established, and the triad tacticity was accurately evaluated by ^{13}C NMR of *ipso* carbon of phenyl group (S = 136.7, H = 136.9, and I = 137.1 ppm) to be $S : H : I$ = 60 : 32 : 8.

SILYLATION OF LOW-DENSITY SILICA AND BRIDGED POLYSILSESQUIOXANE AEROGELS

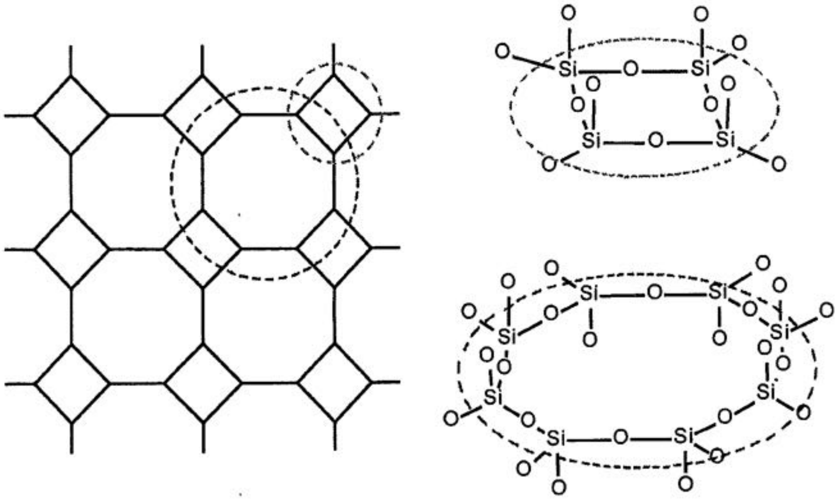
Kimberly A. DeFriend, Douglas A. Loy, Kenneth V. Salazar and Kennard V. Wilson, Jr.
Los Alamos National Laboratory
Polymers and Coatings Group, MST-7
Materials Science and Technology Division
Los Alamos, NM 87545

Silica and bridged polysilsesquioxane aerogels are low-density materials that are attractive for applications such as thermal insulation, porous separation media or catalyst supports, adsorbents, and cometary dust capture agents. However, aerogels are notoriously weak and brittle making it difficult to handle and machine monoliths into desired forms. This complication prevents the development of many applications that would otherwise benefit from the use of the low-density materials. Here, we will describe our efforts to chemically modify and mechanically enhance silica-based aerogels using chemical vapor techniques *without* sacrificing their characteristic low densities. Monolithic silica and organic-bridged polysilsesquioxane aerogels were prepared by sol-gel polymerization of the respective methoxysilane monomers followed by supercritical carbon dioxide drying of the gels. Then the gels were reactively modified with silylating agents to demonstrate the viability of CVD modification of aerogels, and to determine the effects of silylation of surface silanols on the morphology, surface area, and mechanical properties of the resulting aerogels.

NEW ORGANOSILION SHEET POLYMERS

M.A.Boucher[1,2], D.E.Katsoulis[3], M.E.Kenney[1].
[1]Department of Chemistry, Case Western Reserve University, Cleveland OH, 44106-7078; [2]Currently at the Department of Chemistry and Biochemistry, Denison University, Granville OH, 43023-0514; [3]Resins and Inorganics, Dow Corning Corporation, Midland, MI 48686-0994.

The synthesis and characterization of a series of monopendent group organosilicon sheet polymers from the naturally occurring mineral apophyllite, $KCa_4Si_8O_{20}$(F,OH)_8H_2O, was carried out. In this series the pendent siloxy groups were $C_nH_{2n+1}(CH_3)_3SiO$ (n = 1,4,6,10 or 18). The intersheet spacings were determined by X-ray powder diffraction, and were found to correlate with the pendent group chain length. Multiple pendent-group polymers were also synthesized where a short polar chain, such as $(NCC_3H_6)(CH_3)_2SiO$, was grafted on the backbone in conjunction with a long chain. One such a polymer is $[((n\text{-}C_{18}H_{37})(CH_3)_3SiO)_x((NCC_3H_6)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A--$ODM_2$-$CM_2$. These sheet polymers formed gels with both polar and non-polar solvents. The sheets in these gels were well separated (as determined by X-ray powder diffraction). The index of refraction of the sheet polymers was determined by measuring the index of refraction of the gels they formed and noting the degree of transparency of the gels, From the results of this study, it is clear that polymers with a given index of refraction can be made by proper choice of the pendent groups.

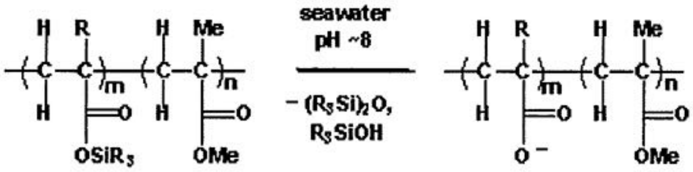


Silicate backbone in apophyllite, $KCa_4Si_8O_{20}$(F,OH)_8H_2O

DEVELOPMENTAL AND SYNTHETIC CHALLENGES IN TRIORGANOSILYL-BASED MARINE ANTIFOULANT COATINGS –HIGH THROUGHPUT APPROACHES

Mark A. Aubart, Michael B. Abrams, Rob T. Boaron*, Marisa Hull, Dana Kobeda, David Mountz, Ron Siebenlist*, Gary S. Silverman, Scot A. Swan, Kenneth Tseng
Atofina Chemicals, Inc., 900 First Avenue, King of Prussia, PA 19406 and *Atofina Vlissingen B.V., Haven 9850, 4389 PD Vlissingen Oost, Netherlands

Triorganosilyl (meth)acrylate-based polymers have been developed as environmentally friendly alternatives to triorganotin-based binders in marine antifoulant paints. These paints rely on the seawater-induced erosion behavior of polymeric binders (see example below) to control the release of added biocides. This paper focuses on two challenging areas of the commercial development of such products: basic product development and monomer synthesis. Initially, identification of silyl monomers and polymers that effectively balance chemical reactivity and macroscopic physical properties in the final polymer film will be discussed. In the second (and main) area of focus, the dehydrogenative coupling of triorganosilanes to unsaturated carboxylic acids will be presented as an economical route to key silyl monomers. The use of high throughput, parallel synthetic techniques as a tool to realize these goals will be a common theme.



Preparation of C_{60}-polysiloxane Hybrids Materials

Takahiro Gunji*, Yosuke Sakai*, Koji Arimitsu*, Yoshimoto Abe*, and Robert West**
*Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510 Japan
**Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison, WI 57306-1396 USA

Since the discovery of the preparative-scale isolation of buckminsterfullerene (C_{60}), C_{60} has attracted many scientists because of its beautiful and symmetrical shape. It is well known as a new material with unique electrical and optical properties such as an optical limiter. The low solubility of C_{60} in common organic and polar solvents, however, provides a formidable obstacle on the application as an advanced material. In this paper, we will paper, we will report a convenient hydrosilylation of C_{60} with sila-functional silanes by using platinum catalyst to obtain C_{60}-polysiloxane hybrids with aim to develop a new approach for the fabrication of C_{60} containing novel materials.

Hydrogen hexachloroplatinate (IV) was dissolved in a mixture of toluene and small amount of ethanol, and then anhydrous calcium sulfate was added. After stirring for 6 h, calcium sulfate was filtered. Into this solution, C_{60} and triethoxysilane were added and then stirred at room temperature for 4 days. Solid materials were filtered and toluene was evaporated under reduced pressure. The residue was added diethyl ether and the insoluble solid was filtered. Silylated C_{60} was obtained by evaporating diethyl ether from the filtrate.

An ethanol solution of silylated C_{60} and silanol terminated polydimethylsiloxane (STPDS, M_n=400-700) was subjected to reflux for 8 h. The mixture was poured into a schale, made of polymethylpentene, and aged in an electrical furnace at 100 °C or 150 °C for a certain period to provide C_{60}-polysiloxane hybrid gel film.

Into a mixture of silylated C_{60}, tetraethoxysilane (TEOS), ethanol, and hydrochloric acid was added and then stirred for 1 day. The hydrolyzate was subjected to dip-coating on various substrates and aged in an electrical furnace at 80 °C for a certain period to provide C_{60}-polysiloxane hybrid coating films.

Silylated C_{60} was isolated as a brown pasty liquid in the yield of 30 %. The formula was estimated to be $H_3C_{60}[Si(OEt)_3]_3$ due to the peak at $m / z = 1213$ (M + 1) by means of FAB mass analysis.

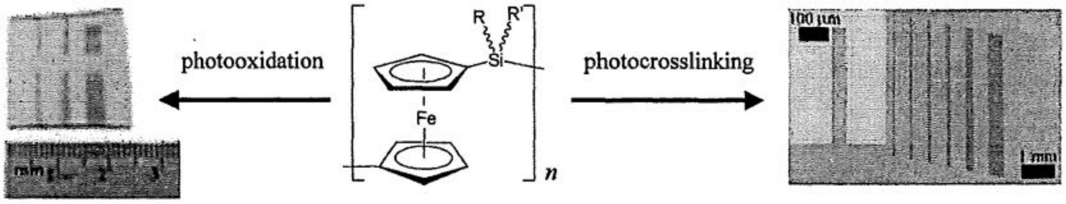
Transparent and homogeneous C_{60}-polysiloxane hybrid gel films, which were colored in light brown and rubber-like, were obtained by aging the ethanol solution of silylated C_{60} and STPDS in the molar ratios of $Si / C_{60} = 500$ and 1000 for 19 days in the presence of dibutyltin(IV)dilaurate as a catalyst.

C_{60}-polysiloxane hybrid coating films were prepared by aging for 1 day. The pencil hardness and adhesive strength, which were evaluated based on JIS K5400 protocol, were 8H and 8 point, respectively. When heating time was increased to 7 days, pencil hardness and adhesive strength were increased to 9H and 10 point, respectively.

PHOTOCONTROL OF POLYFERROCENYLSILANES

Paul W. Cyr,[*,†] Edward H. Sargent[†] and Ian Manners[*]
[*] Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada.
[†] Edward S. Rogers Sr. Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario M5S 3G4, Canada.

Metal-containing polymers are of considerable interest in materials science. The presence of metal atoms in macromolecules can be used to impart unique electrical, optical or magnetic properties, as well as to provide a functionality that can be chemically modified.[1] Polyferrocenylsilanes (PFSs, see figure) represent a class of organometallic polymers that have been successfully demonstrated as materials exhibiting promising utility in a number of applications.[2] The presence of the ferrocene unit in the main chain of PFSs provides an electrically and optically addressable unit in the polymer. Recent work from this laboratory has demonstrated the potential for the use of light to modify the properties of PFSs. A photooxidation method has been developed which can be used to controllably alter the conductivity of PFS films by several orders of magnitude and to prepare photoconducting materials.[3] This method thus allows the photopatterning of conductive PFS materials. In addition, photolithography of PFS derivatives over several length scales has been achieved, allowing the spatial deposition of crosslinked metallopolymer networks.[4]



PFS

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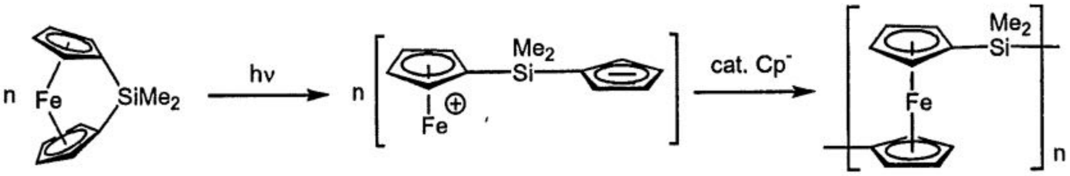
PHOTOCHEMICALLY-INDUCED RING-OPENING POLYMERIZATION OF SILA[1]FERROCENOPHANES

Makoto Tanabe, Sara C. Bourke, and Ian Manners
Department of Chemistry, University 'of Toronto, 80 St. George Street, Toronto, Ontario Canada M5S 3H6

Thermal, anionic, and transition metal-catalyzed ring-opening polymerizations (ROP) of sila[1]ferrocenophanes have been investigated extensively.[1] The mechanisms for these ROP routes have also been studied in detail. All polymerization routes to date involve the cleavage of the Si-Cp$_{ipso}$ bond of sila[1]ferrocenophane. However, highly strained, boron-bridged ferrocenophanes have been reported to undergo ring-opening reaction by the insertion of iron or cobalt fragments into the Fe–Cp bond.[2] The photoinduced polymerization of sila[1]ferrocenophanes using cyclopentadienyl anion as an initiator affords high molecular weight polymers on irradiation with UV-Vis light. The mechanism for new polymerization route is proposed to proceed via Fe–Cp bond cleavage.



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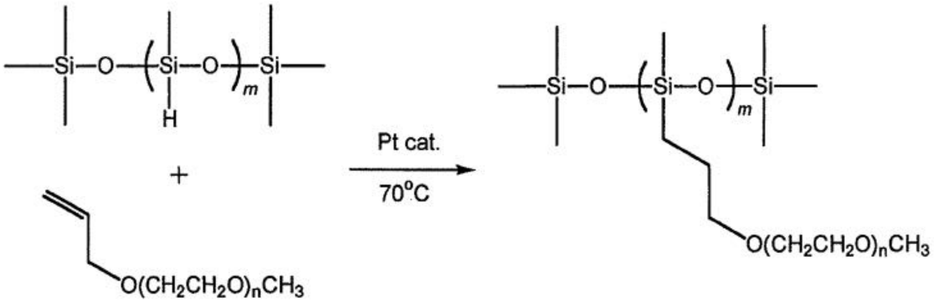
LIQUID SILOXANE COPOLYMERS FOR APPLICATION IN HIGH ENERGY DENSITY LITHIUM BATTERIES

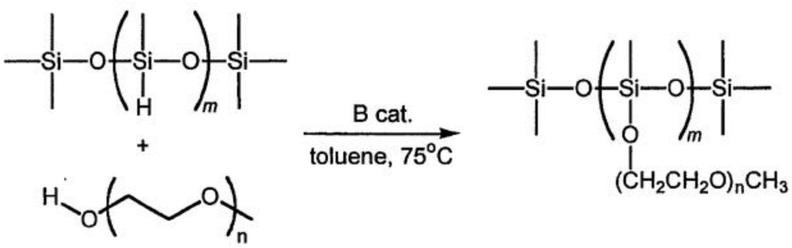
Nicholas A.A. Rossi, Zhengcheng Zhang, and Robert West
Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison, WI 53706, USA
e-mail: rossi@chem.wisc.edu

We have recently investigated polyethylene oxide (PEO) based liquid polymer electrolytes for application in lithium batteries. Because PEO is a highly crystalline material at room temperature, recent research has focused on the combination of PEO with more flexible, amorphous polymers. Polysiloxanes are highly flexible polymers with low glass transitions. Therefore, we have synthesized PEO-siloxane copolymers via two routes: 1) hydrosilation and 2) dehydrogenative coupling. Our aim is to achieve low viscosity polymer electrolytes with conductivites of over 1 x 10^{-3} Scm^{-1} for commercial application. To this end, we have synthesized pure copolymers of varied lengths, compositions, and structures in order to determine the most suitable candidates.

1) hydrosilation:



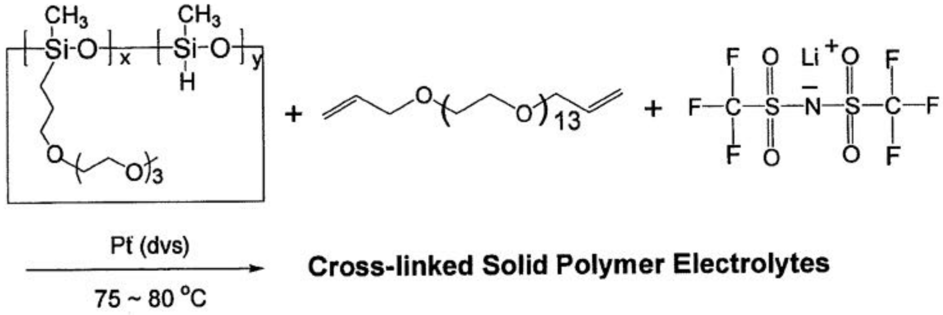
2) dehydrocoupling reaction



NOVEL NETWORK-TYPE POLYMER ELECTROLYTES BASED ON OLIGOETHYLENEOXY-FUNCTIONALIZED CYCLOPENTASILOXANES FOR USE IN LITHIUM POLYMER BATTERIES

Zhengcheng Zhang [1], Leslie J. Lyons [2], Khalil Amine [3] and Robert West [1]
[1] Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, 1101 Univ. Ave., Madison, WI 53706
[2] Department of Chemistry, Grinnell College, Grinnell, IA 50112
[3] Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

A new class of polymer electrolytes has been synthesized by partial hydrosilylation of pentamethylcyclopentasiloxane (D_5^H) by oligo(oxyethylene) methyl ether side chains, followed by cross-linking with an _,_-diallyl poly(ethylene glycol) cross-linker. The ionic conductivities of these cross-linked network polymers were measured by the AC impedance method after doping with $LiN(CF_3SO_2)_2$. The maximum conductivity _$_{RT}$ =5.48x10^{-5} S/cm occurred for the network with low cross-linking density at a doping level of EO/Li$^+$ =28:1 and increased to 1.14x10^{-4} S/cm at 37 °C. The variable temperature conductivities of the cross-linked network electrolytes followed the VTF equation, indicating that polymer segmental motion assists the ion transport.



IMPACT OF BLOWING AGENTS ON SILICONE SURFACTANT SELECTION FOR THE STABILIZATION OF RIGID POLYURETHANE (PUR) AND POLYISOCYANURATE (PIR) FOAMS

Kenrick M. Lewis
GE Silicones – OSi Specialties, 771 Old Sawmill River Rd, Tarrytown, NY 10591

The 1987 Montreal Protocol and its subsequent amendments, Federal legislation and Department of Energy regulations have all combined to effect mandatory elimination of chlorofluorocarbons (CFC's) from rigid PUR and PIR foam formulations and to establish a timetable for the substitution of alternate blowing agents. These regulations have also necessitated changes in the raw materials and additives used to manufacture the foams. Silicone surfactants are essential additives in the manufacture of rigid foams. Among other properties, they influence compatibilization of raw materials, flowability, thermal insulation and compressive strength. This presentation will show how the mandatory changes in blowing agent use have engendered the development of new silicone surfactants to yield foams, blown with reduced CFC-11 levels and alternate blowing agents, which satisfy industry performance criteria and government regulatory standards.

NOVEL HYDROGEN ELECTRODE ON THE ELECTROSYNTHESIS OF HIGH YIELD SILANE OLIGOMERS

Xinwei Wang, Youxin Yuan, and Israel Cabasso
The Michael Szwarc Polymer Research Institute and Department of Chemistry,
State University of New York - ESF, Syracuse, New York 13210

Silane oligomers and polymers are preferably used as the binding precursor for silicarbide ceramics.[1] Electrosynthesis of the silane oligomers using a sacrificial anode, such as Al, Mg, Cu and Ag, has been investigated extensively since it was discovered by Hengge.[2] However, these anodes are either expensive or suffer from severe passivation during electrolysis. Hydrogen electrode formed by using Pt-coated porous graphite rod can be applied in electrosynthesis of silane oligomers,[3] but at low efficiency due to the poor dispersion of hydrogen. We wish to report here of a novel design of a hydrogen electrode. This hydrogen electrode consists of three layers, the bottom fine frit glass layer that creates even hydrogen dispersion, the electrical conductive transitional carbon layer, and the highly dispersed Pt/C catalyst top layer containing 0.12 – 0.35 mg/cm^2 of Pt.

Electrolysis of $MePhSiCl_2$ was conducted in a THF/HMPA(1/1, v/v)/$Bu_4N^+{\bullet}ClO_4^-$ electrolyte. A series of oligosilane $H\text{-}[MePhSi]_n\text{-}H$ ($n = 2 – 7$) were obtained at high yield as identified by GC-MS, and a moderate yield (~12% current efficiency) of polysilane with M_n ~ 6800 g/mol was also isolated. The yield and composition of oligomers can be controlled by adjusting the Pt loading, monomer concentration, current density, and electricity passing through the electrolysis cell. With an increase in Pt loadings, the fractions of oligomers with $n \geq 3$ increase. The formation of large oligomers ($n \geq 3$) and polymers was also favorable at the high monomer concentration (1.25 mol/L) and the low current density (1.0 mA/cm^2). Figure 1 indicates that as the more electricity is consumed, the formation of oligomer (n= 2-8) increases rapidly until 1.4F/mol of electricity is completed, after which polymer formation became significant.

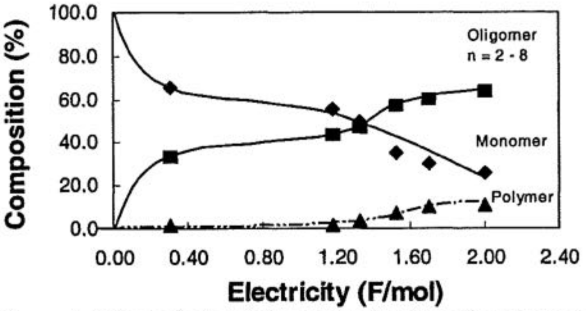


Figure 1. Effect of electricity on the fraction of monomer, and the yield of oligomers $-[SiMePh]_n-$ and polymer. Electropolymerization conditions: Pt loading of H_2 electrode 0.12 mg/cm^2, current density 6.25 mA/cm^2, 1.0 mol/L of $MePhSiCl_2$. During the electrolysis, samples were removed at various time, reduced with $LiAlH_4$, and analyzed with GC-MS and GPC.

Acknowledgement: This project is financially supported by Dow Corning.

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Pt-SILICONES RESERVOIRS AND THEIR APPLICATIONS IN HYDROSILYLATION CATALYSIS

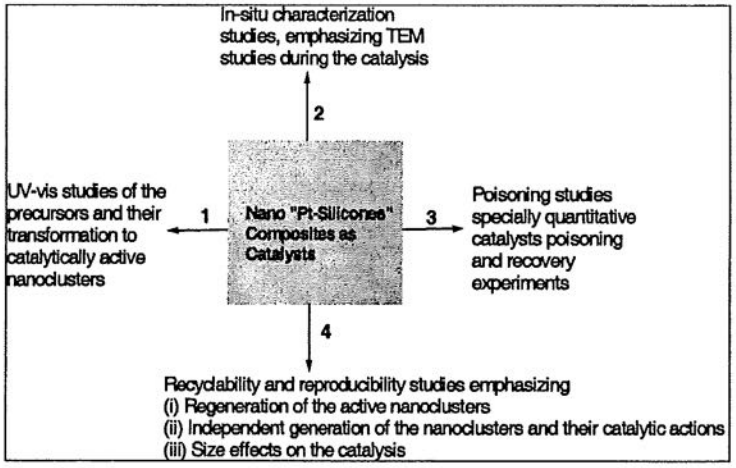
Bhanu P. S. Chauhan

Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry and Graduate Center, City University of New York at The College of Staten Island, 2800, Victory Boulevard, Staten Island, New York 10314

Nanosized metal particles are effective catalysts for chemical transformations because of their large surface areas. Since metal nanoparticles tend to lose reactivity as they precipitate or aggregate, stabilizers such as polymers, ligands or surfactants are used in these preparations to prevent agglomeration and to control the particle size. This process may result, however, in strong adsorption of the stabilizers on the active sites of the metal nanoparticles, leading to a loss of catalytic activity. Hence, there is a need for new nanoparticle technologies that provide the improved protection with minimal surface deactivation.

In this presentation, we will report synthesis and characterization of polysiloxane encapsulated Pt-nanoparticles and their applications to hydrosilylation catalysis. These materials are prepared by sequestering metal ions with hydropolysiloxanes followed by chemical reduction to yield the corresponding zerovalent metal nanoparticles. We will demonstrate that our method enables routine formation of stable nanometallic reservoirs in organic solvents avoiding particle aggregation during the storage as well as nucleation and growth process.[1,2] Catalytic activity of such nanoparticles will be discussed in detail.

A problem that has caused considerable consternation in the study of nanocluster catalysis is the difficult task of distinguishing homogeneous, single-metal-complex catalysts from soluble nanocluster or colloid (vide supra) catalysts. The literature in this area dates back to about 1980 and includes contributions from Maitlis, Whitesides, Crabtree, Collman, Lewis and Finke. In the present catalysis, studies as outlined in Figure were performed to critically investigate the catalytic action of "Pt-siloxane nanoconjugates".



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CROSS-LINKED SILICON BASED POLYMER NANOWIRE FORMATION BY HIGH ENERGY CHARGED PARTICLES

S. Tsukuda,[1] S. Seki,[1] S. Tagawa,[1] M. Sugimoto,[2] K. Jimbo,[3] and A. Kohyama[3]

ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka,[1] JAERI Takasaki, 1233
Watanuki, Takasaki, Gumma,[2] and IAE, Kyoto University, Uji, Kyoto,[3] Japan

In recent years, the effects of deposited energy density on chemical products in solid polymer have been examined, and the difference in the types of radiation-induced reactions has been ascribed to a variation in the density of reactive intermediates. The spatial distribution of energy deposited by charged particles plays a significant role in promoting chemical reactions in target materials. However, the detailed mechanisms of chemical reactions promoted by the incident particle track in polymeric materials have not yet received significant attention. In polysilane derivatives, the dominant reaction has reported to be a cross-linking reaction to give a nano-gel in the chemical core, whereas main-chain scission occurs outside of the core area.[1-3] The size (length and thickness) and number density of the nano-wires can be controllable by changing the parameters of the incident ion beam and the molecular size of the target polymer, and the selective adhesion and orientation of nano-wires on a substrate is also possible.

Silicon carbide (SiC) fiber, which has high tensile strength and good thermal resistance, is one of the most promising candidates as a reinforcement fiber for used with ceramic matrix composites in high-temperature applications. Generally, SiC fiber is synthesized from polycarbosilane (PCS) as a precursor by melt-spinning, curing, and pyrolysis. SiC fiber has been obtained from polycarbosilane-polyvinylsilane (PCS-PVS) blend polymer by electron beam curing, the fiber has been shown to be very fine and flexible.

Based on the concept of single-track gelation, the present study demonstrates the formation of cross-linked polymer nano-wires with controlled size using polysilanes and a variety of Si-based polymers. The size controllability of the nano-wires is discussed in relation to the efficiency of the cross-linking reaction of the polymer materials.

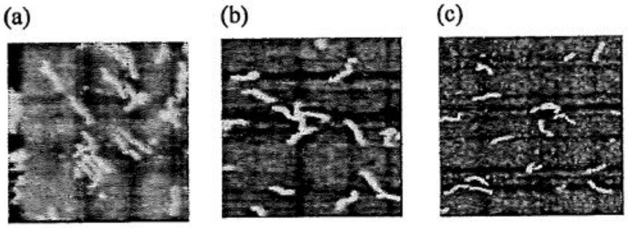

Figure. AFM images of nano-wires showing the variation in size with molecular weight. Nano-wires were formed using Xe ion beam by irradiating poly(methylphenylsilane) with decreasing molecular weight in the order of (a) to (c).

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SILYLATED BIMETALLIC COMPOUNDS AS SINGLE-SOURCE PRECURSORS TO BINARY AND TERNARY METAL CHALCOGENIDE MATERIALS

Iliana Medina, Joel T. Mague, Mark J. Fink
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Group III/VI semiconductors have received much attention due to their possible applications as semiconductors, photoconductors and light emitters. The related ternary and quaternary materials ($CuInS_2$ or $CuGa_yIn_xSe_2$) are of particular interest for solar cells. Recently many researchers have expressed a need for precursor compounds containing both group 13 and group 16 chalcogen in a single molecule, the so-called single-source compounds. Reports on compounds based on silicon-containing ligands are very scarce. We are interested in developing silylated derivatives of compounds containing M_2E_2 (M= Ga, In.; E= S, Se) ring cores as CVD precursors to III/VI materials. These compounds have shown to be well suited for further conversion to the appropriate mixed-metal $MM'E_2$ (M= Cu, Ag; M'= Ga, In; E= S, Se) precursors to ternary materials. We report on the synthetic strategy employed to generate these compounds. Their characterization and thermal properties will also be presented.

HOT FILAMENT CHEMICAL VAPOR DEPOSITION OF ORGANOSILICON AND FLUOROCARBON-ORGANOSILICON THIN FILMS.

Hilton G. Pryce Lewis, Shashi Murthy, Shannan O'Shaughnessy, Michael C. Kwan and Karen K. Gleason*
Department of Chemical Engineering, MIT, Cambridge MA 02139
Email: kkg@mit.edu

Hot-filament chemical vapor deposition (HFCVD) is a one-step, solvent-free method, for producing polymeric thin films by thermal decomposition of a precursor gas. Thermal decomposition is achieved using a resistively heated filament wire, and the radical species generated by this process undergo polymerization reactions to form a film on the cooled surface of a substrate. In comparison to plasma-enhanced CVD, HFCVD produces films with better-defined chemical structures since there are fewer reaction pathways available. Deposition of organosilicon HFCVD films onto room temperature substrates from the precursors hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) occurs at high rates (>1 micron/min) and permits systematic control over the incorporation of cyclic and linear siloxane structures. HFCVD has also successfully deposited copolymer thin films consisting of fluorocarbon and organosilicon groups, where the presence of covalent bonds between the fluorocarbon and organosilicon moieties in the thin films has been confirmed by Infrared, X-Ray Photoelectron (XPS) and solid-state 19F, 13C and 29Si Nuclear Magnetic Resonance (NMR) spectroscopy. Employing an initiator (perfluorooctane sulfonyl fluoride, PFOSF) in the HFCVD polymerization of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V3D3) allows rapid deposition of copolymer films at significantly lower filament temperatures. At low filament temperatures, polymerization is initiated by radical species produced by the pyrolysis of PFOSF followed by chain propagation occurs along the vinyl bonds of V3D3, resulting in chains with hydrocarbon backbones and siloxane rings as pendant groups. Films produced by HFCVD are being investigated as potential biopassivation coatings on neurological implants and process optimization has resulted in flexible conformal HFCVD coatings on fine lead wires. Additionally, fluorocarbon organosilicone HFCVD copolymer films can be modified to facilitate the surface attachment of peptides such as poly-L-lysine and the arginine-glycine-aspartic acid (RGD).

"Acrylic Thermosets: A Green Chemistry Alternative to Formaldehyde-based Resins"

Barry Weinstein
Rohm & Haas

Thermosetting binders are used ubiquitously in composite building and construction materials. The most common thermosetting resins are century-old formaldehyde-based resin systems particularly, phenol-formaldehyde (PF, Bakelite). Unfortunately, the inherent reactivity which makes PF resins excellent binders also makes them hazardous to both the environment and human health.

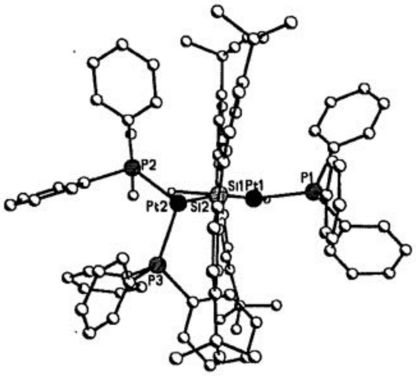
Acrylic thermoset technology offers a green chemistry solution to the myriad of problems associated with formaldehyde-based resins. This patented technology consists of an acrylic polymer based resin with a polyol crosslinker and phosphorous-containing catalyst. Acrylic thermosets are ideal as a green chemistry solution because they are simple, safe and completely remove formaldehyde from the equation. Because the reactivity of the system comes from the catalyst, acrylic thermosets are completely non-toxic and stable at ambient conditions. The only by-product of cure is water generated through a condensation reaction. Used in the place of formaldehyde resin systems, acrylic thermosets offer comparable or superior properties.

Pt-Si MONOMERS, DIMERS, AND TRIMERS

Janet Braddock Wilking, Joyce Corey, Kevin Trankler, Lisa French, Kimberly Dill, and Nigam P. Rath
Department of Chemistry and Biochemistry, University of Missouri-St. Louis
St. Louis, MO 63121

Constrained secondary hydrosilanes such as silafluorene ($H_2SiC_{12}H_8$) and related ring systems [such as $H_2SiC_{12}H_6$-3,6-(t-Bu)$_2$] react with $(Ph_3P)_2Pt(C_2H_4)$ to give stepwise formation of mono-, di- and tri-nuclear Pt-Si containing products. The mononuclear complexes observed, [$P_2Pt(H)SiHR_2$ (**1**) and $P_2Pt(SiHR_2)_2$ (**2**)], were found to be reactive at or above room temperature. The Pt-Si containing monomers then react to form dimers. The dinuclear complexes contain a bridging (Pt···H···Si) unit and a terminal platinum hydride in solution at low temperature. The molecular structure of the dimer $(Ph_3P)_2(H)Pt(\mu\text{-}SiR_2)(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2)Pt(PPh_3)$ [$SiR_2 = H_2SiC_{12}H_6$-3,6-(t-Bu)$_2$ (**3b**)] was confirmed by X-ray crystallography (Figure 1). The differences in the solid state vs. low temperature solution NMR data of (**3b**) will be discussed. With silafluorene, a symmetrical trinuclear complex $[(Ph_3P)Pt(\mu\text{-}SiR_2)]_3$ ($SiR_2 = SiC_{12}H_8$, **4a**) was formed at room temperature possibly from a bimolecular reaction of the unsymmetrical dimer or reaction of a monomer with dimer. Addition of the substituted silafluorene $H_2SiC_{12}H_6$-3,6-(t-Bu)$_2$ to $(Ph_3P)_2Pt(C_2H_4)$ provided a trinuclear complex at elevated temperatures. The sequence leading to the trimer has been probed by reaction of two different dimers as well as addition of a monomer with a dimer. Phosphine and silyl group exchange reactions will also be presented. The implications of the observations will be discussed.

Figure 1. Moleculear structure of $(Ph_3P)_2(H)Pt(\mu\text{-}SiR_2)(\mu\text{-}\eta2\text{-}H\text{-}SiR_2)Pt(PPh_3)$
[$SiR_2 = H_2SiC_{12}H_6$-3,6-(t-Bu)$_2$ (**3b**)]



SYNTHESIS AND STRUCTURE OF 14-ELECTRON DISILENE-PALLADIUM COMPLEX

Mitsuo Kira, Yumiko Sekiguchi, Takeaki Iwamoto, and Chizuko Kabuto
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku,
Sendai 980-8578, Japan. E-mail: mkira@si.chem.tohoku.ac.jp

Considerable attention has been focused on the synthesis and structure of disilene-transition metal complexes. According to the Dewer-Chatt-Duncunson-like consideration, all the known disilene complexes are classified as matallacycles rather than π-complexes, although the π-complex character of the complexes should be sensitive to central transition metals, ligands except the disilene, and substituents on the disilene. We wish herein to report the first 14-electron disilene palladium complex showed a remarkable π-complex character due to the least π-back donation.

Fourteen-electron disilene complex **1** was obtained as red crystals in 85% yield by the reaction of bis(tricyclohexylphosiphine)palladium dichloride with the corresponding 1,2-dilithiodisilane. X-ray crystallographic analysis has shown that **1** is a T-shaped tricoordinate 14-electron palladium complex bent angles around the Si=Si bond (δ) of less than 10 ° and the Si=Si bond length (r) of 2.273 (1) Å (Fig. 1). In comparison of the structural parameters of **1** with those of the corresponding 16-electron complex **2**, δ and r of which were 27.3 ° and 2.3180(8) Å, respectively,[1] complex **1** would be classified as a π-disilene complex rather than a metallacycle due to the least π-back donation among the known disilene complexes.

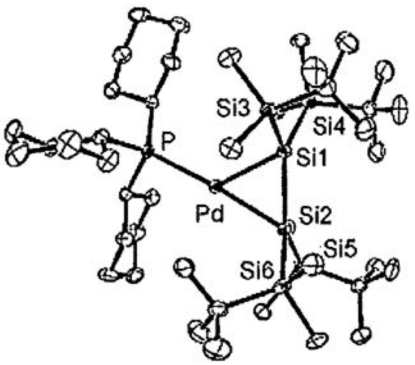
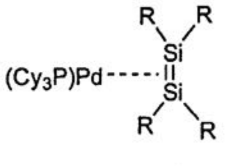
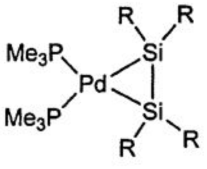


Fig. 1. Molecular structure of **1**.



1



2

Cy = Cyclohexyl
R = *t*-BuMe$_2$Si

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ACTIVATION OF Si-H AND Si-Si BONDS BY PALLADIUM BISPHOSPHINE COMPLEXES: EVIDENCE FOR LONG LIVED σ-COMPLEXES

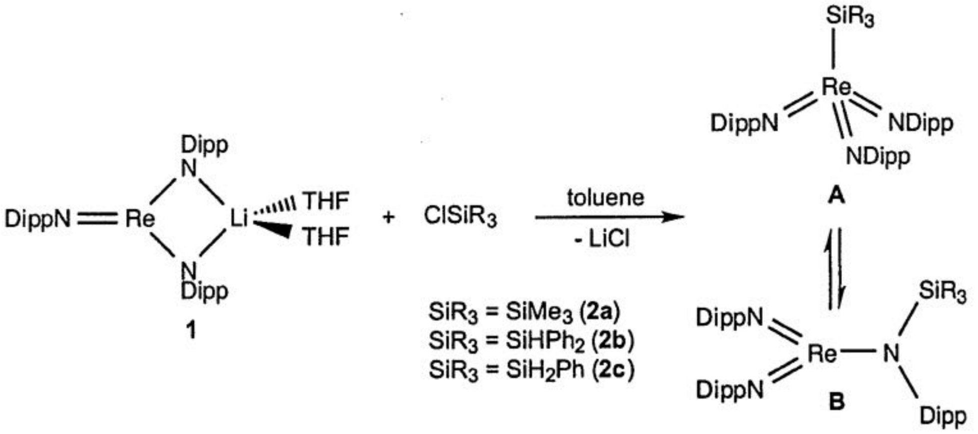
Mark J. Fink, Joel T. Mague, and Robert C. Boyle
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

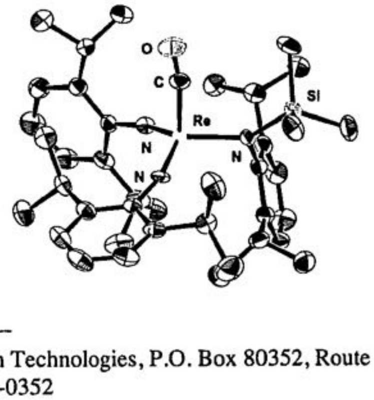
The reaction of tertiary hydrosilanes (R_3SiH) with the zero-valent palladium complex $[Pd(\mu\text{-dcpe})]_2$, gives the novel silyl palladium hydrides $(dcpe)Pd[SiR_3]H$. These complexes undergo both associative and dissociative exchange with free silane, and are fluxional at room temperature. The kinetics and temperature dependent kinetic isotope effects associated with the fluxional process suggest the intermediacy of Si-H σ-complexes. The intermediacy of Si-H σ-complexes is further confirmed by rapid exchange of the palladium hydride with the α-silyl hydrogen in the complex $(dcpe)Pd[Si^tBu_2H]H$. Finally, evidence for the possible existence of the corresponding Si-Si σ-complexes of palladium will be presented.

Synthesis and Reactivity of Tris(imido) Rhenium Complexes Containing Rhenium-Main Group Element Bonds. Silicon-Carbon Bond Activations of $PhSiH_3$ by Silyl Complexes.

John Gavenonis[1] and T. Don Tilley
Department of Chemistry
University of California, Berkeley
Berkeley, California 94720-1460

A series of complexes of the $(DippN{=})_3Re$ (Dipp = 2,6-$^{i}Pr_2C_6H_3$) fragment containing rhenium-main group element bonds are reported. Treatment of $(DippN{=})_3ReCl$ with $(THF)_3LiSi(SiMe_3)_3$ or 2 $^{t}BuLi$ and 4 THF afforded the reduced, Re(V) complex $(THF)_2Li(\mu,\mu\text{-}NDipp)_2Re({=}NDipp)$ (**1**). Compound **1** reacted readily with main group element halides to give complexes with silyl, germyl, stannyl, phosphido, and selenido ligands. The silyl complexes exist in equilibrium between the $(DippN{=})_3ReSiR_3$ (Re(VII), **A**) and $(DippN{=})_2ReN(SiR_3)Dipp$ (Re(V), **B**) isomers (SiR_3 = $SiMe_3$ (**2a**), $SiHPh_2$ (**2b**), SiH_2Ph (**2c**)). Complexes **2a** and **2b** reacted with $PhSiH_3$ to give products arising from Si-C bond activation.





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[1] Current address: DuPont Titanium Technologies, P.O. Box 80352, Route 141 and Henry Clay Road, E352/151, Wilmington, DE 19880-0352

DESIGN AND SYNTHESES OF HETEROGENEOUS CATALYSTS AND CATALYST SUPPORTS DERIVED FROM METAL SILOXIDE MOLECULAR PRECURSORS

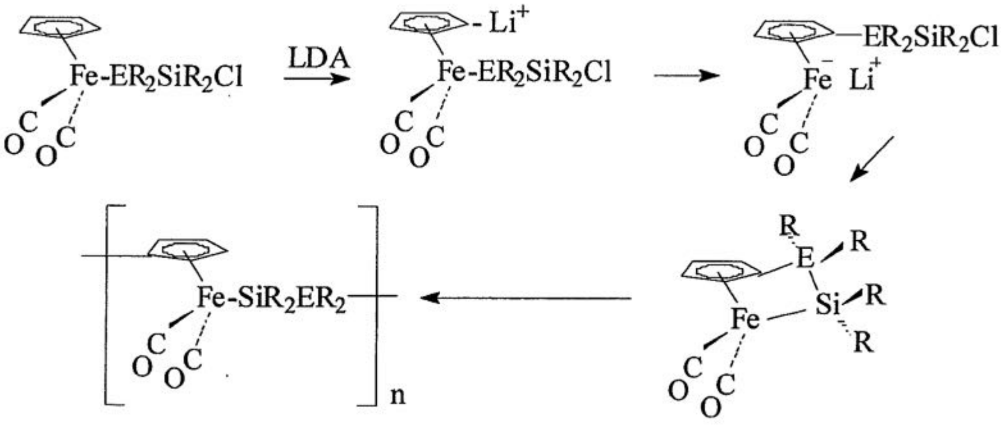
Richard L. Brutchey and T. Don Tilley
Department of Chemistry, University of California, Berkeley, Berkeley, California
94720-1460 and the Chemical Sciences Division, Lawrence Berkeley National
Laboratory, 1 Cyclotron Road, Berkeley, California 94720.

Abstract: Herein we describe the syntheses of transition metal tris(*tert*-butoxy)siloxy complexes of the type $(RO)_nM[OSi(O^tBu)_3]_m$ (where M = Ti, Zr and Ta) and the use of these oxygen-rich ***molecular precursors*** toward the development of molecularly controlled transition metal oxide-silica catalysts and catalyst supports. These molecular precursors can be thermolytically converted to highly dispersed transition metal oxide-silica materials or used to introduce site-isolated metal centers onto the surface of mesoporous silica supports. Several of these materials were shown to be active cyclohexene oxidation catalysts. Additionally, homogeneous hybrid inorganic/organic transition metal oxide-silica materials were obtained via a co-thermolytic route using molecular precursors and $(EtO)_3Si\text{-}R\text{-}Si(OEt)_3$ compounds.

CARBOSILA-, CARBOGERMA-, AND RELATED TRANSITION METALLACYCLES AND THEIR RING OPENED POLYMERS.

Hemant K. Sharma, Paula Apodaca, Francisco Cervantes-Lee and Keith H. Pannell
Department of Chemistry, University of Texas at El Paso, El Paso, TX. 79968, USA.

Thermal, transition metal-catalysed and base-catalysed ring opening of small cycles is a long-standing method for formation of polymeric materials. To obtain transition metal atoms in the backbone of the polymer one needs the formation of relatively rare metallacyclobutane species. [1]-Sila-ferrocenophanes, and their related germa- and stanna- analogs fit this description and have been successfully synthesized and ring-opened to produce a Pandora's Box of interesting polymers and complexes. The cyclopentadienylirondicarbonyl group, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-, can be thought of as containing half a ferrocenyl grouping and we have recently discovered that formation of metallacyclo-butanes and –pentanes can be effected and that furthermore, under suitable conditions they can be ring-opened to form a new class of organometallic polymer containing $(Fe\text{-}Si\text{-}E\text{-}C)_n$ repeating units, E = C, Si, Ge. A typical synthetic routing is noted below.



We acknowledge the support of the Welch Foundation (AH-0546) and the Department of Energy through the USA-Mexico Materials Corridor program.

COMPOSITION-DRIVEN CHIRAL SELECTION IN OPTICALLY ACTIVE POLYALKYLARYLSILANE AGGREGATES

Wenqing Peng and Julian Koe
Department of Chemistry, International Christian University, Tokyo

In our investigation of chiral selection in optically active polyalkylarylsilanes, we have designed a series of polyalkylarylsilane homo- and copolymers bearing substituents in either *para-* or *meta-* positions on the phenyl rings (see Chart 1). Reversal of aggregate chirality of polyalkylarylsilanes is achieved by simple structural modification of an achiral side chain by substitution of an *n*-butyl or 2-methoxyethoxy group in either *para* or *meta* positions of the phenyl rings (see Fig. 1).

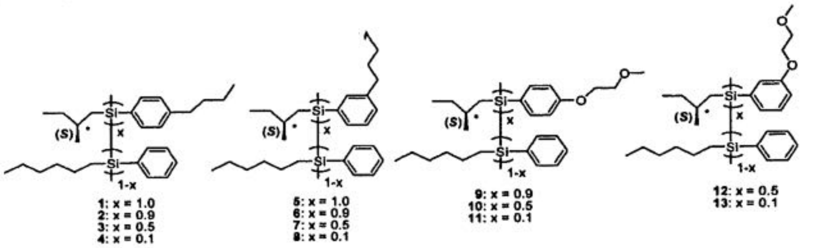


Chart 1. Chemical structures of polysilanes **1-13**

Figure 1. CD spectra of (a) polymer **1** and (b) polymer **2** aggregates prepared at various isooctane/ethanol ratios.

Inversion of aggregate chirality was also achieved by changing the mole ratio of chiral and achiral units. This aggregate chirality inversion depends neither on the positions of the substituents on the phenyl rings (*para-* or *meta-* positions) nor on the properties of the substituents (*n*-butyl or 2-methoxyethoxy group). Only the chirality of polymer **3** aggregates can be switched by solvent effects (THF/MeOH solvent ratios and solvent addition order). These effects may results from the different steric requirements for the achiral side groups, together with the morphology of polysilane aggregates. Further work to understand the mechanism of the chiral selection is continuing.

SYNTHESIS AND PROPERTIES OF PHENYL-SUBSTITUTED OLIGOSILANES WITH WELL-DEFINED STRUCTURES

Ichiro Imae and Yusuke Kawakami
Graduate School of Materials Science,
Japan Advanced Institute of Science and Technology [JAIST]
1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

σ-Conjugated polysilanes have been attracting great attention as a novel class of photo- and electroactive materials.[1] In studying the properties of conjugated polymers, the corresponding oligomers with well-defined structures are often synthesized and their properties are studied related with their chemical structures. More recently, it was found that some of π-conjugated oligomers were not simply studied as model compounds, but even showed superior properties to the corresponding polymers and were applied to photo- and electroactive materials.

Although there are numerous reports on their synthetic methods and some spectroscopic studies of oligosilanes with well-defined structures as model compounds of polysilanes, their electronic properties are little reported. In order to investigate the relationship between the electronic properties of oligosilanes and their chemical structures, we have investigated the band gap energies and oxidation potentials of permethylated oligosilanes which have only σ-electron system and found that they decreased with increasing their chain length.[2]

For the further investigation of the electronic properties of oligosilanes, oligosilanes having phenyl substituents as π-electron system were synthesized and their electronic properties were investigated.

Electronic absorption spectra of α,ω-dimethyloligo(diphenylsilane)s (monomer – heptamer) showed remarkable red-shift with increasing the chain length of the oligosilanes. It was also found that the electrochemical oxidation potentials of these oligosilanes decreased with increasing their chain length by cyclic voltammograms. The ionization potentials estimated by ultraviolet photoemission spectra showed similar trend to the oxidation potentials by cyclic voltammograms.

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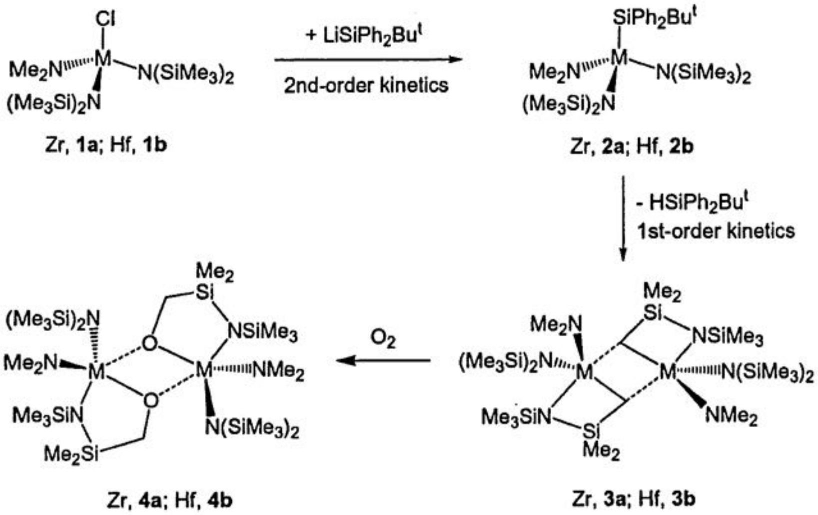
γ-HYDROGEN ABSTRACTION BY SILYL LIGANDS. PREPARATION OF METALLACYCLIC COMPLEXES AND KINETIC STUDIES OF THE REACTIONS

Xiang-Hua (Bruce) Yu, Zi-Ling (Ben) Xue

Department of Chemistry, The University of Tennessee, Knoxville, TN 37996

Reactions of $(Me_2N)M[N(SiMe_3)_2]_2Cl$ (M = Zr, **1a**; Hf, **1b**) with $LiSiPh_2Bu^t$ give unstable silyl complexes $(Me_2N)M[N(SiMe_3)_2]_2[SiPh_2Bu^t]$ (M = Zr, **2a**; Hf, **2b**). The silyl ligands in **2a** and **2b** undergo γ-hydrogen abstraction with $-N(SiMe_3)_2$ ligands yielding four-membered ring metallocyclic complexes **3a** and **3b**. The kinetics of the consecutive reactions to give **3a** has been studied. **3a** and **3b** were also found to react with O_2 to yield the five-membered metallocyclic complexes **4a** and **4b**. These studies will be presented and compared with the kinetic studies of the γ-hydrogen abstraction reaction of Ta silyl amide $(Me_2N)_3Ta[N(SiMe_3)_2](SiPh_2Bu^t)$.

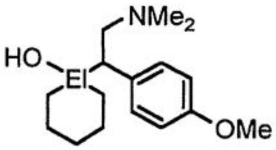


SYNTHESIS AND PHARMACOLOGICAL CHARACTERIZATION OF SILA-VENLAFAXINE, A SILICON ANALOGUE OF THE ANTIDEPRESSANT VENLAFAXINE

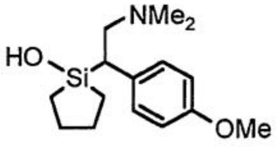
Jürgen O. Daiß,[1] William Bains,[2] Graham A. Showell,[2] Julie Warneck,[2]
and Reinhold Tacke[1]

[1]Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany,
and [2]Amedis Pharmaceuticals Ltd,
162 Cambridge Science Park, Milton Road, Cambridge CB4 0GP, U.K.
E-Mail: r.tacke@mail.uni-wuerzburg.de

In context with our systematic studies on silicon-based drugs (for recent publications, see refs. [1–4]), sila-venlafaxine (**1b**) and its derivatives **2** and **3** were prepared in multistep syntheses, starting from tetrachlorosilane. As the parent carbon compound venlafaxine (**1a**), its sila-analogue **1b** is a potent serotonin/noradrenaline reuptake inhibitor. The syntheses of *rac*-**1b**, (*R*)-**1b**, (*S*)-**1b**, *rac*-**2**, and *rac*-**3** as well as the crystal structure analyses of *rac*-**1b**·HCl, (*R*)-**1b**·HBr, *rac*-**2**, *rac*-**3**, and *rac*-**3**·HCl will be presented. In addition, the pharmacological properties of *rac*-**1a**, *rac*-**1b**, *rac*-**2**, and *rac*-**3** (structure–activity relationships) will be reported.



El = C: **1a**; El = Si: **1b**



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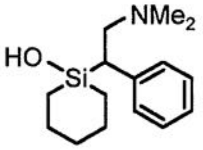

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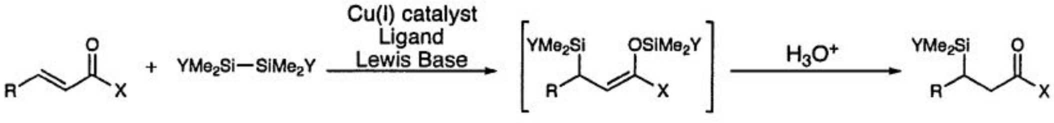
COPPER(I)-CATALYZED DISILYLATION OF ELECTRON-DEFICIENT ALKENES UTILIZING A LEWIS BASE-ACTIVATION STRATEGY

Christopher T. Clark, Karl A. Scheidt
Department of Chemistry
Northwestern University
2145 Sheridan Rd
Evanston, IL 60208

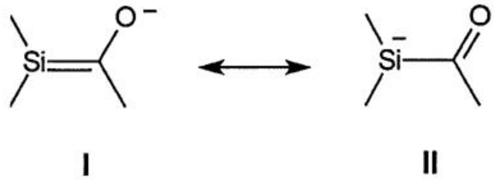
An improved strategy for the disilylation of electron-deficient alkenes has been developed. Lewis base-activated disilanes in the presence of a copper(I) catalyst effect the disilylations of enones, alkylidene malonates, –,––unsaturated amides, and –,––unsaturated acyloxazolidinones. Following acidic hydrolysis, this process yields synthetically useful ––silyl carbonyl compounds in moderate to high yield that can be further transformed to give ––substituted, ––hydroxy carbonyl compounds. The development of this methodology, studies of substrate scope, possible mechanisms, and lead enantioselective results will be discussed.



2-SILENOLATES: HEAVY ENOLATES WITH A POTENTIAL IN STEREOSELECTIVE SYNTHESIS

Arnaud Martel,† Tamaz Guliashvili,† Andreas Fischer,‡ Patrik Akselsson,†
Ibrahim El-Sayed,† and Henrik Ottosson†
† Department of Chemistry (Organic Chemistry), Uppsala University, 751 24 Uppsala, Sweden, and ‡ Department of Chemistry (Inorganic Chemistry), Royal Institute of Technology, 100 44 Stockholm, Sweden.

Recently, we reported the first X-ray structural determination of a 2-silenolate.[1] This is also the first structural characterization of an enolate in which one C atom has been replaced by a heavier group 14 element. As a continuation of this work, we now report the structure of 1-amino-2-silenolates. It was revealed that our potassium 2-silenolates are stable at ambient temperature and that they are mainly described by resonance structure **II** in which negative charge is placed on Si. The Si atom is therefore strongly pyramidal and the SiC bond corresponds to a Si-C single bond.



The pyramidal structure around Si and the separation of Si from K^+ observed in the crystal structures allow us to consider the Si atom as a potential chiral center[2] with only three substituents. In a combined computational and synthetic effort, we now work toward realization of such chiral 2-silenolates.[3,4] The computational study gives us an understanding of how the substituents influence the Si inversion barrier and it allows us to select the most promising targets for our syntheses. The particularly high stability of 1-amino-2-silenolates, and the structural characteristics of the nucleophilic center at silicon, should offer a range of potential applications of these species in synthetic organic chemistry.

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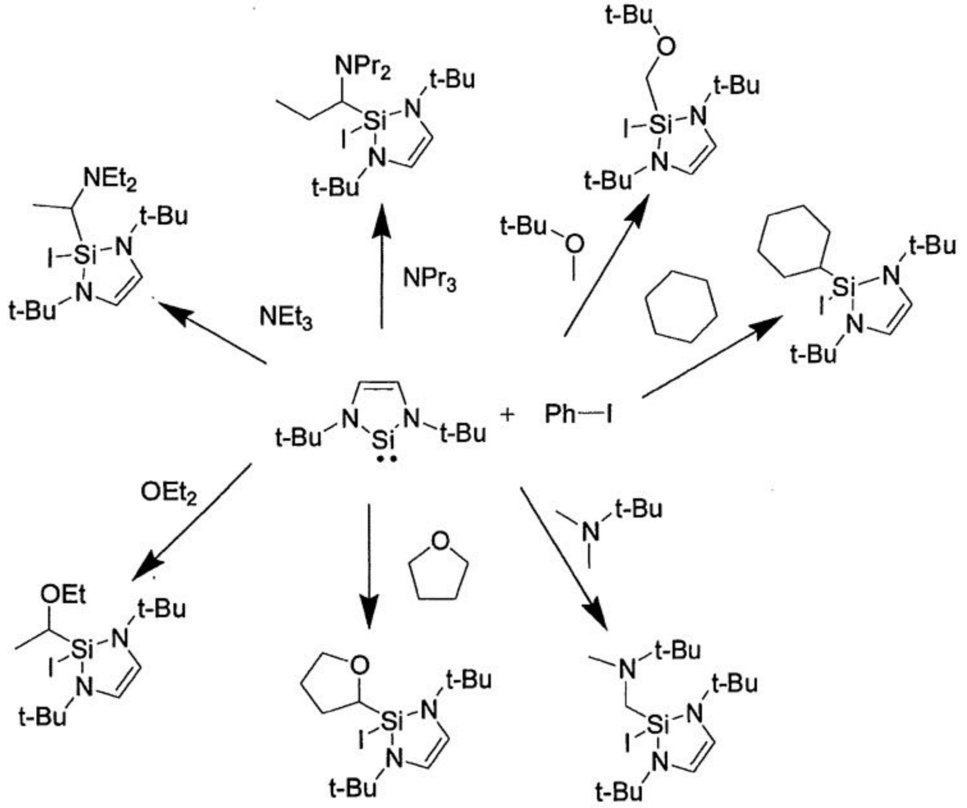
CH-ACTIVATION OF ALKANE, ETHERS, AND AMINES USING A MIXED SILYLENE/ARYL HALIDE REAGENT

Randon H. Walker and Mark M. Banaszak Holl

Chemistry Department, University of Michigan, Ann Arbor, MI 48109-1055

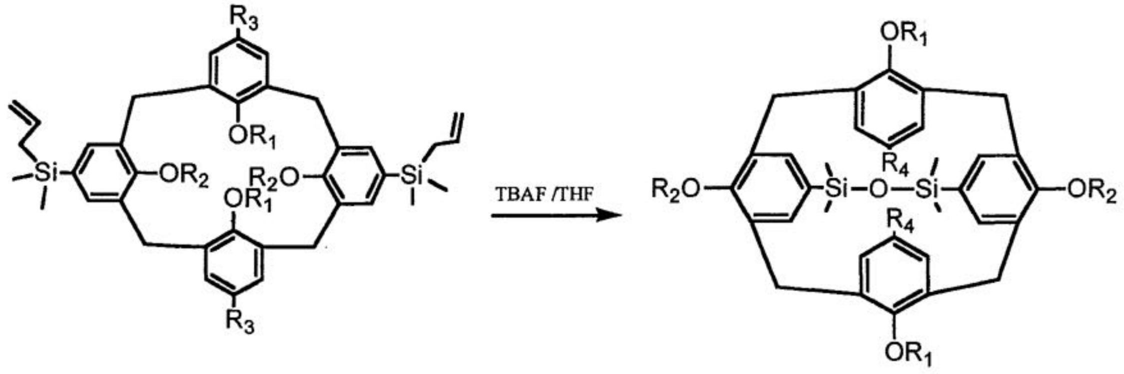
Intermolecular CH-activation of alkanes, ethers, and amines has been achieved using a mixed silylene/aryl halide reagent. The reaction represents a new method for the formation of Si-C bonds. The general reaction, effects of functional groups, and regiochemistry will be discussed. The context of this reaction in terms of other group 14 CH-activations will also be provided.



SYNTHESIS OF CALIX[4]ARENES CONTAINING A DISILOXANE BRIDGE AS POTENTIAL ANIONIC RECEPTORS

Paul F. Hudrlik, Liping Zhang, Wondwossen Arasho, Jaeeock Cho, and Anne M. Hudrlik
Department of Chemistry, Howard University, Washington, DC 20059

Calixarenes are of interest in the preparation of host molecules for molecular recognition. Since silicon can expand its valence shell and form pentacoordinate or hexacoordinate intermediates, calix[4]arenes with silicon substitutents at the upper rim (wide) might be hosts for anionic species. Calix[4]arenes containing a disiloxane bridge across the upper rim were synthesized by treatment of the corresponding bis(allyldimethylsilyl)calix[4]arenes with tetrabutylammonium fluoride in THF. The allyldimethylsilylcalix[4]arene ethers were prepared by halogen–lithium exchange reaction of the corresponding bromo compounds, followed by treatment with allylchlorodimethylsilane/triethylamine. Interesting conformation changes of the upper rim silylated calix[4]arenes will be discussed.



1. R_1 = OMe, R_2 = OBn, R_3 = H
2. R_1 = OPr, R_2 = OPr, R_3 = H
3. R_1 = OPr, R_2 = OPr, R_3 =SiMe$_2$(allyl)

4. R_1 = OMe, R_2 = OBn, R_4 = H
5. R_1 = OPr, R_2 = OPr, R_4 = H
6. R_1 = OPr, R_2 = OPr, R_4 =SiMe$_2$OH

SILOXANE BIOCATALYSIS

Alan R. Bassindale[1], Kurt F. Brandstadt[2], Thomas H. Lane[2], Peter G. Taylor[1]
[1]Department of Chemistry, Open University, Milton Keynes, England
[2]Dow Corning Corporation, Midland, MI 48686

The intricate siliceous architectures of diatom species have inspired our exploration of biosilicification. Although research has progressed in the area of silica biosynthesis, the molecular mechanisms of these interactions are effectively unknown. Since previous studies often failed to recognize the chemistry of silicic acid and its analogues, this model study is believed to be the first rigorous study to demonstrate biocatalysis at silicon. Our data suggests that homologous lipase and protease enzymes catalyze the formation of siloxane bonds under mild conditions. In particular, the active site of bovine pancreatic trypsin, a proteolytic enzyme, was determined to selectively catalyze the *in vitro* condensation of silanols. Conversely, although trypsin would theoretically catalyze of the hydrolysis of a siloxane bond due to the law of microscopic reversibility, the reverse reaction was not favored. Furthermore, trypsin as well as several other proteins and polypeptides promoted the hydrolysis of alkoxysilanes in a non-specific manner.

"Sweet Silicones"
Biocatalytic Reactions to form Organosilicon Carbohydrate Macromers

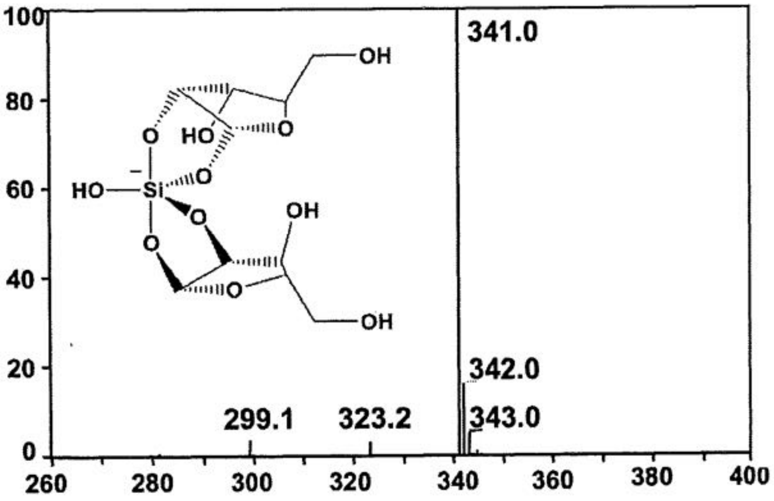
Bishwabhusan Sahoo[1], Kurt F. Brandstadt[2], Thomas H. Lane[2], and Richard A. Gross[1]
[1]Polytechnic University, Brooklyn, New York 11201
[2]Dow Corning Corporation, Midland, Michigan 48686

An enzymatic route for the synthesis of organosilicon carbohydrates was discovered and studied. Immobilized lipase B from *Candida antarctica* (Novozyme 435®) catalyzed the formation of regioselective ester bonds between carboxylic acid-endblocked organosilicones and a C1-O-alkylated sugar under mild reaction conditions (i.e. low temperature, neutral pH, solventless). Specifically, the acid-endblocked organosilicones reacted with the primary hydroxyl group at the C6 position of α,β-ethyl glucoside during the regioselective esterification. The pure organosilicon-sugar conjugates were prepared in a one-step reaction without performing any protection-deprotection steps. It was observed that the lipase-catalyzed reactions did not require activation of the acid groups. In comparison to organic materials, the hydrophobic organosilicon molecules were acceptable substrates. Given the ability to perform selective reactions and maintain the integrity of the siloxane bonds, lipases appear to be useful catalysts in the efficient synthesis of structurally defined organosilicon carbohydrate bioconjugates.

SILICATE COMPLEXES OF SUGARS IN AQUEOUS SOLUTION

Joseph B. Lambert,[1] Gang Lu, [1] and Vera Kolb[2]
[1]Department of Chemistry, Northwestern University, Evanston, IL 60208
[2]Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141

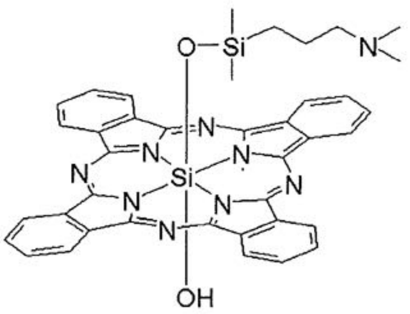
Certain sugars react readily with basic silicic acid to form soluble 2/1 (sugar/silicic acid) silicate complexes. Failure of monohydroxy compounds to give soluble products under these conditions indicates that the sugar silicates are chelates: five-membered diolato rings. Only furanose forms react. Pyranose sugars are stable under these conditions. Because all glycosides fail to react with silicic acid, reaction appears to involve the anomeric position (C1 in aldoses, C2 in ketoses), which has a more acidic hydroxy group. Reaction is completed only when the anomeric hydroxy group is cis to an adjacent hydroxy group. The appropriate furanose form must have sufficient natural abundance and solubility to provide an observable product, as measured by ^{29}Si and ^{13}C NMR spectroscopy. These structural and practical constraints rationalize the successful reaction of the monosaccharides ribose, xylose, lyxose, talose, psicose, fructose, sorbose, and tagatose and the disaccharides lactulose, maltulose, and palatinose. Glucose, mannose, galactose, and sucrose, among others, failed to form complexes. This high selectivity for formation of sugar silicates may have ramifications in prebiotic chemistry.



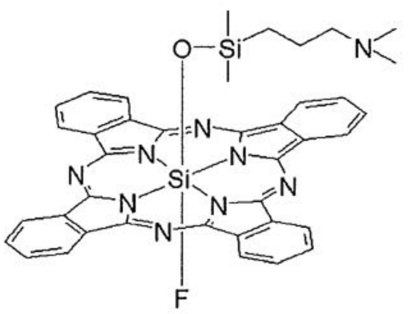
THE ORGANOSILICON DRUG Pc 4 AND ITS FLUORO ANALOGUE, Pc 175

M. Guo and M. E. Kenney
Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106-7078

The organosilicon drug Pc 4 is in a Phase 1 clinical trial for metastatic dermal cancer at University Hospitals of Cleveland. Plans are underway for an additional trial of it at University Hospitals. Because of the interest in Pc 4, additional analogues of it have been made. One is Pc 175, a fluoro analogue. This analogue has been made with Pc 4 as a precursor and also by two simpler approaches. A brief account of the work being done on Pc 4 and of the chemistry of Pc 175 will be given.



Pc 4



Pc 175

Silylated Polyurethane (SPUR^{SM}) Sealants: Property tailoring

Patrice Lehmann, Roy Griswold GE Advanced Materials, Tarrytown, NY

Silane terminated polyurethanes are receiving increased attention in sealant and adhesive applications. Selected organofunctional silanes react with conventional urethane pre-polymers to form silane "endcapped" or silylated polyurethane resins (SPUR^{SM}). At room temperature, in the presence of moisture and an appropriate cure catalyst, the reactive alkoxy silane end-groups of these polyurethanes hydrolyze then condense to form stable siloxane (Si-O-Si) 3-D networks.

This paper considers various approaches to the design of such polymers and formulation of their sealants in order to reach desired sealant properties. Discussed will be conventional polyurethane chemistry, varying pre-polymer composition and synthesis. Additionally, the silanes used as endcappers and adhesion promoters also affect final properties.

NEW CONDENSATION PROCESS LEADING TO THE FORMATION OF SILOXANE BOND

Slawomir Rubinsztajn and James A. Cella
GE Global Research Center
1 Research Circle
Niskayuna, NY 12309

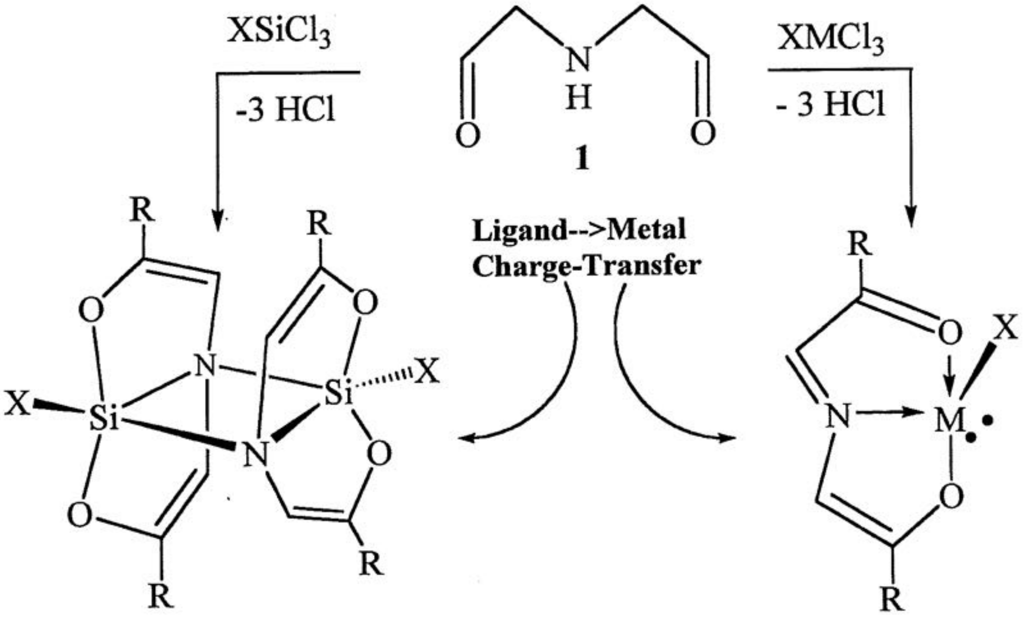
Abstract

There are many condensation reactions between organofunctional silanes or organofunctional polysiloxanes that lead to formation of a siloxane bond with elimination of low molecular byproducts such as water, alcohol, carboxylic acid, amine or hydrogen. We have recently discovered a new reaction between organo-hydrosilanes and alkoxysilanes in the presence of tris(pentafluorophenyl)boron. The reaction proceeds rapidly at room temperature producing a siloxane bond and releasing an alkane by-product. These reactions enable facile preparation of siloxanes that would be difficult to obtain with existing chemistries. The scope and mechanistic aspects of these new processes will be discussed.

Intramolecular Electron-Transfer in Hypervalent Silicon-Complexes and Related Systems

Matthias Driess,* Nicoleta Dona, Klaus Merz
Department of Inorganic Chemistry, Fakulty of Chemistry
Ruhr-University Bochum, Universitätsstrasse 150, D-44801 Bochum
E-mail: matthias.driess@rub.de

One of the basic aims in coordination chemistry is that one can tune the chemical functionality of a coordinated atom by choosing a suitable ligand system capable of intramolecular (reversible) electron transfer. While the latter is well established in transition metal coordination chemistry with many chelate ligand systems, tuning the valence state (high oxidation state vs. low oxidation state, magnetism) is much more difficult for the main-group elements. Here we present that the diketoamine ligand **1** can serve as a electron-rich chelate ligand even towards silicon(+4), germanium(+4) and tin(+4) atoms. Interestingly, the reaction of the diketoamine ligand **1** with common halosilanes affords the unusual dimeric silanes **2**, while halogermanes and halostannanes lead to the hypervalent carbene-homologues **3** (see below). The latter products are the result of intramolecular electron-transfer reactions from the ligand backbone to the group 14 atom. These and other surprising results will be discussed in my contribution.



2: X = halogen, alkyl, aryl

3: M = Ge, Sn; X = halogen

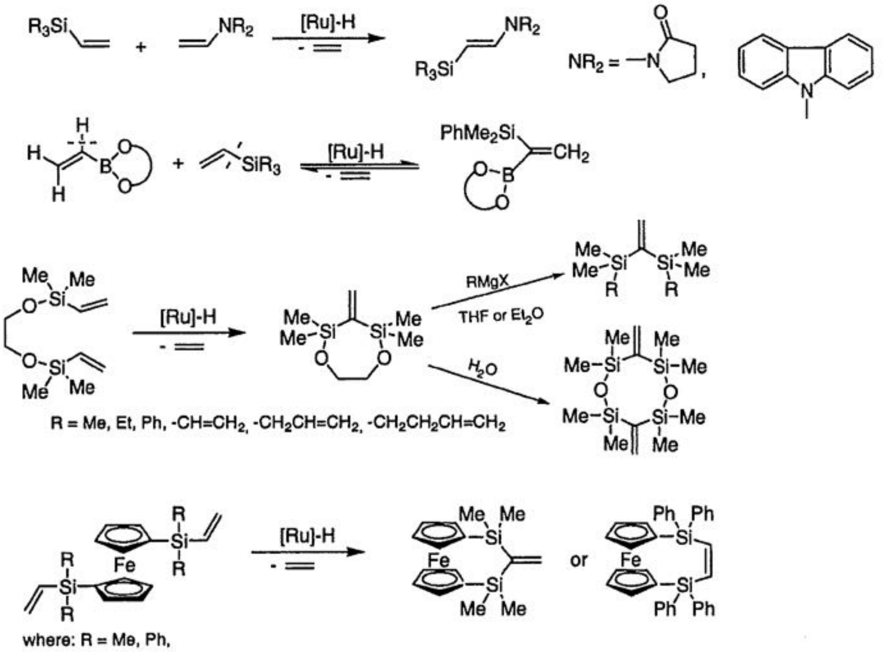
STEREO- AND REGIO-SELECTIVE SYNTHESIS OF COMPOUNDS WITH VINYLSILICON FUNCTIONALITY VIA RUTHENIUM CATALYZED SILYLATIVE COUPLING – RECENT ADVANCES

Bogdan Marciniec

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland, marcinb@main.amu.edu.pl

The two catalytic reactions occurring between the same parent substances, i.e., silylative coupling (also called trans-silylation) and cross-metathesis of functionalized such as styrene and vinyl- and allyl-substituted hetero(O, N. S, B)alkenes with vinylsubstituted silicon compounds have been used for the synthesis of well-defined molecular compounds with vinylsilicon functionality. On the other hand, divinylsilicon derivatives in the presence of Ru (as well as Rh and Ir) compounds containing or generating M-H and/or M-Si bond undergo silylative coupling polycondensation and/or ring closing to give unsaturated polymeric and/or cyclic organosilicon compounds (for reviews see [1]).

The communication present recent advances on stereo- and regio-selective synthesis of linear and cyclic organosilicon compounds with vinylsilicon functionality based on the ruthenium catalyzed silylative coupling reactions have been presented. Their products cannot be obtained by the metathesis procedures (see the below examples).



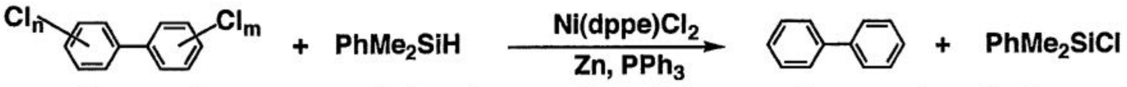
1a. B.Marciniec, C.Pietraszuk, *Current Organic Chemistry*, 7, 691(2003).
b.B.Marciniec, C.Pietraszuk, in Handbook of Metathesis, *Verlag Chemie*, R.Grubbs ed.Chap.2.13, p.455 (2003).

ORGANOSILICON AND ORGANOMETALLIC WAY TO EFFICIENT DECHLORINATION OF POLYCHLORINATED ARENES

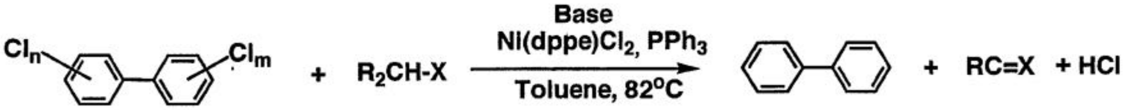
Hideki Sakurai,* Satoshi Onai, and Takanobu Sanji
Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki Noda, Chiba 278-8510, Japan

Large amounts of polychlorinated arenes, such as polychlorobenezenes and polychlorobiphenyls, are left untreated. It is clear that these left chemical compounds become one of the threats for global environment. However, dechlorinative hydrogenation of aromatic-chlorine bonds is one of the difficult organic functional transformations. Exploitation of the efficient method of the dechlorinative hydrogenation is thus meaningful not only from scientific but environmental point of view.

It is demonstrated that hydrosilanes can reduce these chemicals efficiently in the presence of an inexpensive nickel-based catalyst. Thus polychlorobenzenes and polychlorobiphenyls are converted to benzene and biphenyl quantitatively under relatively mild reaction conditions. The reaction could provide a practical method of treating these chemicals. Furthermore, it is evidenced that cascade catalyst systems composed of nickel and other transition metal complexes are also effective for clean reduction.



The reaction was extended to the use of much inexpensive organic reducing reagents. Polychlorobenzenes and polychlorobiphenyls are thus reduced quantitatively.



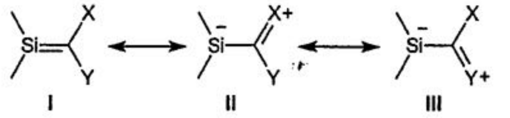
- Present address: Miyagi Organization For Industry Promotion, Kamisugi 1-14-2, Aoba-ku, Sendai 980-0011, Japan; e-mail: sakurai-h516@gamma.ocn.ne.jp

ZWITTERIONIC SILENES FROM OLIGOSILYLAMIDES: THEIR FORMATION AND TRAPPING REACTIONS

Henrik Ottosson, Tamaz Guliashvili, Arnaud Martel, and Ibrahim El-Sayed
Department of Chemistry (Organic Chemistry), Box 599, Uppsala University,
751 24 Uppsala, Sweden.

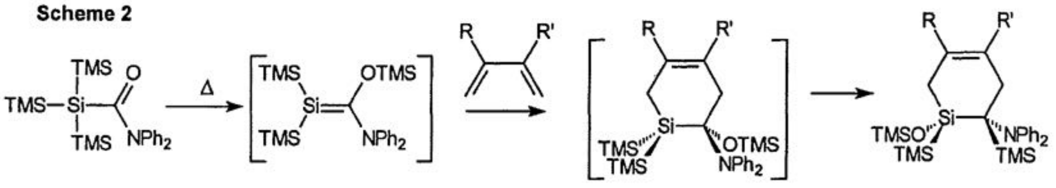
Silenes with π-electron donating substituents at the C atom are influenced by zwitterionic resonance structures **II** and **III** that place negative charge at Si (Scheme 1). It was earlier shown by Apeloig and Karni that this reversed Si=C bond polarization is the most important single electronic factor that reduces the reactivity of silenes,[1] and our quantum chemical calculations indicated that silenes dominated by the zwitterionic resonance structures are Si-C single rather than Si=C double bonded and that they have markedly pyramidal Si atoms.[2] One of our goals is now to find silenes that react selectively, that are less air and moisture sensitive, and that are less prone to dimerize than many of the presently investigated silenes, and we reason that zwitterionic silenes with π-donor substituents at C are good candidates in this regard. Silenes with increased selectivity in reactions with e.g. dienes could find applications in organic synthesis.

Scheme 1



X, Y = NR_2, OR, SR, O^-

Scheme 2



R, R' = H, Me, OMe, CO_2Me

We form transient zwitterionic silenes through thermolysis of *tris*(trimethylsilyl)silylamides and trap them with 1,3-dienes (Scheme 2).[3,4] The silenes formed react selectively and quantitatively to yield the [4+2] cycloadducts, which is in contrast to several naturally ($Si^{\delta+}=C^{\delta-}$) polarized silenes. Moreover, we see no dimerization adducts and the sensitivity of the silenes to air and moisture is so low that their formation and subsequent trapping reactions can be carried out under standard reflux conditions. An interesting aspect of the trapping reactions is that electron-poor dienes react faster than electron-rich dienes, indicating that these cycloaddition reactions are inverse electron-demand Diels-Alder reactions.

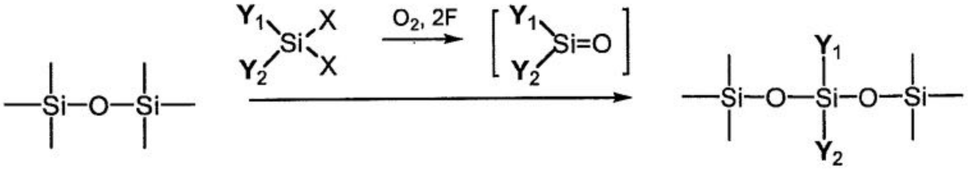
1. Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **1984**, *106*, 6676.
2. H. Ottosson, *Chem. Eur. J.* **2003**, *9*, 4144.
3. I. El-Sayed, T. Guliashvili, R. Hazell, A. Gogoll, H. Ottosson, *Org. Lett.* **2002**, *4*, 1915.
4. T. Guliashvili, A. Martel, I. El-Sayed, A. Fischer, H. Ottosson. In preparation.

ELECTROGENERATION OF SILANONES(?): NEW SYNTHETIC ROUTE TO FUNCTIONALIZED SILOXANES

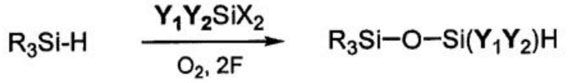
Viatcheslav JOUIKOV and Robert KEYROUZ
Laboratory of Molecular and Macromolecular Electrochemistry,
UMR 6510 CNRS, University of Rennes I, 35042 Rennes,
FRANCE

Diorganyl silanones have not as yet been observed in solutions at room temperature, though their intermediacy was inferred in a number of reactions of silicon compounds carrying vicinal X and OR groups, whose combination provides a stable leaving product, RX. The analysis of reactions, where the formation of silanones was thus supposed, allowed us to develop a method for *in situ* electrogeneration of what we believe to be silanone intermediates and to involve them into the reactions with different substrates, the method which provided an efficient synthetic tool for the preparation of functional siloxanes.

We have recently shown [1] that electrochemical activation of molecular oxygen in the presence of dichloro or dialkoxysilanes ($Y_1Y_2SiX_2$, X = Cl, OAlk) results in the formation of very potent $\leftarrow Y_1Y_2SiO \rightarrow$ group transferring intermediates. Although not characterized directly, these transient species allowed a series of interesting synthetic reactions. Thus a selective insertion of a Y_1Y_2SiO fragment (Y_1, Y_2 = Alk, Ph, H, vinyl, OAlk, $(CH_2)_nCF_3$, $(CH_2)_nCl$, $(CH_2)_nOH$, $(CH_2)_nNH_2$) into permethylated siloxanes was performed, resulting in linear or cyclic siloxanes with the extended backbone carrying different functional groups.



When trapping electrogenerated silanones with hydrosilanes, various insertion products were synthesized with two additional functional groups at the Si-H carrying silicon.



$$R_3Si\text{-}H \xrightarrow[O_2,\ 2F]{Y_1Y_2SiX_2} R_3Si{-}O{-}Si(Y_1Y_2)H$$

Further developments of this process such as performing the electrosynthesis in ionic liquids [2], using atmospheric air as an O_2-providing reagent, elucidating the reaction mechanism and the nature of oxygen species triggering the reaction will be presented.

References:

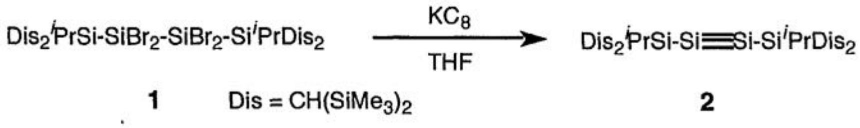
[1] D. Fattakhova, V. Jouikov and M. Voronkov, *J. Organomet. Chem.*, **513** (2000) 170;
R. Keyrouz and V. Jouikov, *New J. Chem.*, **27** (2003) 902.
[2] B. Martiz, R. Keyrouz, S. Gmouh, M. Vaultier and V. Jouikov, *Chem. Comm.*, 674 (2004).

Stable Disilyne with a Silicon-Silicon Triple Bond, $Dis_2{}^iPrSi\text{-}Si\equiv Si\text{-}Si^iPrDis_2$: A New Entry for the Multiple Bond Chemistry

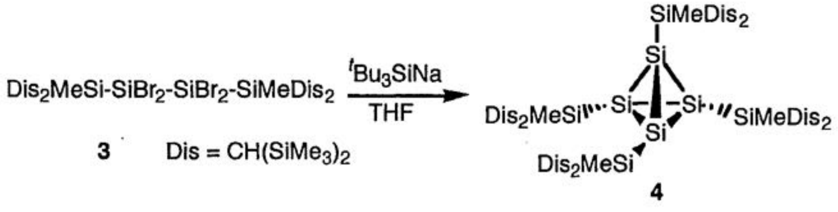
Akira Sekiguchi, Rei Kinjo, Masaaki Ichinohe, and Masafumi Toyoshima

Department of Chemistry, University of Tsukuba,
Tsukuba, Ibaraki 305-8571, Japan

After the breaking of the so-called "double-bond rule" by the preparation of the first stable heavy alkene analogues stable both in the solid state and solution, silene >Si=C< and disilene >Si=Si< in 1981, many stable unsaturated silicon compounds have been synthesized to date. However, stable silicon-silicon triply bonded compounds (disilynes, $RSi\equiv SiR$) are still unknown, despite several attempts to synthesize them, except for the transient existence as intermediates. We report here the first successful synthesis of a stable and isolable compound with a silicon-silicon triple bond. We have designed the bis[bis(trimethylsilyl)methyl](isopropyl)silyl group as a new protecting group of a disilyne. $Dis_2{}^iPrSi$-substituted disilyne (**2**) was successfully synthesized by the reaction of $Dis_2{}^iPrSi\text{-}SiBr_2\text{-}SiBr_2\text{-}Si^iPrDis_2$ (**1**) (Dis = $CH(SiMe_3)_2$) with two equivalents of KC_8 in THF at –78 °C, and was isolated as yellow crystals in quantitative yield. Compound **2** is air and moisture sensitive, but thermally stable. The structure of **2** was unambiguously determined by X-ray analysis. The Si-Si bond is not linear, but is *trans*-bent with angle of 137.44(4)°. The $Si\equiv Si$ bond length is 2.0622(9) Å, which is 13.5% shorter than a normal Si-Si bond (2.34 Å) length and 4.3% shorter than Si=Si double bond lengths (ca. 2.15 Å).



The choice of the protecting substituents is very crucial, and Dis_2MeSi-substituted tetrasilatetrahedrane was obtained when $Dis_2MeSi\text{-}SiBr_2\text{-}SiBr_2\text{-}SiMeDis_2$ was reacted with ${}^tBu_3SiNa$ in THF.[1)] The details will be reported.



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1) M. Ichinohe, M. Toyoshima, R. Kinjo, and A. Sekiguchi, *J. Am. Chem. Soc.*, **125**, 13328 (2003).

WHAT DOES IT TAKE TO SUPPRESS SIGMA DELOCALIZATION IN AN OLIGOSILANE?

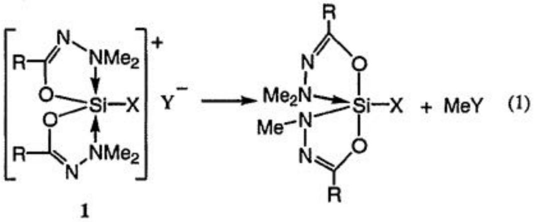
Josef Michl, David W. Rooklin, Annika Bande, Martina Peters, and Thorsten Schepers
Department of Chemistry, University of Colorado, Boulder, CO 80309-0215

Experimental and computational (TD DFT) data are combined to address the issue of conformational dependence of the effect of sigma electron delocalization on the energy of the lowest singlet sigma-sigma* excitation in linear and cyclic peralkylated oligosilanes. Specifically, we ask whether there are conformational constraints under which a doubling of the number of SiSi bonds in an oligosilane, say from Si_3Me_8 to Si_5Me_{12}, will fail to cause a reduction of the HOMO-LUMO gap and a decrease of the lowest singlet sigma-sigma* excitation energy. A qualitative rationalization of the results is provided in terms of the simple ladder C model, operating at the Hückel level of molecular orbital theory. The results make it clear that sigma delocalization is cyclic, even in linear oligosilane chains, and that conformational effects exercise their influence by interconverting Hückel and Möbius orbital arrays. This perspective makes it obvious why the planar all-anti zig-zag conformation provides maximum effective delocalization of sigma electrons, and why cyclooligosilane are not aromatic, regardless of ring size.

REACTIVITY OF SILICONIUM-ION COMPLEXES: CC BOND FORMATION THROUGH INTER-CHELATE REARRANGEMENT

Boris Gostevskii, Akella Sivaramakrishna, Inna Kalikhman and Daniel Kost
Department of Chemistry, Ben Gurion University, Beer-Sheva 84105, Israel

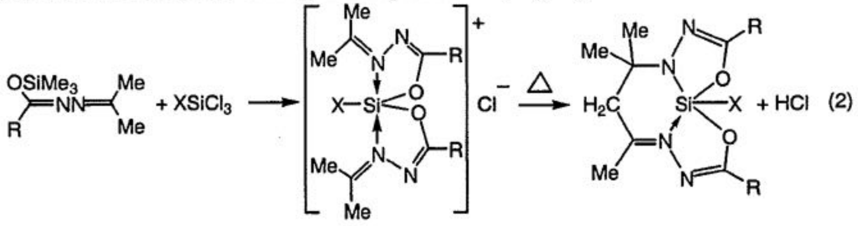
We have recently reported[1] the facile preparation and manipulation of pentacoordinate siliconium-ion salts (**1**), and their unexpected methyl halide elimination reaction in cases of bulky ligands X (Eq. 1).



1

X = t-Bu, Cyclohexyl
R = Me, Ph, CH_2Ph, t-Bu
Y = Cl, Br, I

In the absence of N-methyl groups, in complexes (**2**), a skeletal molecular rearrangement takes place, forming a new carbon-carbon bond between the two chelate rings resulting in a third ring with silicon at the bridgehead position (Eq. 2).



2 **3**

R = Me, Ph, CF_3
X = Me, C_6H_{11}

Both of these reactions seem to be driven by the same driving force: the transformation of a formal silyl cation stabilized by coordination of *two* donor groups to a neutral tetravalent (pentacoordinate) silane with a single coordination bond.

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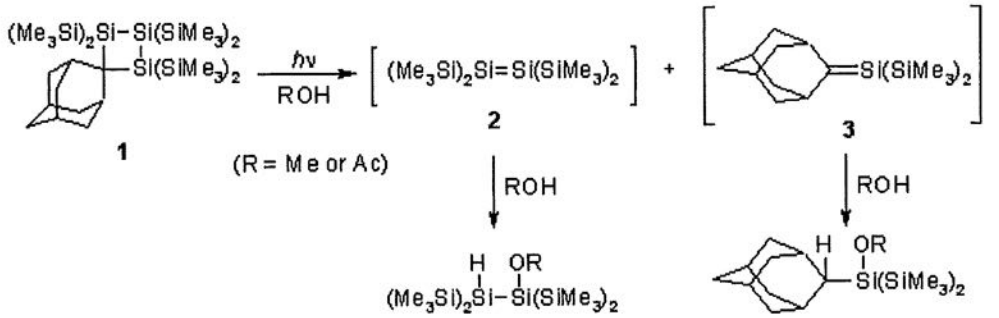
[1] Kost, D.; Gostevskii, B.; Kocher, N.; Stalke, D.; Kalikhman, I. *Angew. Chem. Int. Ed.* **2003**, *42*, 1023.

PROTONATION OF THE SILICON-CARBON DOUBLE BOND. A KINETIC STUDY OF THE ADDITION OF ALCOHOLS AND ACIDS TO A STABILIZED SILENE IN SOLUTION.

William J. Leigh, Thomas R. Owens, Yitzhak Apeloig, and Dmitry Bravo-Zhivotovskii.

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1 and *Department of Chemistry & the Lise Meitner-Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa 32 000, Israel*

UV photolysis of trisilacyclobutane **1** in solution in the presence of methanol or acetic acid yields the products of 1,2-addition of the trapping agents to tetrakis(trimethylsilyl)-disilene (**2**) and 1,1-bis(trimethylsilyl)-2-adamantylidenesilene (**3**) as transient intermediates. The two compounds have been detected directly by laser flash photolysis of **1**, as long-lived species absorbing with $\lambda_{max} = 410$ nm (**2**; $\tau \sim 750$ ms) and $\lambda_{max} = 340$ nm (**3**; $\tau > 1$ second) in dry, deoxygenated hexane solution. Both species are sensitive to oxygen, reacting with rate constants on the order of 10^6 $M^{-1}s^{-1}$. Addition of small amounts of methanol (0.045 M) to the solution reduces the lifetime of the disilene to 68 μs, but does not affect that of the silene significantly. The silene exhibits a similar lifetime in deoxygenated acetonitrile solution, and the lifetime is reduced upon addition of molar quantities of methanol. The reaction appears to proceed with pure second order kinetics in methanol/acetonitrile mixtures and exhibits a bimolecular rate constant on the order of 10 $M^{-1}s^{-1}$. The silene reacts somewhat faster with the more acidic, less nucleophilic alcohol 2,2,2-trifluoroethanol, and faster still with acetic, chloroacetic, and trifluoroacetic acids. The rate constants correlate with the pK_a^{DMSO} of the alcohol or acid, and a Bronsted plot of the data is linear with a slope ($-\alpha$) of -0.18 ± 0.02. No evidence for reaction is observable with strongly nucleophilic, non-acidic reagents such as *n*-butyl amine. The results are consistent with a mechanism in which reaction is initiated by protonation of the Si=C bond, analogous to the Markovnikov electrophilic addition mechanism of alkene chemistry.

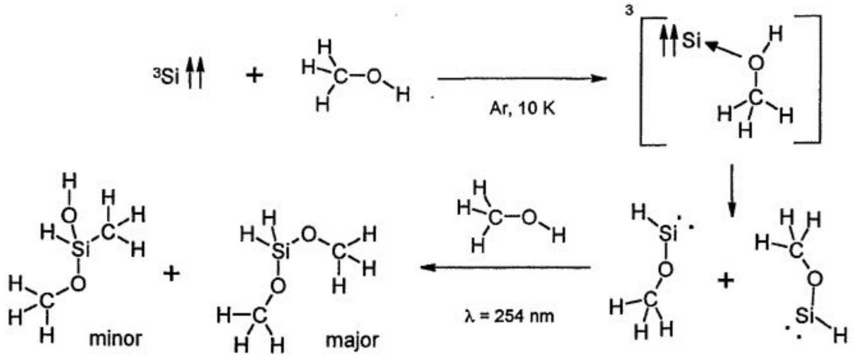


The Direct Reaction of Silicon with Methanol: A Matrix Spectroscopist´s View

Günther Maier*, Jörg Glatthaar
Institute of Organic Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58
D-35392 Giessen, Germany

The copper-catalyzed "direct reaction" of silicon with alcohols like methanol or ethanol is of growing interest in silicone industry. Trialkoxysilanes, the major reaction products, are important starting materials for the production of silicone precursors.[1]

The fundamental reaction steps seem to be fully understood: Silicon forms a surface-bound alkoxysilylene through insertion into the O-H bond, which is attacked by a second molecule of alcohol. The dialkoxysilanes are then oxidized with the help of the copper catalyst under formation of tri- and tetraalkoxysilanes.



We tried to model these reactions through co-condensation of atomic silicon with varying amounts of methanol. Two independent studies[2,3] on this topic have already been published. But there were still some inconsistencies. The present study clarifies the situation: Silicon atoms react with methanol under formation of methoxysilylene. No long-living n-adduct of a silicon atom and methanol was detected. Also no traces of a C-O bond insertion product could be observed. The insertion into the bond between the methyl group and the oxygen only takes place in the second reaction step. For instance, higher concentrated matrices containing adducts of methoxysilylene and methanol form mixtures of dimethoxysilane (major product) and hydroxy(methoxy)methylsilane (minor product) upon activation with UV light. With CH_3OD or CD_3OD the reaction is completely changed. First, now the silicon atoms form stable n-adducts. Second, on irradiation only C-O bond insertion occurs.

The results of this study are compared with the experimental findings in our recently published studies on the reaction of silicon atoms with methyl halides and dimethyl ether.

[1]K. M. Lewis, R. Nelson, S. R. Cromer, C.-L. O`Young, A. T. Mereigh, **WO 2002060909**

[2] G. Maier, H. P. Reisenauer, H. Egenolf *Monatshefte f. Chem.* **1999**, *130*, 227-235.

[3] V. N. Khabashesku, K. N. Kudin, J. L. Margrave, L. Fredin *J. Organomet. Chem.* **2000**, *595*, 248-260.

Experimental and Theoretical Studies of the Gas-Phase Reactions of SiH_2 + H_2O (D_2O) and SiH_2 + HCl. Kinetic and Quantum Chemical Studies.

by **Rosa Becerra,** *Instituto de Quimica-Fisica 'Rocasolano', C.S.I.C., Madrid, Spain,* **Matthew J. Almond, Nicola Goldberg, Robin Walsh,** *School of Chemistry, University of Reading, Whiteknights, Reading, UK.*, **J. Pat Cannady,** *Dow Corning Corporation, Midland, MI, USA,* and **J. Steven Ogden,** *Department of Chemistry, University of Southampton, Highfield, Southampton, UK*

Time-resolved gas-phase kinetic studies of the title reactions have been carried out using laser flash photolysis to generate and monitor SiH_2

(i) The $SiH_2 + H_2O$ (D_2O) reaction was studied over the pressure range 5-400 Torr with SF_6 as bath gas at 297 K and at 345 K. The pseudo first order rate constants, k_{obs}, for [SiH_2] decay gave good fits to the quadratic equation:

$$k_{obs} = k_a + k_b[H_2O] + k_c[H_2O]^2$$

Furthermore the rate constant k_b was found to be highly pressure (SF_6) dependent. Rate constants (both k_b and k_c) at 345 K were about half those at 297 K. Isotope effects, k_{bH}/k_{bD}, were in the range 1.0–1.15, suggesting no involvement of H- (or D-) atom transfer in the rate determining step. The mechanism proposed involves the initial formation of the zwitterionic donor-acceptor complex, $H_2Si\cdots OH_2$ in a vibrationally excited state which can either be stabilised by collision with SF_6 or react further with H_2O (or D_2O). RRKM modelling shows that the reaction is close to the low pressure limit for this third body assisted association reaction. The mechanism is further supported by *ab initio* calculations at the G3 level which show that, whereas $H_2Si\cdots OH_2$ is unable to undergo direct isomerisation to silanol, SiH_3OH, due to a high energy barrier, the H_2O catalysed reaction is a barrierless process. This is the first example of a gas phase catalysed reaction of a silylene.

(ii) The SiH_2 + HCl reaction was studied at 10 Torr total pressure in SF_6 bath gas at five temperatures in the range 296-611 K. The second order rate constants fitted the Arrhenius equation :

$$\log(k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (-11.51 \pm 0.06) + (1.92 \pm 0.47\ \text{kJ mol}^{-1})/RT\ln 10.$$

The data are consistent with formation of a weakly bound donor-acceptor complex, which reacts by two parallel pathways to form SiHCl + H_2, either directly, or indirectly via SiH_3Cl^*. This interpretation is also supported by G3 calculations.

Full details of the kinetics and theoretical calculations will be given at the meeting.

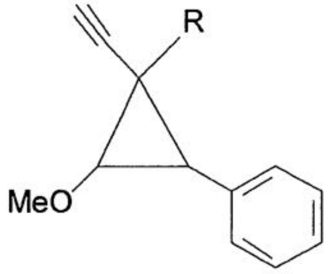
ALKYNE CYCLOADDITION REACTIONS OF DISILENES: THE REAL STORY

Kim M. Baines, Stephen E. Gottschling, and Kaarina K. Milnes
Department of Chemistry, *The* University *of* Western Ontario
London, Ontario, Canada N6A 5B7
e-mail: kbaines2@uwo.ca

In a single issue of *Advances in Organometallic Chemistry* (Vol. 39, 1996) three groups of authors, Brook and Brook, West and Okazaki and ourselves independently noted that although many reactions of Group 14 (di)metallenes are now reported, the mechanisms of these reactions remain unknown. In recent years, we have examined the mechanism of addition of carbonyl compounds to Group 14 dimetallenes using mechanistic probes to investigate the nature of the intermediate (if any) involved in these reactions.

We have employed *trans*-(2-phenyl)cyclopropane carbaldehyde and *trans, trans*-(2-methoxy-3-phenyl)cyclopropane carbaldehyde as mechanistic probes in the investigation of the addition of aldehydes to Group 14 dimetallenes. We have provided evidence, for the first time, that aldehydes add to both tetramesityldisilene and tetramesitylgermasilene in a stepwise manner with the formation of a biradical intermediate.[1] In contrast, no evidence for the formation of a biradical intermediate was found in the addition of aldehydes to tetramesityldigermene.[2]

To examine the nature of the intermediates (if any) in the addition of alkynes to Group 14 dimetallenes, *trans,trans*-(2-methoxy-3-phenylcyclopropyl)ethyne and *trans,trans*-(1-methyl-2-methoxy-3-phenylcyclopropyl)ethyne have been examined as potential mechanistic probes. The behaviour of these compounds under both ionic and radical conditions, the kinetics of rearrangement of the corresponding ✂-cyclopropyl vinyl radical and cation as well as the results of the addition of these alkynes to both tetramesityl- and tetrakis(t-butyldimethylsilyl)disilene will be presented.



R = H, Me

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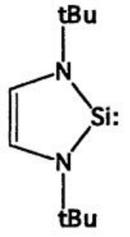
[1] Dixon, C.E.; Hughes, D.W.; Baines, K.M. *J. Am. Chem. Soc.* **1998**, *120*, 11049.

[2] Samuel, M.S.; Baines, K.M. *J. Am. Chem. Soc.* **2003**, *125*, 12702.

RECENT DEVELOPMENTS IN STABLE SILYLENE CHEMISTRY

Nicholas J. Hill and Robert West
Organosilicon Research Center, Department of Chemistry, University of Wisconsin, Madison, 53706 USA email: nickhill@osirc.com

Following the isolation of the thermally stable N-heterocyclic silylenes **1-3** in the mid-1990's several studies have examined their behavior toward a wide range of organic, inorganic and organometallic substrates.[1, 2] Although the behavior of these divalent silicon species is now reasonably well understood, many areas remain unexplored.



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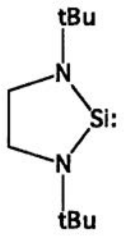

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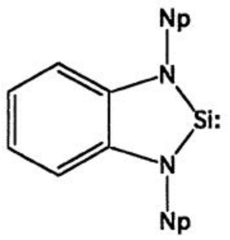
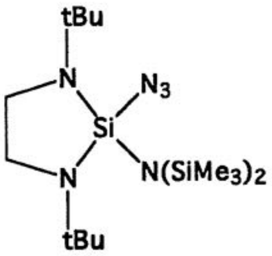
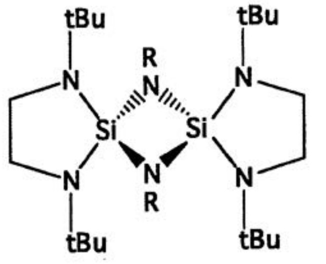
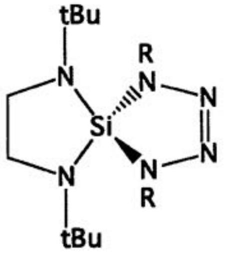


3

Our recent efforts have focused upon the reactions of **2** with bulky organic azides to give a range of structurally diverse species (see below). This work, along with our efforts to develop a range of modified N-heterocyclic silylenes based upon **1** and **2**, will be discussed here.







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POSTER ABSTRACTS

POLYMER SCIENCE & GUITAR STRINGS: KEEPING THE MUSIC ALIVE WITH SURFACE CHEMISTRY

Tony Parker
A. A. Parker Consulting & Product Development
Newtown, PA 18940
Starmacpar@aol.com

The corrosion resistance of musical instrument strings can be improved by minimizing the galvanic couple between the winding and core metals, where the best corrosion resistance is achieved when the metals are galvanically equivalent. Corrosion resistance can also be improved through the use of appropriate metal surface treatments. For the case of phosphor-bronze wound strings, corrosion resistance is improved when the surface is modified with azole compounds such as benzotriazole, and benzimidazzole. Corrosion resistance is also improved when the surface is modified with N-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS). These improvements are most noteworthy when the core of the string is more cathodic in character (i.e. titanium as opposed to steel). The corrosion inhibiting function of benzotriazole and other azole compounds is known to result from a combination of factors inclluding the ability of the azole functionality to chelate with the metal surface to form and oxide-reinforcing polymer network. Unlike other comparative compounds, AAPS possesses analogous molecular-level capabilities, and also provides improved corrosion protection. Collectively, these results provide unique insight into the common molecular level attributes of good corrosion inhibitors.

HYBRID ORGANIC-INORGANIC POLYMERIC NANOCOMPOSITES FOR BIOSENSOR APPLICATIONS

Nuttawee Niamsiri[1], Daniel F. Schmidt[2], Deepak Shah[2], Terri A. Wilson[3], Emmanuel P. Giannelis[2], Carl A. Batt[1]
[1]Department of Food Science, Cornell University, Ithaca, NY USA
[2]Department of Material Science & Engineering, Cornell University, Ithaca, NY USA
[3]Department of Chemical & Biomolecular Engineering, Ithaca, NY USA

Abstract:

Our research focus is on the synthesis of innovatively engineered biodegradable polymeric materials for the development of low-cost, disposable biosensors that can be used for medical diagnostics, for the rapid detection of hazardous biological and chemical contaminants in the environment and food processing industry. Polyhydroxyalkanoates (PHAs) are biopolyesters naturally synthesized by numerous bacteria as carbon and energy storage compounds, and are suitable candidates for the production of novel biodegradable plastics. Since they possess material properties similar to various synthetic thermoplastics and elastomers, they have been extensively studied as environmentally friendly substitutes for conventional petroleum-based polymers such as polypropylene. However, due to the fact that unmodified PHAs possess limited stability towards many standard polymer-processing techniques, the aim of our research group is to develop novel hybrid polymer networks based on PHAs that further expand their applications. To date, we have successfully produced a variety of chemically distinct PHA using specially designed bioreactors. In this project, PHA-PDMS (Polydimethylsiloxanes) hybrids were formed through a crosslinking reaction between functional group present in the PDMS and complementary groups present in the PHA. The resulting material has properties quite similar to standard PDMS rubber, but unlike such PDMS, this material is potentially biodegradable. Additionally, this material represents the first of its kind reported to date. Currently, our primary research goal is to investigate the feasibility of using these novel PHA-PDMS hybrid elastomers for constructing microfluidic networks on chip-based biosensor devices. In addition, our lab is presently characterizing the degradability of the crosslinked PHA-PDMS materials.

Presenting Author:
Nuttawee Niamsiri
Cornell University
Department of Food Science
317 Stocking Hall
Ithaca, NY, 14853, USA
Tel:(607) 255-7902
Fax: (607) 255-8741
nn22@cornell.edu

Contact Author:
Carl A. Batt
Cornell University
Department of Food Science
317 Stocking Hall
Ithaca, NY, 14853, USA
Tel:(607) 255-7902
Fax: (607) 255-8741
cab10@cornell.edu

SILICONE NANOSPHERES FOR POLYMER AND COATING APPLICATIONS

Jochen Ebenhoch and Helmut Oswaldbauer
Wacker-Chemie GmbH
D-81737 München, Germany
Tel.: +49 (0)89 6279 1166 – Fax: +49 (0)89 6279 1706
e-mail: jochen.ebenhoch@wacker.com

Silicone Nanospheres with different particle diameters, crosslinking density and chemical functionalization are accessible by aqueous hydrolysis-condensation sequences of silane and siloxane precursors and subsequent isolation. Grafting of functionalized particles with organopolymers resp. surface modification results in nanosized silicone domaines, which are readily dispersible in monomeric and polymeric systems. A variety of these versatile, tailor-made products have been launched by WACKER on a commercial scale.

Properties of thermosetting and thermoplastic resin systems are subject of improvement to meet increasing performance requirements of end-users. One way to enhance material properties is to incorporate nano-modifier, based on elastomeric silicone particles, which are optionally grafted with acrylic or other polymers to control dispersibility, viscosity and other parameters. For example epoxy resin formulations could be modified with silicone nanosheres to improve low-stress behavior, resp. fracture toughness properties, even at very low particle loading levels. Based on Silicone Core-Shell technology, WACKER developed products, which enable manufacturing of highly transparent materials with improved RT and low-temperature (-40°C) impact resistance combined with high weatherability.

There are not many industrial fields, where key requirements are of the same complexity, as for coating applications. Improvement 0fscratch resistance is a challenge for today's liquid automotive topcoat and powder coating systems. On the other hand, impact resistance of waterborne and powder coats are currently not sufficient and have to be improved to meet today's requirements. WACKER Silicone Nanospheres offer a solution for both problems – significantly higher scratch resistance by using functionalized and/or grafted highly crosslinked silicone particles and better impact resistance by incorporation of Core-Shell particles with elastomeric silicone rubber cores.

Synthesis and Size-control of Si Nanoparticles Prepared by a Solution Route

Jing Zou and Susan Kauzlarich

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

Abstract:

Silicon nanoparticles (NPs) have great promise for applications, such as tunable lasers, optoelectronic devices and biological tag. This group has demonstrated the production of silicon NPs by a simple room temperature reduction route. This method allows for both size control and surface passivation. We have recently achieved size control and successfully terminated the nanoparticles by a silanization method. The NPs have been characterized by TEM/HRTEM, FTIR, UV-vis, PL, and NMR. The terminated product is stable both in solvents and exposed to air / water. The long-term stability of these NPs was determined by measurement of their photoluminescence and compared to other terminated Si NPs. The optical property of Si NPs before and after silanization treatment was also examined. ^{29}Si solid state NMR was employed to study and compared various terminated Si NPs, such as alkoxyl-terminated NPs and silanization-terminated NPs. The termination and characterization will be presented in details.

Solution Synthesis and Characterization of Si & Si/Ge Nanoparticles.

Katherine A. Pettigrew, Philip P. Power, and Susan M. Kauzlarich, Department of Chemistry, University of California, Davis, One Shields Ave., Davis, CA 95616, Fax: 530-752-9307, smkauzlarich@ucdavis.edu

Si and Si/Ge alloyed nanoparticles have been prepared by the oxidation of magnesium silicide with bromine. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) confirm the crystalline nature of the nanoparticles. Energy dispersive X-ray spectroscopy (EDS) illustrates that the nanoparticles are composed of silicon and silicon/germanium. Fourier transform infrared (FTIR) spectra are consistent with alkyl-capped surfaces. Fluorescence spectroscopy indicates strong ultraviolet-blue photoluminescence, which is attributed to both quantum confinement and surface termination.

SILYLATED SURFACES: SOME NEW INSIGHTS

Kirsten Weissenbach and Rodney Conn
Degussa Corp. 2 Turner Place Pisacatway NJ 08855

The hydrolysis and condensation of organofunctionaltrialkoxy silanes has been studied using time-dependent ^{29}Si-NMR. It was shown that for aqueous solutions of these materials 1.5 hydroxyl groups per silicon atom proves to be a limit for good performance in surface deposition.

In addition, monomeric and oligomeric aminosilanes were applied to E-glass and the resulting films were investigated by means of AES (Auger Electron Spectroscopy). It was demonstrated that oligomeric cationic aminosilanes exhibit a superior film-formation when compared to the commonly used monomeric aminosilanes. AES depth profiling showed that the films deposited from solutions of the oligomeric silanes were more homogeneous and defect free than those from their monomeric counterparts.

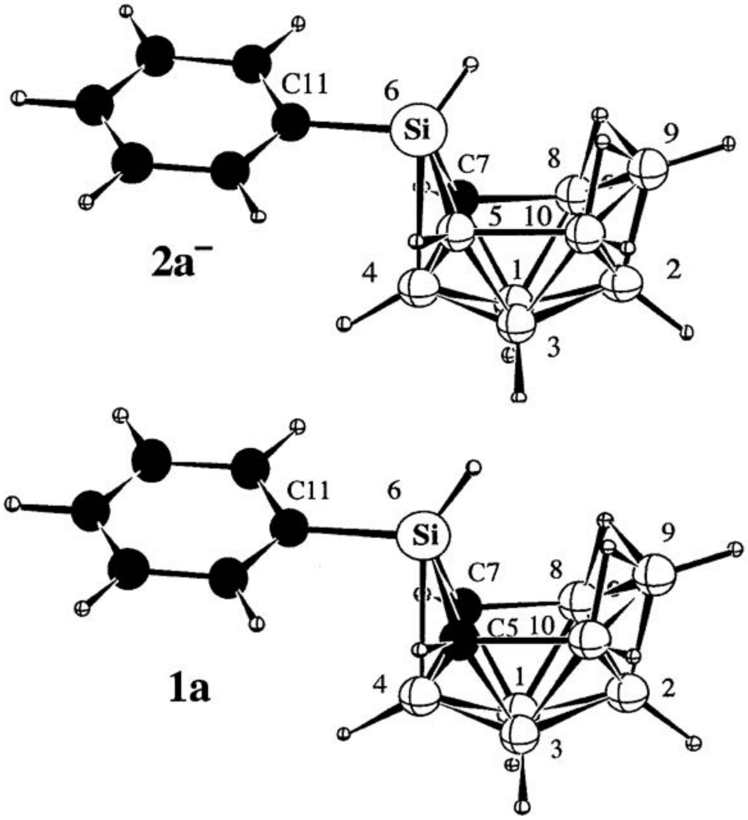
Syntheses and Structural Studies of 10-Vertex Siladicarbaboranes and the First Silamonocarbaboranes

Jude Clapper and Larry G. Sneddon

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

judeclap@sas.upenn.edu, lsneddon@sas.upenn.edu

The first 10-vertex siladicarbaboranes, 6-R-*arachno*-6,5,7-$SiC_2B_7H_{12}$ (R = Ph, **1a** or Me, **1b**) and silamonocarbaboranes, PSH^+(6-R-*arachno*-6,7-$SiCB_8H_{12}^-$) (R = Ph, **2a**$^-$ or Me, **2b**$^-$) have been synthesized via the proton sponge initiated in situ dehydrohalogenation reactions of *arachno*-4,6-$C_2B_7H_{13}$ and *arachno*-4-CB_8H_{14} carbaboranes with $RSiHCl_2$ (R = Ph or Me). DFT/GIAO computations have confirmed that **1** and **2** have *arachno* cage frameworks based on an icosahedron missing two adjacent vertices. In both compounds the silicon and carbon atoms are located in adjacent positions on the open six-membered face.

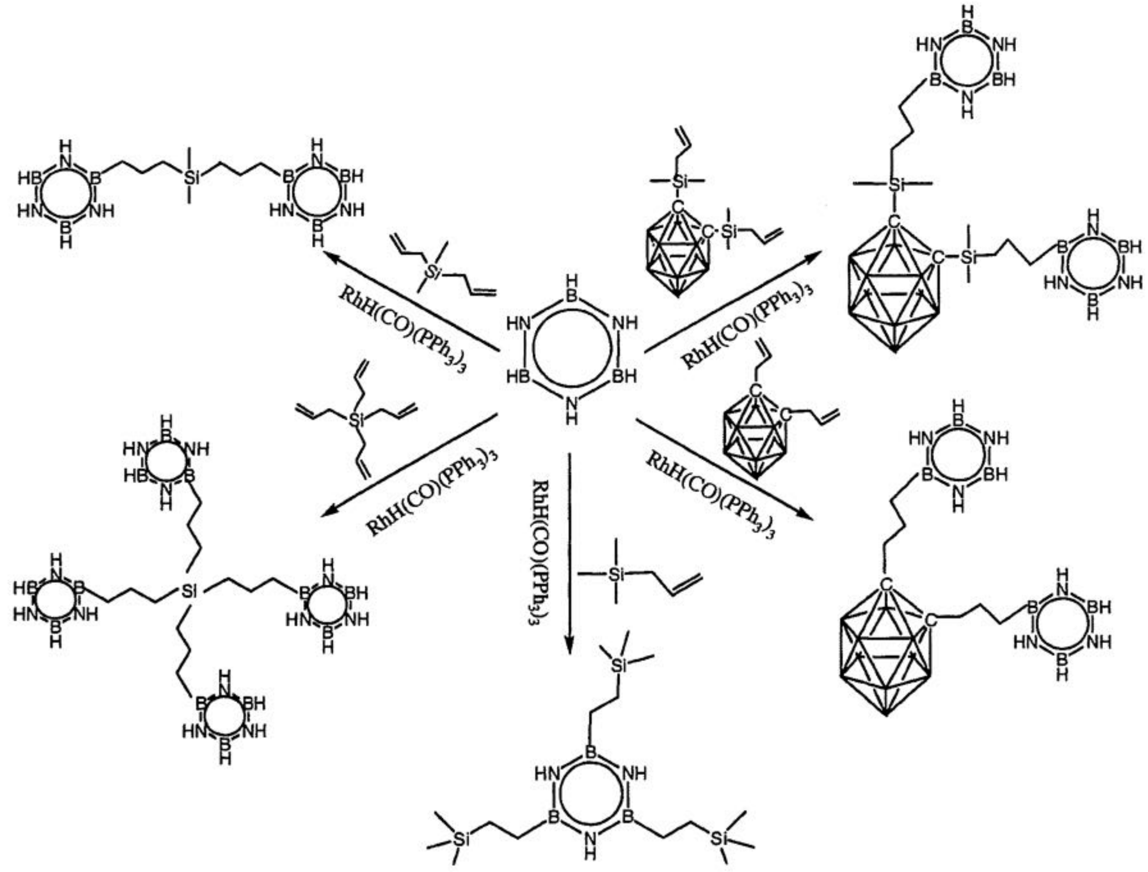


DFT optimized geometries for *exo*-6-Ph-*arachno*-5,6,7-$SiC_2B_7H_{12}$ (**1a**) and *exo*-6-Ph-*arachno*-6,7-$PCB_8H_{12}^-$ (**2a**$^-$) at the B3LYP/6-311G* level.

Design, Synthesis and Ceramic Conversions of Molecular and Polymeric Single Source Precursors to Si-B-C and Si-B-N-C Composite Materials

Xiaolan Wei, Patrick J. Carroll and Larry G. Sneddon
Department of Chemistry, University of Pennsylvania, Philadelphia, PA19104-6323

Molecular precursors to tertiary and ternary composite ceramic materials have been synthesized via titanium-catalyzed decaborane olefin-hydroboration and rhodium-catalyzed borazine olefin-hydroboration. New classes of polymeric precursors have been prepared via both ruthenium-catalyzed ring opening metathesis polymerization (ROMP) of norbornenyldecaborane and norbornenyltrimethylsilane and platinum-catalyzed hydrosilylation copolymerization. The thermal properties, bulk ceramic conversions and characterizations of the ceramics will also be presented.

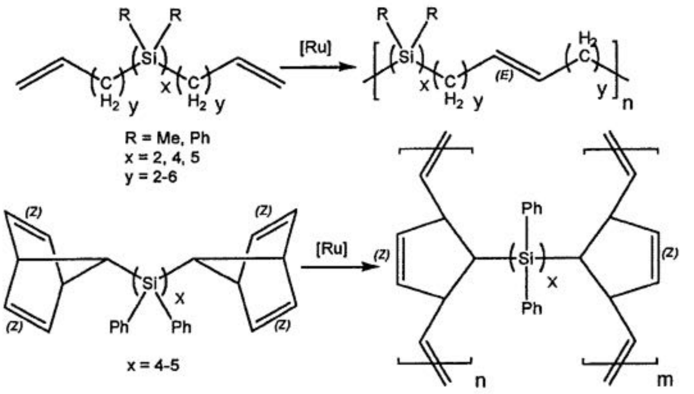


Synthesis of Novel Unsaturated Si-rich Polycarbosilanes and Their Conversion to Electrical Conductive Films

Matthias Driess* and Gabriela Mera
Department of Inorganic Chemistry , Ruhr-University Bochum
Universitätsstrasse 150, D-44801 Bochum, Germany
E-mail: matthias.driess@rub.de

Unsaturated, Si-rich organocarbosilanes are a novel delicate class of materials because they combine electronic and mechanical properties of σ-delocalized polysilanes with those of π-conjugated polyolefins giving hybrid properties such as semiconducting and/or metallic behavior, photoluminescence, photolithography, photoconductivity, and thermochromism.

There are only a few examples of such polymers hitherto known having a disilanediyl-carbon backbone.[1] One part of our current efforts in this field is to develop new convenient pathways to unsaturated, Si-rich polycarbosilanes via catalytic reactions. We found that the Grubbs-catalyst RuCl$_2$(PCy$_3$)$_2$(=CHPh) was can be used in ADMET and ROMP metathesis polymerization of different novel unsaturated organodi-, tetra- and pentasilanes. In fact, we succeeded in the synthesis of several unsaturated title compounds which were used for the preparation of electrical conducting films. The starting materials are insulators in their undoped state but become semiconducting upon exposure of thin films to I$_2$ vapor. Not only that and quite surprising, some "monomeric" precursors lead to metallic conducting thin films with 10^2 S/m, similar to the value of doped polyacetylene. The results on the synthesis and characterization of the precursors as well as the characterization of the electrical conducting thin films will be discussed.



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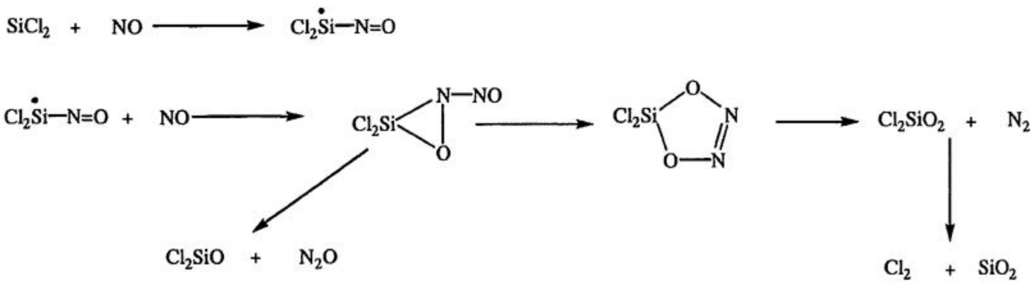
[2] Gabriela Mera, Matthias Driess; *Organosilicon Chemistry VI,* **2004**, in print.

HIGH TEMPERATURE REACTIONS OF Si_2Cl_6 WITH OXIDES OF NITROGEN

Nicola Goldberg,[a] J.Steve Ogden,[b] Matthew J. Almond,[a] Robin Walsh,[a] Jenny Lee,[a] J.Pat Cannady,[c] and Rosa Becerra[d].
[a] School of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD;
[b] Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ; [c] Dow Corning Corporation, Mail Stop 128, 2200 W.Saltzburg Rd, PO Box 994, Midland, MI, 48686-0994, USA; [d] Instituto de Quimica-Fisica 'Roscolano', C.S.I.C., C/Serrano 119, 28006, Madrid, Spain.

The thermal route to dichlorosilylene from pyrolysis of Si_2Cl_6 has been investigated using both mass spectrometry and matrix isolation techniques. There was no direct evidence for the formation of $SiCl_2$ as under the conditions used it would probably polymerise and not reach the spectrometer. The formation of $SiCl_2$ was confirmed by employing a known "trapping" agent, namely buta-1,3-diene. This reaction has been investigated by Chernyshev et al[1] and involves addition to one of the C-C double bonds to form a silacyclopentene, which was detected by mass spectrometer and infrared.

Dichlorosilylene was then reacted with N_2O and NO. The observed products from the N_2O reaction were $SiCl_2O$, its polymers and N_2. This confirms the mechanism suggested by Safarik et al[2] based on their kinetic experiments. On reacting $SiCl_2$ with NO, $SiCl_2O$, its polymers, Cl_2 and N_2O were all observed. The following mechanism for this reaction is proposed and is based on an extension of the mechanism of Sandhu et al[3] :



This mechanism is supported by ab-initio calculations at the MP2 and G3 levels.

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DOES SILYLENE REACT WITH "UNREACTIVE" MOLECULES? EXPERIMENTAL AND THEORETICAL STUDIES OF THE GAS-PHASE REACTIONS OF SiH_2 WITH CO, CO_2, AND N_2.

by **Rosa Becerra,** *Instituto de Quimica-Fisica 'Rocasolano', C.S.I.C., Madrid, Spain,* **J. Pat Cannady**, *Dow Corning Corporation, Midland, MI, USA.*, and **Robin Walsh,** *School of Chemistry, University of Reading, Whiteknights, Reading, UK*

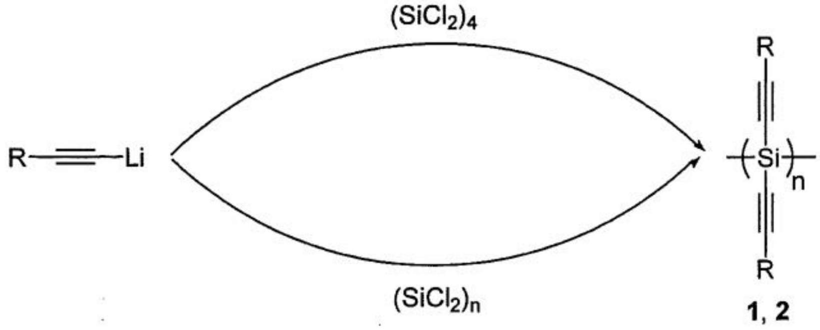
Time-resolved gas-phase kinetic studies of SiH_2, generated by laser flash photolysis, have been carried out to obtain rate constants for its reactions with CO, CO_2 and N_2.

Our findings show that while there is clear-cut evidence for reaction with both CO and CO_2, no evidence could be found for reaction with N_2 even with pressures of N_2 up to 500 Torr. Second-order rate constants and activation parameters will be reported at the meeting, including limiting values for the reaction with N_2. Detailed quantum chemical (ab initio) calculations of the potential energy surfaces for all three reactions have been carried out and will also be reported. These surfaces support the kinetic findings.

SYNTHESIS OF POLY(ETHYNYLSILANE)S

Wenqing Peng, Julian Koe
Department of Chemistry, International Christian University, Tokyo

Poly{bis(trimethlysilylethynyl)silane} (**1**) and poly{bis(phenylethynyl)silane} (**2**) have been prepared by two different routes (see Chart 1). Firstly, reaction of trimethylsilylethynyllithium or phenylethynyllithium with octachlorocyclotetrasilane at -80℃ and warming to room temperature; secondly, reaction of the lithium compounds with perchloropolysilane at 70 ℃. Both routes gave perethynylpolysilanes with similar Mw (about 2000), and no crosslinking was found during the reactions. The polysilanes $-\!\!\left[\mathrm{Si(C{\equiv}C{-}R)_2}\right]\!\!-_n$ (R= trimethylsilyl or phenyl) were characterized by SEC, NMR, IR, UV and fluorescence. The polysilanes are yellow (**1**) or yellow brown (**2**). The polysilanes do not show the characteristic (σ-σ^*) UV transition of Si-Si conjugation in the main chain for normal polysilanes, except for a long tail to 300 nm. They have good solubility in THF, $CHCl_3$ and toluene and also exhibit good film-forming ability. These two polysilanes may be of interest as non-linear optical materials, and further investigation is continuing.



1, 2

1 R = $(CH_3)_3Si$
2 R = Ph

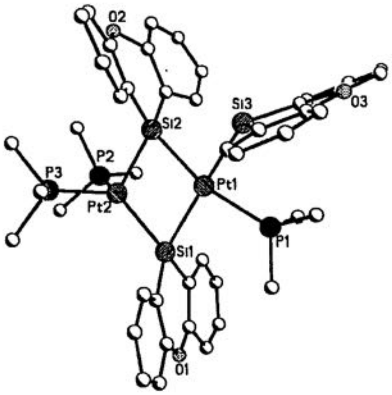
Chart 1 Synthetic route for poly(ethynylsilanes)

Pt-Si DIMERS PREPARED FROM SILICON HETEROCYCLES

Lisa French, Janet Braddock Wilking, Joyce Corey, Victoria Speedie, Michael Rutherford, and Nigam P. Rath
Department of Chemistry and Biochemistry, University of Missouri-St. Louis
St. Louis, MO 63121

The reactivity of silicon heterocyclic compounds, such as 10,10-dihydrophenoxasilin ($H_2SiC_{12}H_8O$, **1**), 2,8-dimethyl-10,10- dihydrophenoxasilin ($H_2SiC_{14}H_6O$, **2**) and 2,8-dibromo-5-methyl-10,10-dihydrophenazasiline ($H_2SiC_{13}H_9Br_2N$, **3**) with Pt(0) and Pt(II) phosphine complexes including $(Me_3P)_2PtMe_2$ and $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ have been examined. These reactions proceed through reactive mononuclear complexes (either $P_2Pt(H)(SiHR_2)$ or $P_2Pt(SiHR_2)_2$) and stable dinuclear complexes are isolated as the major product. For example, the reaction of (**1**) with $(Me_3P)_2PtMe_2$ gave the novel unsymmetrical dimer (**4**) that contains three silicon units. The structure of (**4**) was confirmed by X-ray crystallography (see Figure 1). In contrast, the reaction of (**1**) with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ produced a symmetrical dinuclear complex, $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2)]_2$ (**5**). The methyl-substituted oxasilin ring system (**2**) reacted with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to give a monomer initially, followed by the formation of yet a different unsymmetrical dimer, $(Ph_3P)_2(H)Pt(\mu\text{-}SiR_2)(\mu\text{-}\eta^2\text{-}H\text{-}SiR_2(Pt(PPh_3)$ (**6**). However, over the course of a week the dimer (**6**) produced a unique trimer, $[(Ph_3P)Pt(\mu\text{-}SiR_2)]_3$ (**7**). The phenazasiline (**3**) reacted with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ to give an unsymmetrical dinuclear complex, (**8**) analogous to (**6**) as the isolated product.

Figure 1. Molecular structure of $(Me_3P)_2(?H)Pt(\mu\text{-}SiR_2)_2Pt(PMe_3)(SiHR_2)$ ($SiR_2 = SiC_{12}H_9O$, **4**)



BIS(PYRIDYL) LIGANDS BASED ON ORGANOSILICON LINKERS – COMPLEX FORMATION WITH LATE TRANSITION METALS

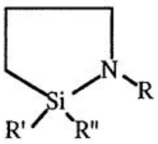
Parbati Sengupta, Hongming Zhang, Chinwon Rim, and David Y. Son*
Department of Chemistry, Southern Methodist University, Dallas, TX 75275-0314

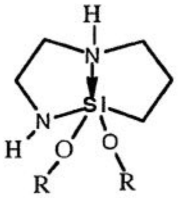
A series of new bis(pyridyl) ligands have been synthesized from 2-ethynylpyridine and various bis(chlorodimethylsilyl) starting materials. By appropriate choice of the organosilicon spacer, flexibility in the ligand can be varied. The air-stable ligands readily form crystalline metal complexes with late transition metals including silver, copper, and palladium. The complexes were characterized by X-ray crystallography and NMR spectroscopy. Depending on the metal, these ligands are either chelating or form macrocyclic complexes. Other bis(pyridyl) ligands can be prepared in good yields from various pyridyl alcohols and bis(chlorodimethylsilyl) compounds. Although these ligands are stable to purification on silica gel, they readily decompose on treatment with silver salts in protic or aprotic solvents.

Cyclic Azasilanes: Volatile Coupling Agents for Nanotechnology

Barry Arkles, Youlin Pan, Gerald L. Larson
Gelest, Inc.
11 East Steel Rd.
Morrisville, PA 19067

New cyclic azasilanes have been synthesized for the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles and chemical vapor deposition (CVD) consistent with nanoscale features. A facile method for the formation of Si-N bonds which comprises heating aminoalkoxysilanes in the presence of a neutral ammonium salt catalyst has been developed. Compounds ranging from simple azasilacyclopentanes to pentacoordinate azasilacycloctanes, as shown below, were prepared.



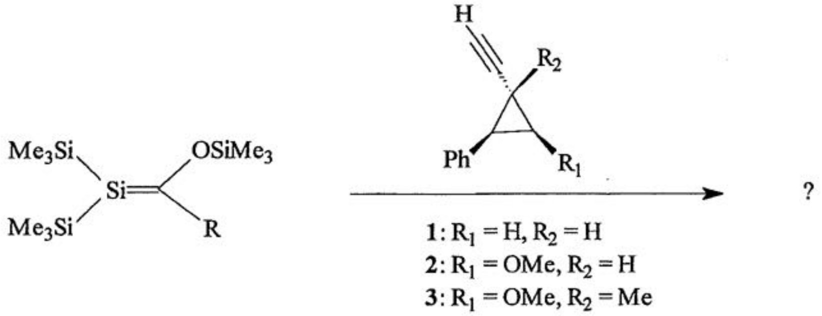


Ring-opening reactions of cyclicazasilanes with hydroxyl groups including carbinols and silanols occurs nearly quantitatively in minutes at room temperature. Treatment of inorganic surfaces, including nanoparticles and oxidized silicon wafers, with cyclic azasilanes demonstrates higher density monolayer deposition by a ring-opening reaction than acyclic alkytrialkoxysilanes and alkylaminotriallkoxysilanes.

ALKYNE CONTAINING MECHANISTIC PROBES: DEVELOPMENT AND APPLICATION

Kaarina K. Milnes, Kim M. Baines
The University of Western Ontario, Department of Chemistry, London, Ontario,
CANADA, N6A 5B7

Three alkynes have been developed for use as mechanistic probes: *trans*-2-phenylcyclopropylethyne (**1**), *trans,trans*-2-methoxy-3-phenylcyclopropylethyne (**2**), and *trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropylethyne (**3**). Kinetic and reactivity studies have shown that alkynes **2** and **3** are able to discriminate between a cyclopropyl vinyl radical and cyclopropyl vinyl cationic intermediate. In an addition reaction, this difference in the behaviour of the two types of intermediates allows for the determination of the nature of the mechanistic pathway being followed. The application of these new alkynyl mechanistic probes for the cycloaddition reactions of Brook-type silenes will be discussed.

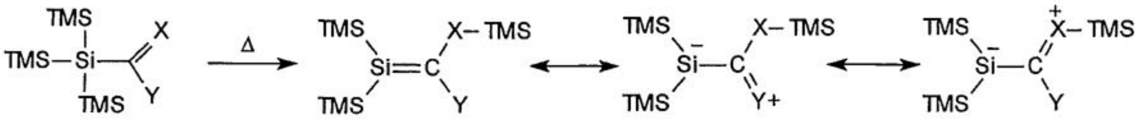


A COMPUTATIONAL STUDY ON THE THERMOLYTIC FORMATION OF SILENES INFLUENCED BY REVERSED Si=C BOND POLARITY

Tamaz Guliashvili, Arnaud Martel, Anders Eklöf, and Henrik Ottosson
Department of Chemistry (Organic Chemistry), Box 599, Uppsala University,
751 24 Uppsala, Sweden.

Formation of silenes can be achieved thermolytically through the 1,3-shift of a trimethylsilyl group from Si to the O atom of a *tris*(trimethylsilyl)silylated carbonyl compound.[1-3] The silenes formed can be stable at ambient temperatures or they can be transient species possible to trap with e.g. 1,3-dienes. Essential for their stability are the relative energies of the starting carbonyl compound and the formed silene, as well as the height of the energy barrier that separates the two species. Using quantum chemical calculations we have now explored this rearrangement in a series of trisilylsilyl substituted carbonyl compounds, but also in silylated imines, amidines, thioketones, thioesters, and thioamides (Scheme 1). The silenes formed will be influenced to various extents by reversed Si=C bond polarization, i.e. $Si^{\delta-}=C^{\delta+}$ rather than the natural $Si^{\delta+}=C^{\delta-}$ bond polarization.

Scheme 1



X = O, S, or NR
Y = OR, SR, or NRR'

The orientation of the π-electron donating groups at the C-end of the silene is important for the degree of reverse Si=C bond polarization, and this also affects their reactivities. Whereas the silene generated from *N,N*-dimethylamino-*tris*(trimethylsilyl)silylamide is only trapped with 1,3-dienes at high temperatures and after long time the *N,N*-diphenylamino-*tris*(trimethylsilyl)silylamide is trapped at moderate temperatures and in shorter time.[3] We will now discuss how the orientation of the amino group relates to the height of the barrier for the [4+2] cycloaddition reaction between 1,3-butadiene and a 2-amino-2-siloxy-silene.

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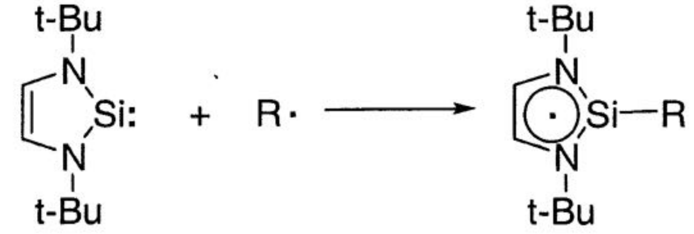
RADICAL REACTIONS OF A STABLE *N*-HETEROCYCLIC SILYLENE: EPR STUDY AND DFT CALCULATION

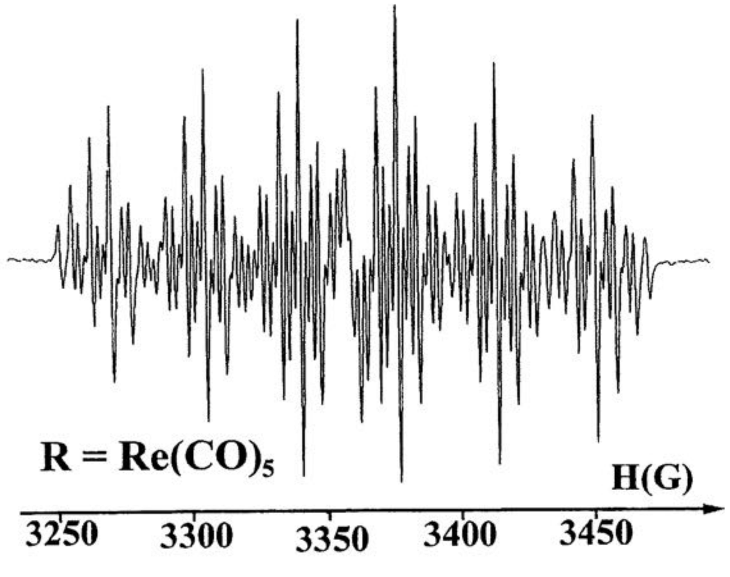
Boris Tumanskii[a], Pauline Pine[a], Nicholas J. Hill[b], Robert West[b] and Yitzhak Apeloig[a]

[a] Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel
[b] Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Chemical species which involve divalent silicon atoms are key intermediates in numerous thermal and photochemical reactions of organosilicon compounds. The field of stable silylenes commenced with the synthesis of stable *N*-heterocyclic compounds and has led to an elaborate chemistry.

We present here results of EPR studies and DFT calculation of adducts of stable silylenes with free radicals from different sources such as: 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO); $Hg[P(O)(OPr\text{-}i)_2]_2$; $(CO)_5Re\text{-}Re(CO)_5$; $(CO)_3CpM\text{-}MCp(CO)_3$, M = W, Mo and toluene. The experimental and calculated *hfc* constants and spin density contributions are in agreement with the molecular structure: in investigated radicals the unpaired electron is delocalized.

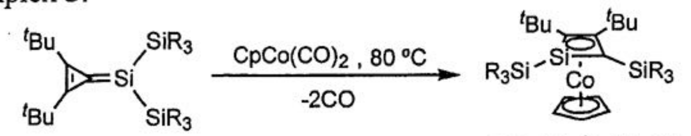




X-RAY AND THEORETICAL STUDIES OF SILACYCLOBUTADIENE COBALT COMPLEXES

Yoshihiro Kon, Kenkichi Sakamoto, Chizuko Kabuto and Mitsuo Kira
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan.

Much attention has been focused on silacyclobutadiene derivatives as silicon-containing cyclic 4π electron systems. Although silacyclobutadiene derivatives were generated as transient species, [1, 2] neither silacyclobutadienes nor their transition metal complexes have been synthesized as isolable compounds. We wish herein to discuss the structural characteristics of silacyclobutadiene cobalt complex **1**, which was synthesized as red crystals in 64% yield (Eq. 1), on the basis of the X-ray and theoretical studies of **1** and a model complex **3**.



(1)

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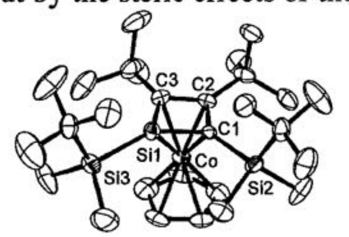
1, R$_3$Si = ^{t}BuMe$_2$Si

The silacyclobutadiene ring skeleton in complex **1** is planar but has no apparent twofold Si1–C2 axis; while the two Si–C bond lengths in the ring (1.757(5) and 1.799(5) Å) were close, the two C–C bond lengths (1.450(8) and 1.559(7) Å) were remarkably different from each other (Fig. 1). The structural feature of **1** is quite different from those of cyclobutadiene complexes, which usually have square four-membered rings. In order to understand the reason for the unusual ring structure of **1**, we performed theoretical calculations for model complex **3** at the B3LYP/LanL2DZ level. At the optimized structure, the four-membered ring of **3** was almost planar and has an apparent twofold Si1-C2 axis; no differences were observed between the two Si–C bond lengths (1.88 Å) and between the two C–C bond lengths (1.47 Å) in the ring. The unusual ring structure observed for **1** would not be caused by the electronic effects of silicon introduced in the cyclobutadiene ring but by the steric effects of the bulky substituents.



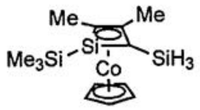


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Fig. 1. ORTEP drawing of **1**.

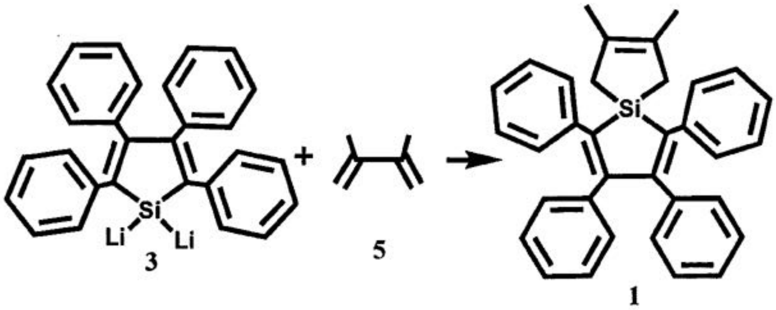
References
1. Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 1315.
2. Kon, Y.; Ogasawara, J.; Sakamoto, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9310.

REACTION OF 1,1-DILITHIOSILOLES WITH 2,3-DIMETHYLBUTA-1,3-DIENE

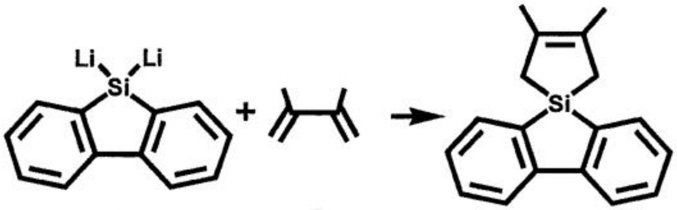
Irina S. Toulokhonova and Robert West*

Organosilicon Research Center, Department of Chemistry, University of Wisconsin - Madison, 1101 University Ave, WI 53706, Madison, USA
e-mail: west@chem.wisc.edu

Unexpected products **1** and **2** were formed in the reaction of 1,1-dilithio-2,3,4,5-tetraphenylsilole **3** and 1,1-dilithiosilafluorene **4** with 2,3-dimethyl-1,3-butadiene **5** in THF:



3 **5** **1**



4 **5** **2**

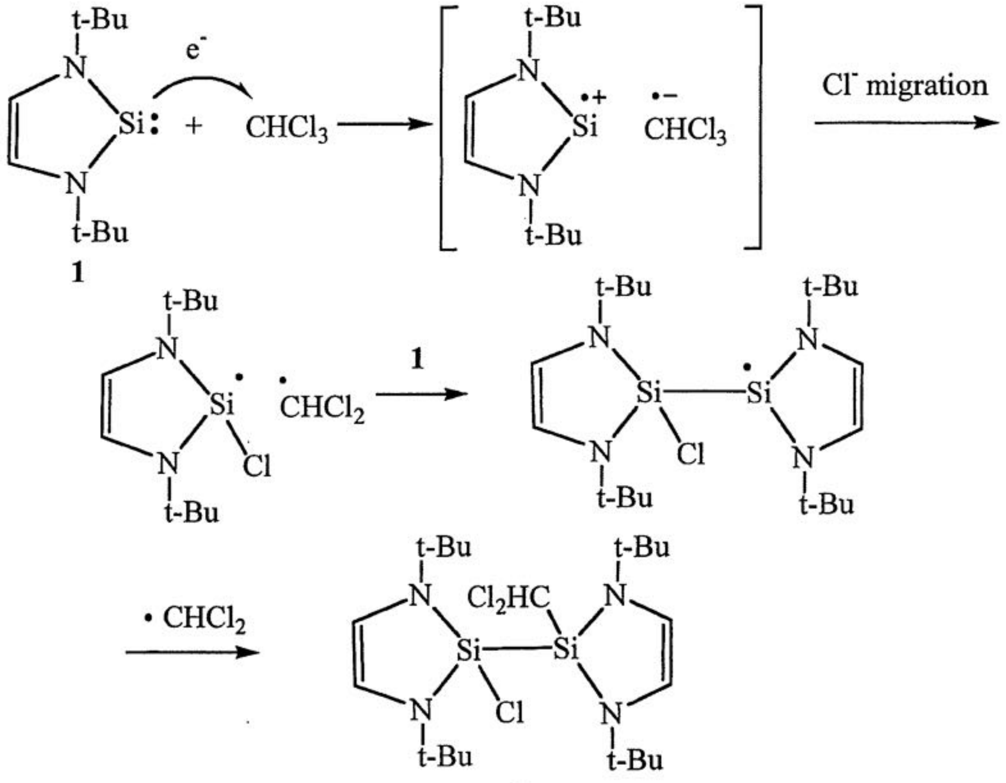
The structure of **1** and **2** were established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and X-ray crystallography.

Photophysical properties of products **1** and **2** will be presented, and possible mechanisms for the formation of **1** and **2** will be discussed.

MECHANISTIC INTERPRETATION FOR REACTION OF A STABLE SILYLENE WITH CHLOROFORM

Akinobu Naka and Robert West
Organosilicon Research Center, University of Wisconsin, Madison, Wisconsin 53706

A large variety of reactions have been reported for stable silylene **1**. The reaction of **1** with chloroform and many other halocarbons afforded the unexpected 2:1 adducts in high yield.[1] In order to determine the mechanism for this reaction, we carried out the reaction of **1** with chloroform. When 0.03 mL of chloroform was added to a solution of **1** (0.070 g, 0.36mmol) in 0.05 mL of C_6D_6, the mixture turned bright yellow. ^1H and ^{13}C NMR spectra for the mixture showed 2:1 adduct **2**, in addition to 1,1,2,2-tetrachloroethane **3** (1.3%). The formation of **3** clearly indicates that dichloromethyl radical is produced as a reactive intermediate. The scheme illustrates a possible mechanistic interpretation for the reaction of **1** with chloroform.



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Reference

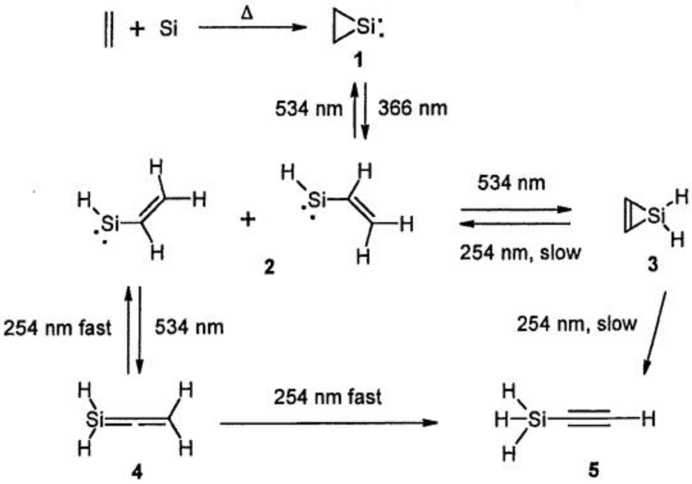
(1) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.*, **2002**, *124*, 4186.

1-Silaallene, a Key Intermediate in the Isomerization of Vinylsilylene into Silylacetylene

Jörg Glatthaar
Institute of Organic Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58
D-35392 Giessen, Germany

Vinylsilylenes and 1-silaallenes may play an important role in the thermal and photochemical isomerizations of silirenes[1a,b] and ethynyl-substituted silanes[1c]. Recently the first stable 1-silaallene was prepared by West et al.[2] In contrast to quantum mechanical calculations of the parent compound[3] (classical allenic C_{2v} structure on all levels of theory[3a]) this molecule has a slightly bent geometry.

Evidence that the unsubstituted 1-silaallene can be accessed directly was demonstrated in a matrix isolation study by Maier and coworkers. [4] Weak IR absorptions of 1-silallene could be tentatively assigned in the photochemical transformation of silacyclopropanylidene **1**, prepared from the reaction of silicon atoms with ethylene.



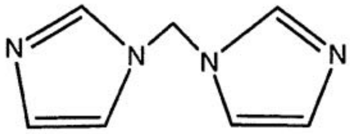
I have reinvestigated this reaction in a more detailed study, applying an improved silicon evaporation oven. Upon irradiation of a matrix containing vinylsilylene **2** with 534 nm-light, 1-silaallene **4** was generated together with 2-silirene **3**. The observed IR-bands and the UV-absorption at 260 nm are in accordance with an allenic C_{2v}-structure. On irradiation with 254 nm allene **4** isomerizes very fast to silylacetylene **5** (via a new hydrogen abstraction/addition reaction pathway) and back to silylene **2**.

[1] (a) R. Becerra, H. Monty Frey, B. P. Mason, R. Walsh, *J. Chem. Soc. Chem. Commun.* **1993**, 1050-1052. (b) T. J. Barton, S. A. Burns, G. T. Burns, *Organometallics* **1983**, *2*, 199-200. (c) S. K. Park, *J. Photoscience* **2002**, *9*, 1-4.
[2] G. E. Miracle, J. L. Ball, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1993**, *115*, 11598-11599.
[3] (a) N. Sigal, Y. Apeloig, *Organometallics* **2002**, *21*, 5486-5493; (b) P. N. Skancke, D. A. Horvat, W. T. Borden, *J. Phys. Chem. A* **1999**, *103*, 4043-4048.
[4] G. Maier, H. P. Reisenauer, H. Egenolf, *Eur. J. Org. Chem.* **1998**, *7*, 1313-1317.

Synthesis and NMR Characterization of Bis-Imidazole Complexes of Silanes

Tatiana Eliseeva, Wendy Lewis, Matthew Panzner, Matthew Espe, Claire A. Tessier, Wiley Youngs
Department of Chemistry, University of Akron, 190 E Buchtel Commons,
Akron, OH 44325

The biodeposition of silica appears to involve the interaction of proteins with ortho-silicic acid, the proteins acting as enzymes at ~ neutral pH and ambient temperature. As the model for such interactions; we have begun a study of the reactions of bis-imidazoles with silanes. The imidazole functionality will model histidine sites and the distance between the two imidazoles can be varied. The first bis-imidazole in this study is 1,1'methylene bis-imidazole (**1**).



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The reaction of **1** with trichlorophenylsilane in ratios 1:1, 1:2, 2:1 have been examined. Characterization of the products by solid state ^{29}Si MNR suggested that 5-or6-coordinate products have been obtained.

OLIGOSILOXANES OF THE TYPE Q_2M_6 FROM THE TRIMETHYLSILYLATION REACTION OF COMPLEX SILICATES

Martín Caudillo, Ramón Zárraga and Jorge Cervantes.
Facultad de Química, University of Guanajuato, Guanajuato, Gto., 36050, MEXICO.
E-mail: jauregi@quijote.ugto.mx

In recent report[1], we have observed that one of the main products of trimethylsilylation (TMS) reactions of complex silicate mixtures obtained as flotation process tails of gold and silver sulfides ores, are Q_2M_6 oligosiloxanes derivatives. This conclusion was obtained because of the presence of anortite as one of the silicates contained in the flotation tails. Anortite is soluble in HCl and the reactivity in TMS reaction is expected. If the original structure of anortite is preserved after the TMS reaction, Q_2M_6 is suggested to be one of the major products.

In order to get a better support of this result, an specific sample of the silicate labradorite, from the same family of anortite, was used in TMS. Other possible sources of Q_2M_6 such as the pyroxene augite was also studied. Further flotation of anortite ores and the TMS results using this source will be discussed.

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[1] J. Cervantes, J. J. Guzman, E. Rodríguez, G. Mendoza-Díaz, M. Caudillo and M. Nájera. J. of Silicon Chem., (2004), in press.

ABOUT THE NATURE OF SILICEOUS ROCK SILICA

Ofitserov E.N., Ubaskina J.A., Fetjuhina E.G., Kroncheva O.A.
Ulyanovsk State University
432670, Ulyanovsk, Tolstoi street, 42
RUS+(8422) 327071, e-mail: baseou@mail.ru

Today it is very impotent to find a new sources for chemical manufacture.
It is used in general an artificial silica as a raw material for silicon organic chemistry at the time of the constant growth of application of its products.
However there is a very available, suit for silicon organic synthesis silica from siliceous rocks. This silica is consists from diatom skeletons. Such silica is usually considered as amorphous. It means that this amorphous silica has to have a near order in structure.
Our research is devoted to abnormal behavior of a silica formed by diatoms. We used the diatomite which is an origin sedimentary siliceous rock formed from diatom silt for our research.
It has been observed the growth of the diatomite silica solubility with the increasing of the rock calcination temperature till 950°C instead of waiting decreasing of the solubility.
It has been noted agglomeration of particles, thermal destruction of elements and high tension of Si-O bonds according to microscope analysis and IR – specters. The amorphous character of substance appeared in such behavior of the diatomite silica.
At this time a X-ray data indicated the crystal structure of diatomite silica. However it is very difficult to isolate a monocrystal from diatomite silica structure. It deals with biogenic character of this one. According to Barskov[1]'s classification the diatomite silica is a biomineral with a matrix structure. This fact is explained the sufficient stability of the diatomite silica to alkalis and to polyphenols that is determined its properties to be a raw material for chemical production.
So the silica of siliceous rocks can not be termed as a fine-crystal and as an amorphous substance, but as a biogenic one. This term is included the specialties of the silica structure and its origin.

[1] Barskov I.V. Biomineralogy and evolution, Paleontology Journal, Moscow, 1982, _ 4, P.5-13

MODELING THE BEHAVIOR OF SILOXANE POLYMERS AS EMULSIFIERS USING MOLECULAR DYNMAICS SIMULATIONS

Justin M. Shorb, Michael E. Silver, and Brent P. Krueger

Hope College Chemistry. 35 E. 12th st. Holland, MI 49423

Due to the fact that silicon-containing molecules are being used more frequently in organic chemistry, it is necessary to extend current organic modeling tools to incorporate silicon. Specifically, this research aims to model a class of siloxane polymers with a silicon-oxygen backbone that behave as oil/water emulsifiers. Specifically, we are interested in modeling the emulsifier mediated air/oil interface. Current work is being done using molecular dynamics packages that include MMFF94 and MM2, two force fields that are already parameterized for silicon. Preliminary results provide initial insight into the behavior of these novel materials as well as comparison for the development of parameters specific to modeling silicon-oxygen polymers in the AMBER molecular dynamics program. AMBER was chosen due to its widespread use and useful polypeptide building software, which can be extended for simple polymer building. We have obtained accurate starting values via *ab initio* calculations using the Gaussian98 quantum mechanics program. Using these initial values, molecular dynamics parameters have been optimized to match experimental IR spectral measurements using a genetic algorithm program PARMSCAN.

APPLICATION OF MICROSTRUCTURED HEATERS FOR THE THERMOLYSIS OF CARBAMATO SILANES

Dr. Th. Frey*, Prof. Dr. L. Rösch*, Dr. Ch. Ruedinger#, Prof. Dr. J. Weis#

*Wacker-Chemie GmbH, Johannes-Hess-Strasse 24, 84489 Burghausen, Germany
#Consortium für el.-chem. Industrie, Zielstattstr. 20, 81379 München, Germany

Mono-, di- and tri-alkoxy functional α,γ,-NCO-Silanes are a group of new organofunctional specialty silanes which find growing use in polymer applications as chain extender or cross linker for adhesives, sealants and coatings. They can be produced from the analogous carbamato silanes by thermal decomposition under methanol elimination. Drawbacks of the established production technology are the low reaction rates at lower temperatures and the large amounts of unwanted decomposition products at reaction conditions favoring higher reaction rates as higher temperatures or higher concentrations.
A high rate and high yield process use the conversion of carbamato silane vapors on a heterogeneous catalyst. A problem of this process could be the vaporization of the carbamato silane especially at higher boiling points. A long residence time at high vaporization temperatures lead to large amounts of higher molecular weight byproducts. The reported experiments made use of microstructured devices with very short residence times for the heating of the carbamato silanes. Carbamato silanes have been heated in microstructured electric heaters followed by flash evaporation with residence times down to 100 ms. The vapors have been converted over a heterogeneous catalyst and quenched with a microstructured heat exchanger. The condensed products have been analyzed by GC-methods. It could be shown that microstructured electric heaters could be used for the superheating of carbamato silanes. For the generation of isocyanato silanes these microstructured devices are superior to conventional heating.

SILANE CROSSLINKING HIGH PERFORMANCE SPRAY FOAMS

Dr. V. Stanjek, Dr. H. Sommer, Dr. R. Weidner
Consortium für el.-chem. Industrie, Zielstattstr. 20, 81379 München, Germany

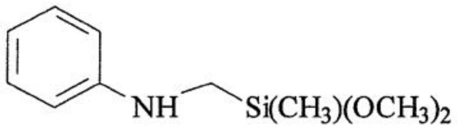
Rigid polyurethane spray-foams provide excellent mechanical and insulation properties. Thus they are widely used especially for insulation in construction and interior applications.

Common rigid foams are cured by reacting a mixture of monomeric isocyanates and/or isocyanate-containing prepolymers either with isocyanate reactive compounds (2-component-system) or with moisture (1-component-system).

However all conventional sprayfoams suffer from the disadvantage, that the foamable composition contains monomeric isocyanates, which are critical with respect to toxicological implications.

Therefore we have developed silane-terminated prepolymers for sprayfoam applications. This new class of sprayfoams is moisture-curable, too, but isocyanate-free and therefore toxicologically save. The cured foam provides an excellent hardness, elasticity and foam structure. The density of the foam is comparable to conventional PU-foams.

The silane-terminated prepolymers for spray foam applications are prepared by a reaction of an isocyanat-terminated prepolymer and an aminosilane. A slight excess of the aminosilane ensures that the product is absolutely isocyanate-free. The key to success is the use of the aminosilane **1** that provides a prepolymer which is much more reactive than conventional silane terminated prepolymers.



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So far two different kinds of silane-crosslinking spray foams have been developed. The first one is not only isocyanate-free but also free of any fluorine containing propellants. The second one possesses an improved inflamability (B2) and is driven by a mixture of fluorine-containing and fluorine-free propellants.

CONTINUOUS PRODUCTION OF ISOCYANATOSILANES USING HETEROGENEOUS CATALYSTS

Dr. Th. Frey*, Prof. Dr. L. Roesch*, Dr. Th. Kammel#, Prof. Dr. J. Weis#

*Wacker-Chemie GmbH, Johannes-Hess-Strasse 24, 84489 Burghausen, Germany
#Consortium für el.-chem. Industrie, Zielstattstr. 20, 81379 München, Germany

Mono-, di- and tri-alkoxy functional α,γ,-NCO-Silanes are a group of new organofunctional specialty silanes which find growing use in polymer applications as chain extender or cross linker for adhesives, sealants and coatings. They can be produced from the analogous carbamato silanes by thermal gas phase decomposition under methanol elimination. Drawbacks of the established production technology are the low reaction rates at lower temperature and the large amounts of unwanted decomposition products at reaction conditions favoring higher reaction rates at higher temperatures together with the backward reaction of isocyanatosilane and methanol to the corresponding carbamatosilane. These disadvantages can be overcome by using a continuous process.

The purified carbamato silane is fed into a thin film evaporator (TFE) and vaporized at a pressure significantly above ambient pressure. Pressure and temperature in the TFE is so that the bottom product contains all high boiling side products and impurities. The vapor distillate of the TFE is fed into a gas phase reactor containing heterogeneous catalyst. The reactor temperature is slightly below the temperature in the TFE. The reaction product is cooled and stripped immediately to withdraw methanol and then purified in a continuous two stage distillation process. The not converted carbamatosilane can be withdrawn in high purity and be recycled to the TFE. It could be shown that the production cost of the isocyanato silane could be significantly decreased, as the variable cost of production can be decreased by recycling not converted carbamatosilane in a continuous process.

Further advantages of the continuous process in a closed loop at moderate reaction temperatures are that no deactivation of the catalyst occurs due to lower temperatures, no byproducts occur in the gas phase reaction and no intermediate product handling is necessary. This is especially important, as NCO-Silanes are labeled to be very toxic substances. Thus, the whole process can be built within containment, the filling of the NCO-Silane and the high boiling waste (bottom product of the TFE) is done via glove boxes.

THERMOLYSIS OF CARBAMATO SILANES IN THE MICROWAVE FIELD

Dr. T. Frey*, Prof. Dr. L. Rösch*, Dr. Ch. Ruedinger#, Prof. Dr. J. Weis#

*Wacker-Chemie GmbH, Johannes-Hess-Strasse 24, 84489 Burghausen, Germany
#Consortium für el.-chem. Industrie, Zielstattstr. 20, 81379 München, Germany

Mono-, di- and tri-alkoxy functional α,γ,-NCO-Silanes are a group of new organofunctional specialty silanes which find growing use in polymer applications as chain extender or cross linker for adhesives, sealants and coatings. They can be produced from the analogous carbamato silanes by thermal decomposition under methanol elimination. Drawbacks of the established production technology are the low reaction rates at lower temperatures and the large amounts of unwanted decomposition products at reaction conditions favoring higher reaction rates at higher temperatures or higher concentrations. The reported experiments made use of microwave heating for reaction rate enhancement. Carbamato silanes have been heated in the microwave field up to temperatures as high as their boiling point. The vapors of the reaction vessel which contained unconverted carbamato silane and the products of the thermal or catalytically enhanced thermal elimination, isocyanato silanes and methanol have been condensed and analyzed by GC-methods. The reaction was performed without catalyst and with homogeneous or heterogeneous catalysts.

It could be shown that the reaction of carbamato silanes to isocyanato silanes could be improved by the application of microwave heating. In the microwave field the reaction rate for the main reaction as well as the selectivity to isocyanato silanes is substantially increased compared to conventional heating.

Stepwise Synthesis of Siloxane Chains

Zhixiang Chang, Mayfair C. Kung and Harold H. Kung*
Department of Chemical Engineering, Northwestern University, Evanston, IL 60208

Abstract

A generalized method to synthesize siloxane oligomer of a definite length with high yield is described. The method was demonstrated by synthesizing disiloxane, trisiloxane, tetrasiloxane, and pentasiloxane, by reacting tris(t-butoxy)silanol sequentially and repetitively with dichlorosilane and silanediol. The method offers the possibility of complete control of the nature of the siloxane oligomer, including the nature and location of the alkyl side chains and point of branching. The chain can also be terminated by reacting an active oligomer with monochloroslane or silanol, such that the resulting oligomer does not possess any reactive ligands.

A NEW DENTAL IMPRESSION MATERIAL WITH REDUCED SULFUR SENSITIVITY

C. ANGELETAKIS and C. LUU (Kerr Corporation, Orange CA, USA)

Contamination of oral surfaces by sulfur containing compounds such as the ones present in latex gloves leads to compromised dental impressions that have to be repeated. **Objectives:** To measure the extent of surface inhibition of polymerization of addition (vinyl) silicones by sulfur compounds and compare this sensitivity with a novel silicone that cures via the Ring Opening Metathesis Polymerization (ROMP) mechanism. **Methods:** The ROMP curable silicone system is composed of end- and pendant functionalized norbornenylethyl polydimethyl siloxane and catalyzed by a ruthenium carbene complex. A stress rheometer (SR 200, Rheometrics Inc.) was used in the plate-plate mode with a gap of 0.5 mm and the top plate oscillating at 1 Hz with an 1% strain limit. Both plates were swabbed with 0, 0.1, 0.5 and 1% hexane solutions of an alkyl thioglycolate ester (Akrostab T-883, Akros Chem.) and air dried. The impression materials were mixed and extruded on the plates and the complex viscosity increase during the setting reaction was followed while the plates were thermostated at 25°C. Three samples each were measured. **Results:** The experimental material shows curing even at the 0.5 and 1.0% thioester levels while the commercial vinyl silicone shows no surface curing at the same levels.

	Exp. impression material (Kerr)				Commercial vinyl silicone			
T-883 (%)	0.0	0.1	0.5	1.0	0.0	0.1	0.5	1.0
Time @ 400Pa.s (s)	41 (7)^{a}	50 (3)^{a}	43 (5)^{a}	43 (1)^{a}	114 (5)	323 (26)	Not Set	Not Set
Time @ 1000Pa.s (s)	152 (12)^{c}	166 (12)^{b,c}	156 (11)^{c}	210 (20)^{b}	187 (5)^{b,c}	453 (26)	Not Set	Not Set
Time @ 5000Pa.s (s)	257(17)^{d}	314 (10)^{e,d}	354 (20)^{e}	613 (10)^{f}	275 (4)^{d}	600 (42)^{f}	Not Set	Not Set

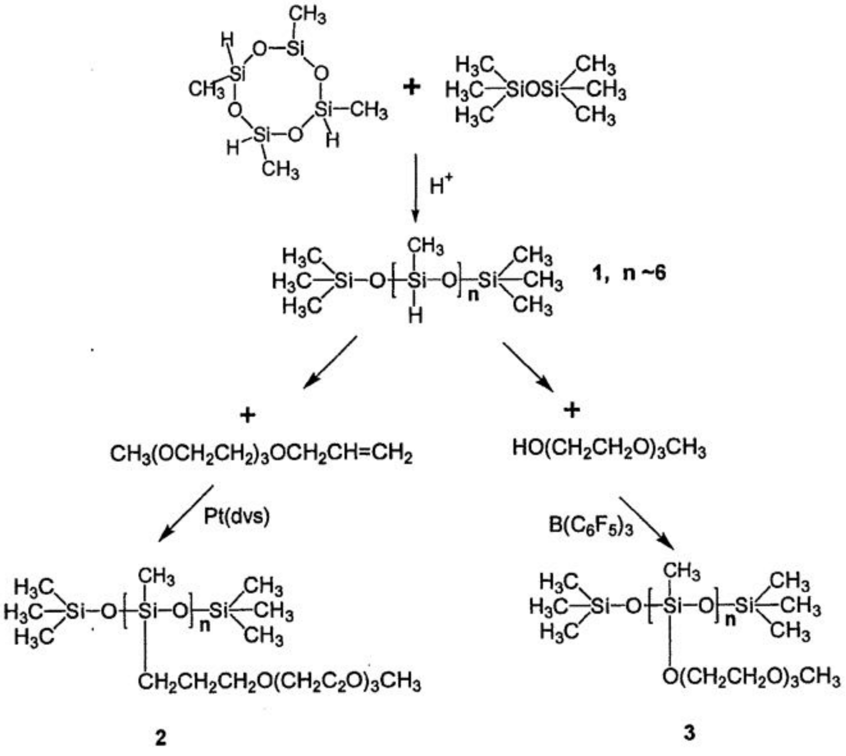
Means with the same letter are not significantly different at $p<0.05$ in the same row

Conclusions: The surface inhibition of polymerization of an experimental silicone material is significantly lower than that of a commercial vinyl addition silicone as shown by exposure to traces of a thioester during cure.

SYNTHESIS AND IONIC CONDUCTIVITY OF SHORT-CHAIN SILOXANES WITH OLIGOETHYLENEOXY COMBS

Zhengcheng Zhang [1], Leslie J. Lyons [2], Khalil Amine [3] and Robert West [1]
[1] Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, 1101 Univ. Ave., Madison, WI 53706
[2] Department of Chemistry, Grinnell College, Grinnell, IA 50112
[3] Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

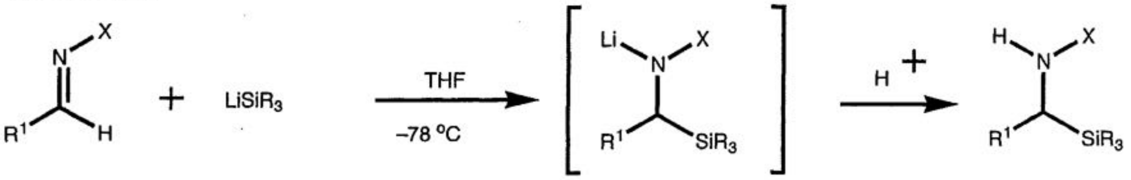
Two types of comb siloxanes based on short-chain polymethylhydrosiloxane (PMHS, **1**) with oligo(ethylene glycol) methyl ether side chains were synthesized by Pt catalyzed hydrosilylation and dehydrogenative silation, respectively. The ionic conductivities of combed siloxanes doped with $LiN(CF_3SO_2)_2$ (LiTFSI) were measured by the A.C. impedance method. Compared with the commercial PMHS (n~33-35) derivatives, the short-chain PMHS (n~6) comb polymers exhibited enhanced conductivity, up to 1.6×10^{-4} S/cm at 25^0C. The oxygen-linked comb siloxane **3** exhibits higher conductivity than the trimethylene-linked one **2** at the same LiTFSI doping level, probably due to its lower viscosity.



SYNTHESIS OF α–SILYL AMINES THROUGH THE ADDITION OF SILYL ANIONS TO IMINES

David M. Ballweg, Rebecca C. Miller, Karl A. Scheidt*
Department of Chemistry
Northwestern University
2145 Sheridan Rd.
Evanston, IL, 60208

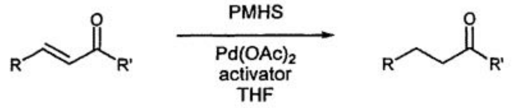
Amines are useful compounds in natural product synthesis and modern medicinal chemistry. Primary amines hold specific interest because of the potential to be difunctionalized. Additionally, the placement of an α-silyl group imparts special properties and provides an additional functional group for future manipulation. Surprisingly, there are relatively few syntheses of primary α-silylamines. we will be presenting the synthesis of α-silylamines using non-enolizable imines and silyl anions in moderate to high yields. The scope of the reaction and synthetic transformations of these compounds will also be discussed.



CHEMOSELECTIVE CONJUGATE REDUCTION OF α,β-UNSATURATED CARBONYL COMPOUNDS WITH POLYMETHYLHYDROSILOXANE

Jill A. Muchnij, Robert E. Maleczka, Jr.
Michigan State University
Department of Chemistry, East Lansing, MI 48824

Polymethylhydrosiloxane (PMHS) is a versatile and inexpensive reducing agent. Reaction of PMHS with an activator such as TBAF, $KF_{(aq)}$, or Triton-B allows for formation of a silicon specie that facilitates reduction under $Pd(OAc)_2$ catalysis. This allows for selective room temperature 1,4-reductions of α,β-unsaturated carbonyl compounds without the need for additional metal additives such as copper or tin.



A VERSATILE AND MILD REDUCING METHOD OF ACTIVATED ALKENES AND ALKYNES, HALIDES, NITRO GROUPS, AND BENZYLIC OXYGENS VIA A COMBINATION OF PALLADIUM ACETATE, POLY(METHYLHYDROSILOXANE), AND AQUEOUS KF

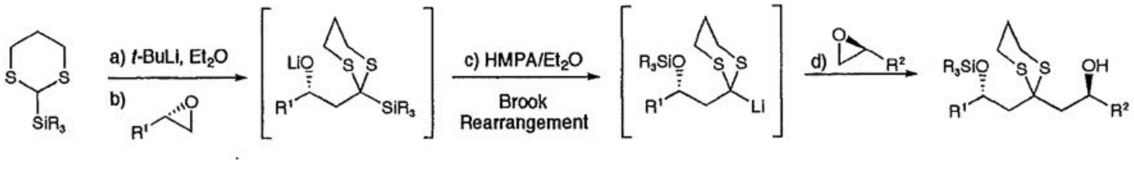
Ronald J. Rahaim, Jr. and Robert E. Maleczka, Jr.*
Michigan State University
Department of Chemistry, East Lansing, MI 48824

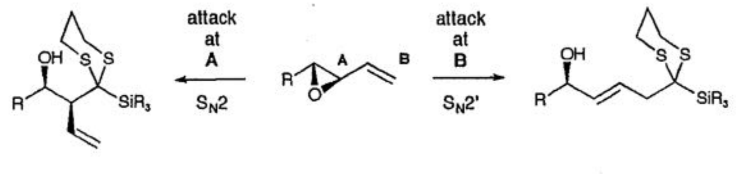
Through our work with poly(methylhydrosiloxane) [PMHS] and transition metal catalysts, we discovered that PMHS reacts with palladium acetate to form a very mild and efficient reduction system. Room temperature reductions of activated alkenes and alkynes, benzylic ketones, chlorides, and nitro groups can be accomplished chemoselectively in short reaction times. Slight modification of the reaction conditions along with the addition of catalytic amounts of chlorobenzene allows for the mild and efficient deoxygenation of benzylic alcohols, epoxides, ketones, and lactones. Studies aimed at understanding the role of the palladium acetate PMHS interaction and the scope of the reductions will be presented.

EVOLUTION OF MULTICOMPONENT LINCHPIN COUPLINGS. REACTION OF 2-LITHIO-2-SILYL-1,3-DITHIANES

Richard J. Fox, Chris Sfouggatakis, Megan A. Foley, Amos B. Smith III
Department of Chemistry, Monell Chemical Senses Center, and
Laboratory for Research on the Structure of Matter
University of Pennsylvania, Philadelphia, PA 19104

Lithiated dithiane anions, important umpolung linchpins in organic chemistry, are frequently exploited for both stereocontrolled generation of a wide variety of protected aldol linkages and for the union of advanced fragments in complex molecule synthesis. In 1997, we disclosed a three-component, one-flask linchpin tactic employing 2-lithio-2-silyl-1,3-dithianes with two different epoxide electrophiles to construct unsymmetrical adducts, exploiting a solvent-controlled Brook rearrangement. More recently, we developed the chemoselective addition of 2-lithio-2-silyl-1,3-dithianes to various vinyl epoxides. Importantly, selectivity between the S_N2 and S_N2' addition manifolds could be easily controlled by appropriately tuning the steric properties of the dithiane anion. The results of the above tactics, as well as additional methodological applications, will be presented.

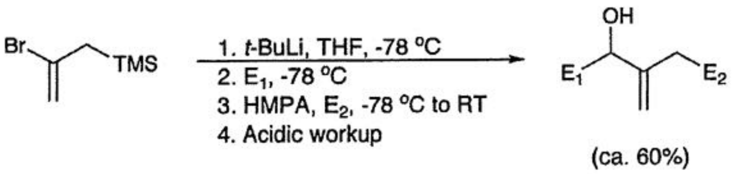




BIFUNCTIONAL MOLECULAR LINCHPINS: A THREE-COMPONENT COUPLING PROTOCOL EMPLOYING 2-BROMOALLYLTRIMETHYLSILANE

Matthew O. Duffey, Amos B. Smith III
Department of Chemistry, Monell Chemical Senses Center, and
Laboratory for Research on the Structure of Matter
University of Pennsylvania, Philadelphia, PA 19104

A new three-component coupling protocol, exploiting 2-bromoallyltrimethylsilane as a bifunctional linchpin, has been developed. The reaction sequence entails the following steps: lithiation of the vinyl bromide, addition of an aromatic or aliphatic aldehyde, execution of a solvent controlled 1,4-Brook rearrangement induced by HMPA to generate an allyl anion, and addition of a reactive second electrophile. Yields are moderate to good.



E_1 = Aliphatic or Aromatic Aldehydes
E_2 = Aldehydes, Ketones, Alkyl Halides, Disulfides

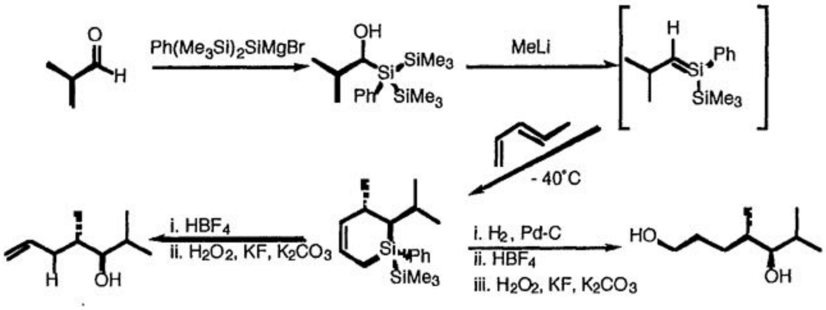
SILENES: NOVEL REAGENTS FOR ORGANIC SYNTHESIS

Mahesh Sanganee,[b] Jonathan D. Sellars,[a] Patrick G. Steel[a*] and Daniel K. Whelligan[a]

a. *Department of Chemistry, University of Durham, Science Laboratories, South Road Durham, DH1 3LE, UK*

b. *GlaxoSmithKline, Gunnels Wood Road, Stevenage, Herts. SG1 2NY, UK*

Although evidence for the existence of silenes was first reported in 1967 there have been minimal efforts at exploiting the unique reactivity of these species in organic synthesis. We have generated silenes through a modified Peterson reaction and these undergo an *in situ* Diels Alder cycloaddition with high diastereoselectivity. After activation, oxidative cleavage of the silane unit provides 1,5-diols and bishomoallylic alcohols in good overall yields. Details of this transformation and extensions to other silenes and substrates will be reported.

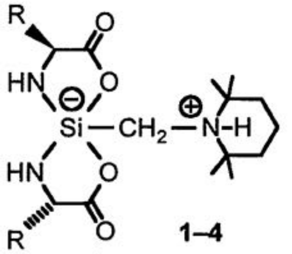


Spirocyclic Zwitterionic λ^5*Si*-Silicates with Two Bidentate Ligands Derived from α-Amino Acids: Synthesis, Structure, and Stereodynamics

Martin Penka, Simona Dragota, Rüdiger Bertermann, Christian Burschka,
and Reinhold Tacke

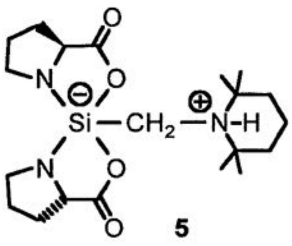
Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
E-mail: r.tacke@mail.uni-wuerzburg.de

In context with our studies on zwitterionic pentacoordinate silicon compounds [1,2], a series of chiral spirocyclic zwitterionic λ^5*Si*-silicates with $Si\mathrm{O_2N_2C}$ skeletons have been synthesized and structurally characterized (solution and solid-state NMR spectroscopy, single-crystal X-ray diffraction), compounds *rac*-**1**, (_,*S*,*S*)-**2**, (*Λ*,*S*,*S*)-**3**_CH_2Cl_2, (*Λ*,*S*,*S*)-**4**_CH_2Cl_2, and (*Λ*,*S*,*S*)-**5**_2CH_2Cl_2. In these compounds, a (2,2,6,6-tetramethylpiperidinio)methyl group and two identical bidentate ligands are bound to the silicon atom. These ligands are twofold deprotonated glycine (**1**), (*S*)-alanine (**2**), (*S*)-phenylalanine (**3**), (*S*)-valine (**4**), and (*S*)-proline (**5**). The stereodynamics of **1**–**5** ((*Λ*)/(_)-isomerization) were studied by NMR spectroscopy. The experimental investigations were complemented by computational studies of related anionic and zwitterionic model species.



1–4

	R
1	H
2	Me
3	CH_2Ph
4	*i*-Pr



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[1] Review dealing with zwitterionic λ^5*Si*-silicates: R. Tacke, M. Pülm, B. Wagner, *Adv. Organomet. Chem.* **1999**, *44*, 221–273.

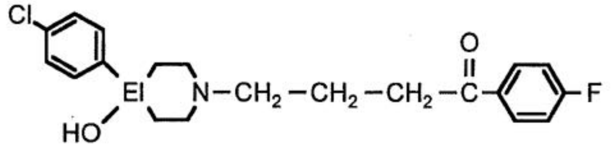
[2] Recent publication dealing with zwitterionic λ^5*Si*-silicates: R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics* **2003**, *22*, 4104–4110.

SYNTHESIS AND PHARMACOLOGICAL CHARACTERIZATION OF SILA-HALOPERIDOL, A SILICON ANALOGUE OF THE DOPAMINE (D_2) RECEPTOR ANTAGONIST HALOPERIDOL

Tilman Heinrich,[1] Barbara Müller,[1] Rüdiger Bertermann,[1] Christian Burschka,[1]
Alexandra Hamacher,[2] Matthias U. Kassack,[2] Bastian Theis,[1] and Reinhold Tacke[1]

[1]Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany,
and [2]Pharmazeutisches Institut, Universität Bonn, An der Immenburg 4,
D-53121 Bonn, Germany
E-mail:r.tacke@mail.uni-wuerzburg.de

In context with our systematic studies on silicon-based drugs (for recent publications, see refs. [1–4]), sila-haloperidol (**1b**) was prepared in multistep syntheses, starting from tetramethoxysilane. Sila-haloperidol is a silicon analogue of the dopamine (D_2) receptor antagonist haloperidol (**1a**), which is in clinical use as an antipsychotic agent. The synthesis and the structure of **1b** in the solid state and in solution will be discussed. In addition, the pharmacological properties (potencies at human dopamine receptors) will be reported.



El = C: **1a**
El = Si: **1b**

[1] J. O. Daiss, S. Duda-Johner, C. Burschka, U. Holzgrabe, K. Mohr, R. Tacke, *Organometallics* **2002**, *21*, 803–811.

[2] R. Tacke, V. I. Handmann, R. Bertermann, C. Burschka, M. Penka, C. Seyfried, *Organometallics* **2003**, *22*, 916–924.

[3] T. Heinrich, C. Burschka, J. Warneck, R. Tacke, *Organometallics* **2004**, *23*, 361–366.

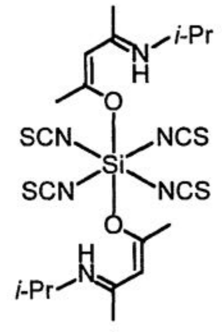
[4] Review: Bains, W.; Tacke, R. *Curr. Opin. Drug Disc. Dev.* **2003**, *6*, 526–543, and references cited therein.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL NEUTRAL HIGHER-COORDINATE SILICON COMPOUNDS WITH MONO-, BI-, TRI-, AND TETRADENTATE LIGANDS CONTAINING *O*- AND *N*-DONOR ATOMS

Oliver Seiler, Christian Burschka, Stefan Metz, Martin Penka, and Reinhold Tacke

Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
E-mail: r.tacke@mail.uni-wuerzburg.de

In context with our studies on higher-coordinate silicon compounds (for recent publications, see refs. [1–3]), we have synthesized the higher-coordinate silicon complexes **1**–**5**, starting from $Si(NCO)_4$ or $Si(NCS)_4$. We report here on the synthesis of compounds **1**–**5** and their structural characterization by single-crystal X-ray diffraction and solid-state NMR spectroscopy.



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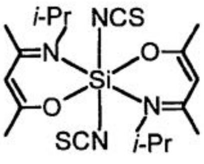

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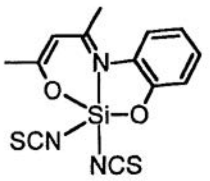

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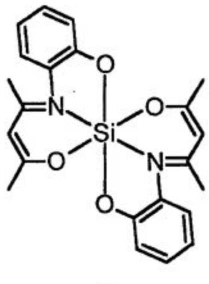

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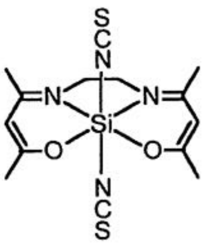

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[1] R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics* **2003**, *22*, 4104–4110.

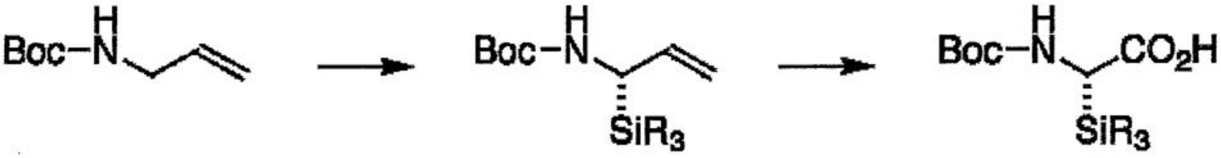
[2] O. Seiler, R. Bertermann, N. Buggisch, C. Burschka, M. Penka, D. Tebbe, R. Tacke, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1403–1411.

[3] R. Tacke, R. Bertermann, M. Penka, O. Seiler, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2415–2420.

ALPHA-TRIALKYLSILYL AMINO ACIDS: PREPARATIONS AND APPLICATIONS

Guodong Liu, and Scott McN. Sieburth, Department of Chemistry, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122, Fax: 215-204-1532, lgd@temple.edu

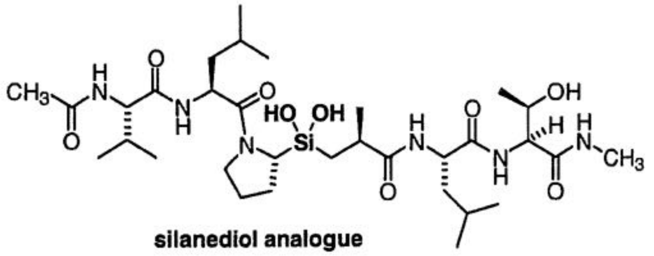
Asymmetric reverse-aza-Brook rearrangement of N-Boc-N-trialkylsilyl allylamine yields an enantiomerically enriched alpha-amino allylsilane. Oxidative cleavage of the alkene leads to a Boc-protected amino acid with the configuration of naturally occurring amino acids (L). Advancements in this methodolgy now make it possible to readily prepare multi-gram quantities of the amino acid precursor in a single operation from the Boc-protected amine.



SILANEDIOL-BASED INHIBITORS OF THE METALLOPROTEASE ANTHRAX LETHAL FACTOR

Madhusudhan Purushotham, Wondwossen D. Arasho and Scott McN. Sieburth
Department of Chemistry, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122, pmadhu@temple.edu

The design and synthesis of silanediol based peptidomimetics as inhibitors of metalloproteases has been successfully applied to thermolysin and angiotensin-converting enzyme. Anthrax Lethal Factor (LF) is a metalloprotease that is produced by the bacteria Bacillus anthracis, and it is directly responsible for death of the infected organism. The design and synthesis of silanediol-based inhibitors of LF will be described.



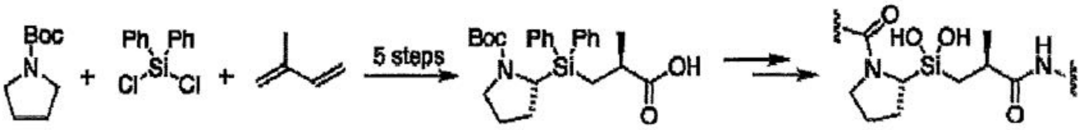
silanediol analogue

EFFICIENT AND ENANTIOSELECTIVE SYNTHESIS OF SILANEDIOL PROTEASE INHIBITORS

Sushmita Sen, Madhusudhan Purushotham, and Scott McN. Sieburth

Department of Chemistry, Temple University, 13th & Norris Streets, Philadelphia, PA 19122, Fax: 215-204-1532, sushmita@temple.edu

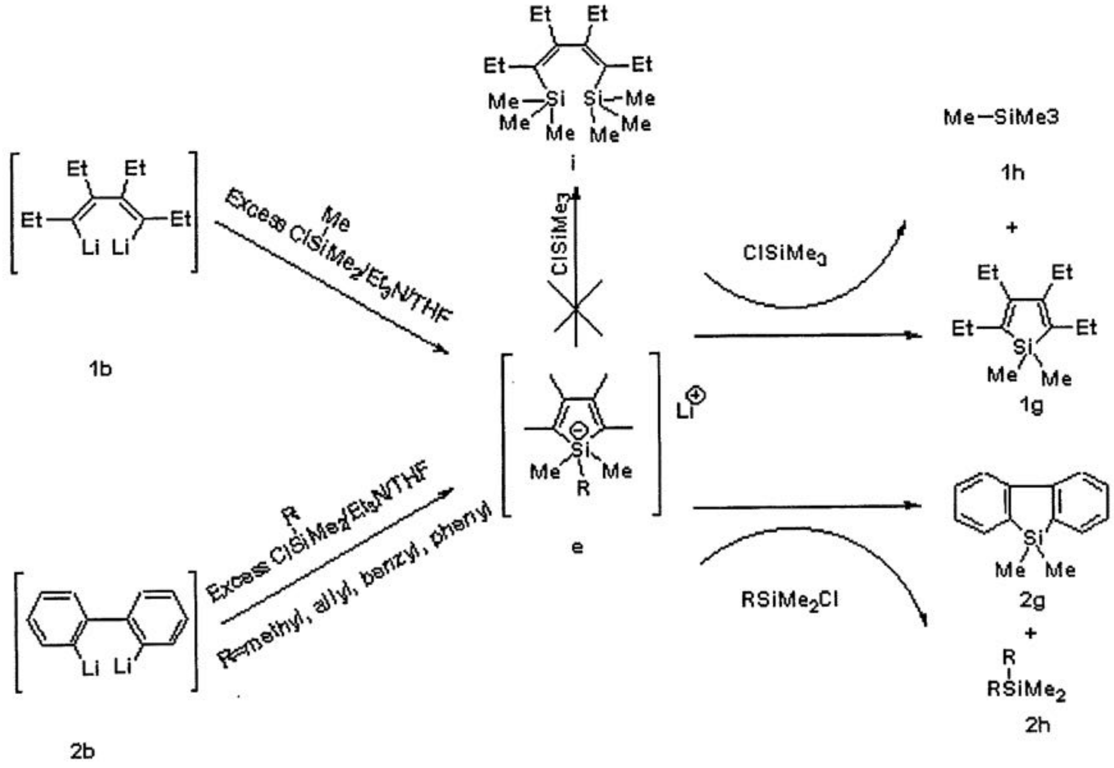
Silanediol-based protease inhibitors have been found to inhibit both aspartic and metalloproteases at low nanomolar concentrations. A new synthetic approach to the preparation of the key diphenylsilane intermediate has now been developed that uses readily available reagents, controls absolute stereochemistry, and can be performed on large scale.



REACTIONS OF DILITHIOBUTADIENES WITH MONOCHLOROSILANES; OBSERVATION OF FACILE LOSS OF ORGANIC GROUPS FROM SILICON

Paul F. Hudrlik, Donghua Dai, and Anne M. Hudrlik
Department of Chemistry, Howard University, Washington DC 20059

Hypervalent (penta or higher) silicon compounds containing electronegative ligands (atoms more electronegative than carbon), such as F or OR, are well known and can be isolated and characterized by x-ray crystallography and NMR spectroscopy. Pentavalent silicates containing only hydrocarbon ligands have been proposed as intermediates in only a few cases. In the course of preparing siloles from dilithiobutadienes and dichlorosilanes, we attempted to characterize dilithiotetraethylbutadiene (**1b**) by reaction with Me_3SiCl. Instead of the expected bis(trimethylsilyl)butadiene (**i**), we obtained dimethylsilole **1g**. In order to study the mechanism of this type of reaction, we also investigated the reactions of dilithiodibenzobutadiene **2b** with different monochlorosilanes. In these reactions, we also obtained a dimethylsilole (**2g**). In each case, the organic group which was lost from the silicon, presumably as an organolithium, was trapped with the unreacted chlorosilane to give the corresponding silane **2h**. Both of the siloles (**1g** and **2g**) were formed in good yields. Pentacoordinate organosilicon species (**e**) are suggested as the key intermediates.

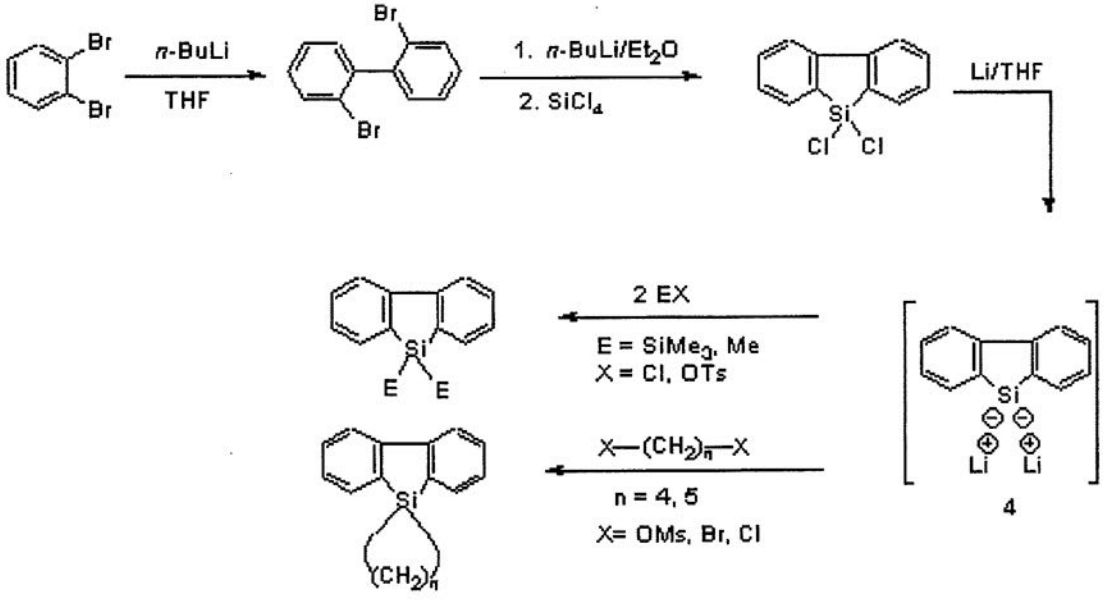


REACTIONS OF SILAFLUORENE DIANIONS WITH MONO- AND DI-FUNCTIONAL ALKYLATING AGENTS

Paul F. Hudrlik, Donghua Dai, and Anne M. Hudrlik
Department of Chemistry, Howard University, Washington DC 20059

Silyl monoanions, with one nucleophilic site, are important synthetic intermediates. They are useful for preparing silicon compounds and for carrying out various synthetic transformations in organic chemistry. Silicon dianions are rare. Silole dianions have been known since the early 1990s, but few reactions of silole dianions have been reported so far. Nucleophilic substitution reactions such as with chlorotrimethylsilane and methyl iodide are known. We have become interested in the potential synthetic applications of the double nucleophilicity of silole dianions, especially, their reactions with dihalides and other difunctional compounds, which might be a practical method for making new silicon-containing heterobicyclic rings.

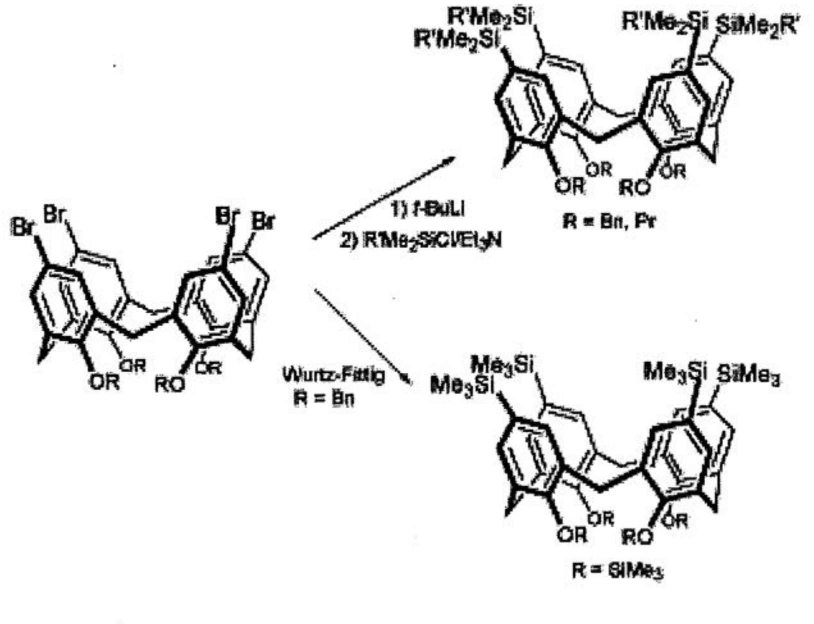
The dilithiosilafluorene dianion **4** was generated using the literature method as shown below. Reactions of this intermediate with various monofuctional and difunctional alkyl halides and sulfonates gave the expected products, including new spirocyclic systems.



METHODS FOR THE SYNTHESIS OF UPPER RIM SILYLATED CALIX[4]ARENES USING HALOGEN-METAL EXCHANGE AND THE WURTZ-FITTIG REACTION

Paul F. Hudrlik, Anne M. Hudrlik, and Wondwossen D. Arasho
Department of Chemistry, Howard University, Washington, D.C. 20059

Calixarenes, which are macrocyclic oligomers made up of phenol units linked by methylene bridges, are receiving increasing attention in the field of supramolecular chemistry because of their potential utility as molecular receptors. In order to enable assessment of silicon groups on the recognition properties of calixarenes, convenient methods were developed to prepare various upper rim silylated calix[4]arenes from halocalixarenes using (1) halogen-metal exchange with *tert*-butyllithium followed by silylation and (2) the Wurtz-Fittig reaction with sodium and trimethylchlorosilane. For the halogen-metal exchange route, the use of the clear supernatant from a mixture of chlorosilane and triethylamine gave the best results. For the Wurtz-Fittig route, procedures which worked well on a small model compound (bromoanisole) resulted in sluggish reactions and product mixtures when applied to a calixarene. However, treatment of a bromo benzyloxycalixarene with sodium and trimethylsilyl chloride in toluene resulted in a facile reaction in which the calixarene was silylated at both the upper and lower rims with loss of the benzyl group.

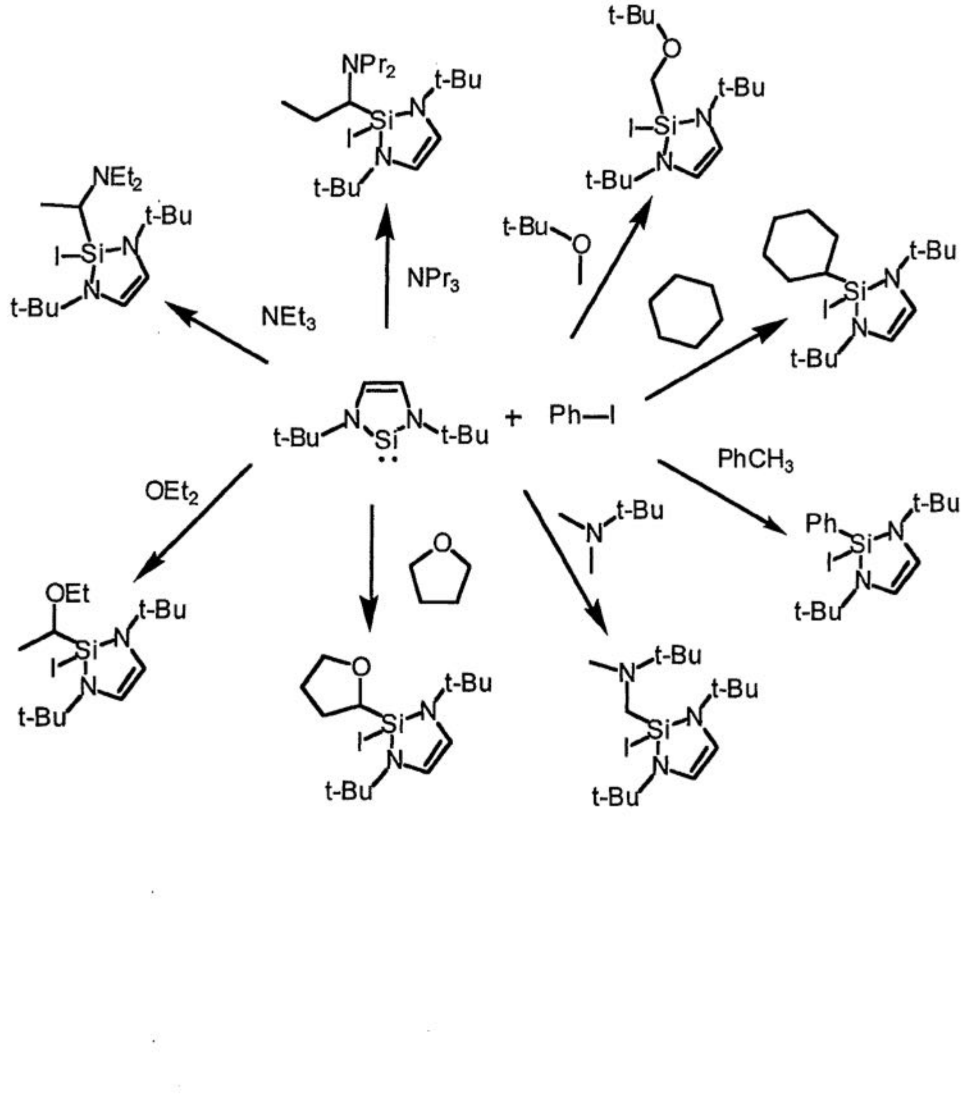


CH-ACTIVATION OF AMINES, ALKANE AND ETHERS WITH A SILYLENE/ARYL IODIDE REAGENT

Randon H Walker and Mark M. Banaszak Holl

Chemistry Department, University of Michigan, Ann Arbor, MI 48109-1055

Intermolecular CH-activation of amines, alkanes, and ethers has been realized using a silylene and aryl iodide as reagents. The reaction provides a new method in regioselectivly forming Si-C bonds. A poster presentation of general reactions shown below, effects of functional groups, and mechanistic work will be presented. Comparison of regioselectivity for this reaction with other CH-activations using a divalent group 14 compound with aryl iodide will also be provided.



PROBING THE MECHANISM OF THE BROOK REARRANGEMENT

Laura Pavelka, Kim Baines, Ian Fleming
The University of Western Ontario, Department of Chemistry, London, Ontario, CANADA, N6A 5B7

The Brook rearrangement is an important rearrangement in organosilicon chemistry described as a 1,2-migration of a silyl group from carbon to oxygen. The mechanism of the Brook rearrangement traditionally involves an intermediate oxyanion in equilibrium with a carbanion, but it has also been suggested that the intermediate could be a pentacoordinated silyl anion. The mechanism for the Brook rearrangement of the disilyl alcohol, 2-methyl-1,1-bis(dimethylphenylsilyl)propan-1-ol, has been investigated to determine the structure of the intermediate in solution. The reaction of the disilyl alcohol with butyllithium in THF-$d_8$was monitored using variable temperature ^{29}Si NMR spectroscopy.

REACTIVITY OF TRIS(TRIMETHYLSILYL)PHOSPHITE (TMSP): CLEAVAGE OF α-LACTAMS (AZIRIDINONES)

Mobin Shazim, Jian Yang, Luis A. Vargas and Ralph Stephani, Queensborough Community College, Bayside, New York and St. John's University, Jamaica, New York

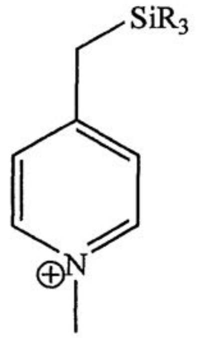
1(1-Adamantyl-3-tert-butylaziridinone **(1)** and 1,3-di-tert-butylaziridinone **(2)** were prepared and reacted with neat TMSP. Results from GC/MS analysis shows formation of silylated tert-butylphosphonic acid in both reactions and N-adamantylacetamide in the case of **1** and N-tert-butylacetamide in the case of **2**. The isolation and the characterization of products and the nature of the reaction will be discussed.

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF β-SILYLATED CARBENIUM IONS

Kathryn Hassall, Sofia Lobachevsky, Jonathan M. White.
School of Chemistry, University of Melbourne, 3010, AUSTRALIA

β-Silyl carbenium ions have long been of interest in organometallic chemistry. This interest arises from the high level of stability arising from the silicon β effect. However, previous attempts to directly observe otherwise unstabilised ions have been hindered by the facile desilylation of these species. We believe that if the rate of desilylation can be reduced, then the lifetime of the species can be increased to an extent that solution and perhaps solid-phase investigations of their structure can be carried out.

In this paper our studies on β-silyl carbenium ions with relatively low electron demand and bulky substituents on silicon are described. These cations include 2- and 4-substituted trialkylsilylsubstituted N-methyl pyridinium ions (1 and 2), trialkylsilylmethyl tropylium (3) and trialkylsilylmethyl cyclopropenium ions (4). Despite the low electron demand of these species, ^{1}H, ^{13}C and ^{29}Si NMR data in solution, and X-ray crystallographic data are consistent with strong hyperconjugation between the carbenium ion and the silicon substituent.



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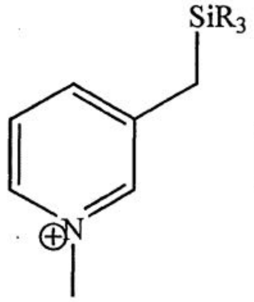

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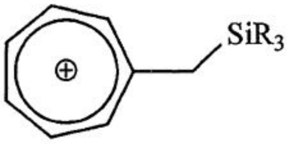

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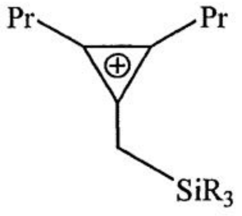
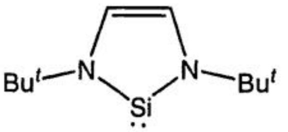


(4)

STILLE REACTIONS CATALYZED BY A SILYLENE-PALLADIUM COMPLEX

Kenneth Lassen, Michael Sangi, and Michael P. Haaf
Center for Natural Sciences, Ithaca College, Ithaca, NY 14850

Stable N-heterocyclic carbenes (**2**) represent an important new class of organometallic ligands, with electronic properties similar to those of some phosphines. These carbenes have been employed in place of phosphines in transition metal catalysts for reactions such as olefin metathesis and carbon-carbon bond forming reactions, in some cases providing superior catalysis. The success of N-heterocyclic carbenes as ligands in metal catalysts invites the study of catalytic properties of analogous silylene-metal complexes. Thus, the incorporation of a stable silylene (**1**) into metal complexes, and their subsequent application as catalysts in organometallic reactions has been a primary focus of our research.



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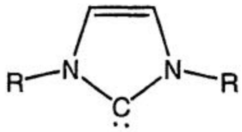


2

R = Bu^t, Mes, e.g.

The catalytic activity of a silylene-palladium complex (**3**) has been demonstrated by means of the Stille reaction (see reaction scheme below), a palladium-catalyzed reaction that affords new carbon-carbon bonds under remarkably mild reaction conditions. Model Stille reactions, employing traditional catalysts such as $Pd(PPh_3)_4$ have been performed and the yields and reaction rates have been compared to those obtained using compound **3** as the catalyst. In some cases, the latter catalyst affords higher yields of coupled product, with lower percentages of undesirable homocoupled products. Preliminary results will be summarized.

3 =

CATALYTIC HYDROSILYLATION EMPLOYING RUTHENIUM COMPLEXES CONTAINING AIR-STABLE PRIMARY AND SECONDARY PHOSPHINES

Shadrick I. M. Paris[1], Frederick Lemke*[1], Eva Hey-Hawkins[2]
[1]Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701
[2]Faculty of Chemistry and Minerology, University of Leipzig, Leipzig, Germany 04103

Metal-catalyzed hydrosilylation is of importance to the silicone industry. Currently, platinum catalysts reign in this area, although alternatives are being investigated. Of these, ruthenium is beginning to show promise, specifically in performing *trans*-addition hydrosilylation to both alkenes and alkynes. Tertiary phosphines allow for both steric and electronic control, but typically do not participate in the insertion process itself. The effect of primary and secondary phosphines on ruthenium-catalyzed hydrosilylation activity would be of great interest, however, few examples of ruthenium-phosphine systems containing primary or secondary phosphines are known. This lack of examples is due to the typical air-sensitivity associated with such ligands, but recently developed air-stable primary and secondary ferrocenylphosphines have opened up the possibility of synthesizing new and interesting complexes. Ruthenium complexes of the formula (p-cym)$RuCl_2PR_3$ (p-cym = *para*-cymene, PR_3 = PH_2CH_2Fc, PH_2Fc, $PH(CH_2Fc)_2$, PMe_3 and PPh_3, Fc = ferrocene) were synthesized and their reactivities towards hydrosilylation studied. The hydrosilylation activity and product distribution of the primary/secondary phosphine analogues were compared with those of the tertiary phosphine analogues. Preliminary data has shown a marked increase in hydrosilylation activity of phenylacetylene with dichloromethylsilane, the order of activity being $PH_2CH_2Fc > PH(CH_2Fc)_2 > PPh_3$ in C_6D_6 at 80 °C. All primary/secondary ruthenium-phosphine complexes are air-stable and have been fully characterized, including x-ray crystallography. The synthesis and reactivities of these complexes will be discussed in full.

RUTHENIUM CATALYZED HYDROSILYATION: SUBSTITUENT AND CONCENTRATION EFFECTS ON THE HYDROSILYLATION OF PHENYLACETYLENES

Nicholas M. Yardy, Shadrick I. M. Paris and Frederick R. Lemke*
Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701

$RuCl_2(PPh_3)_3$ has been observed to catalyze the hydrosilylation and dimerization of phenylacetylenes. The effects of silicon substituents and phenylacetylene substitution were determined. Hydrosilylation of phenylacetylenes was the major reaction observed with $HSiCl_2Me$, whereas with $HSiEt_3$ the major reaction was alkyne coupling. Hydrosilylation was favored as silicon alkyl groups were replaced with silicon chloride groups; however, hydrosilylation activity did drop with $HSiCl_3$. On the phenylacetylene side, a plot of phenylacetylene relative reactivity vs. Hammett σ_p indicated two factors at play: substituent electronegativity and substituent conjugation. The greatest reactivity was observed for *p*-$F_3CC_6H_4C{\equiv}CH$ followed by *p*-$ClC_6H_4C{\equiv}CH$, where the chloride is electronegative and can conjugate with the phenyl ring. The effects of reactant concentrations were also investigated. A linear relationship between the *cis/trans* ratio of β-silylstyrene and $1/[HSiX_3]$ was observed from hydrosilane concentration studies. Also observed was a decrease in the *cis/trans* ratio with increasing ruthenium loading while the *cis/trans* ratio increased with increasing phenylacetylene concentration. The substituent and concentration effects will be discussed with respect to the accepted mechanism for alkyne hydrosilylation.

Novel Process to Produce Organosilanes

Yong Zhang, Yuanyong Jin
Dalian Yuanyong Organosilicon Plant, Dalian, China, 116023

Reaction of chlorobenzene, magnesium and methyltrichlorosilane in the absence of solvents gave methylphenyldichlorosilane and methyldiphenylchlorosilane in 60% yields.

$PhCl+Mg$ _ $PhMgCl$

$PhMgCl+MeSiCl_3$ _ $MePhSiCl_2+MePh_2SiCl+MgCl_2$

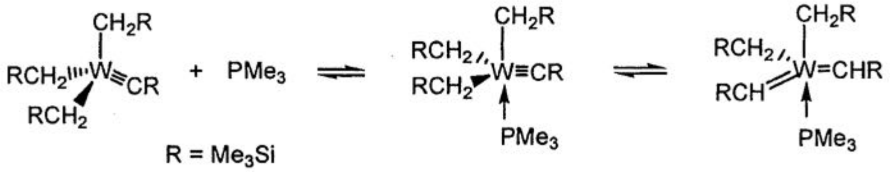
This method was economical process and was suitable for commercial producers. The effects of the molecular ratio of raw materials, initiation time and reaction temperature were discussed.

KINETIC AND THERMODYNAMIC STUDIES OF AN UNUSUAL PMe_3-INDUCED α-H MIGRATION - THE INTERCONVERSION $(Me_3SiCH_2)_3W(\equiv CSiMe_3)(PMe_3) \rightleftharpoons (Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_3)$

Laurel A. Morton, Xianghua Yu, Ziling (Ben) Xue
Department of Chemistry, University of Tennessee, Knoxville, TN 37996

We recently reported the equilibrium between silyl alkylidyne $(Ph_2Bu^tSi)(Bu^tCH_2)_2W\equiv CBu^t$ (**1**) and bis-alkylidene $(Ph_2Bu^tSi)(Bu^tCH_2)W(=CHBu^t)_2$ (**2**).[1] In the presence of PMe_3, alkyl alkylidyne complex $(Me_3SiCH_2)_3W\equiv CSiMe_3$ (**3**) forms a phosphine adduct $(Me_3SiCH_2)_3W(\equiv CSiMe_3)(PMe_3)$ (**4**). **4** undergoes an unusual phosphine-induced α-H migration to form a bis-alkylidene complex $(Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_3)$ (**5**). The bis(alkylidene) tautomer **5** is favored in the **4** $\rightleftharpoons$ **5** equilibrium with K_{eq} ranging from 12.3(0.2) at 278(1) K to 9.37(0.12) at 303(1) K, giving the thermodynamic parameters for the equilibrium: $\Delta H^o = -1.8(0.5)$ kcal/mol and $\Delta S^o = -1.5(1.7)$ eu. The α-H exchange between **4** and **5** follows first-order reversible kinetics. The activation parameters are $\Delta H^{\neq} = 16.2(1.2)$ kcal/mol and $\Delta S^{\neq} = -22.3(4.0)$ eu for the forward reaction (**4** → **5**), and $\Delta H^{\neq} = 18.0(1.3)$ kcal/mol and $\Delta S^{\neq} = -20.9(4.3)$ eu for the reverse reaction (**5** → **4**). Bis-alkylidene complexes are believed to be intermediates in alkyl-alkylidyne scrambling through α-H transfer in $(Bu^tCH_2)_3W\equiv CSiMe_3$ and $(Bu^tCH_2)_3W\equiv {}^{13}CCMe_3$. The **4** $\rightleftharpoons$ **5** equilibrium is a rare direct observation of a bis(alkylidene)-alkylidyne interconversion.

1. Chen, T.-N.; Wu, Z.-Z.; Li, L.-T.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.-J.; Guzei, I. A.; Rheingold, A. L.; Xue, Z.-L. *J. Am. Chem. Soc*, **1998**, *120*, 13519.

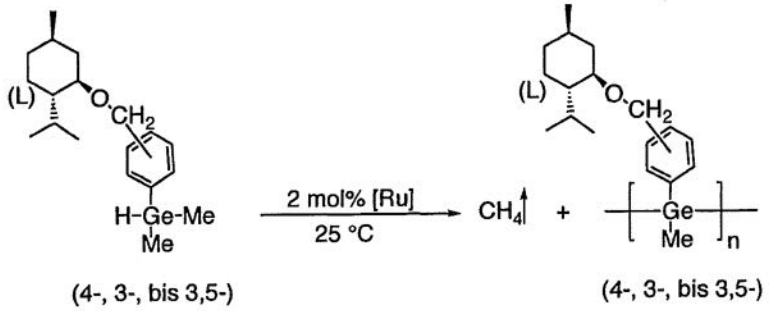


3 **4** **5**

SYNTHESIS AND CHARACTERIZATION OF SCREW SENSE HELICAL POLYGERMANES BEARING REMOTE CHIRAL GROUPS

Yisong Huo and Donald H. Berry*
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323
yisong@sas.upenn.edu

Poly(arylmethyl)germanes containing (*L*)-menthoxymethyl substitution on the aryl ring were synthesized via catalytic demethanative coupling and characterized by a variety of analytical and spectroscopic methods. Preferential screw sense (PSS) helical conformations of the polygermane backbones were revised by analysis of the circular dichroism (CD) spectra. Quite surprisingly, polygermanes containing the identical chiral group ((*L*)-menthoxymethyl) in *meta*- and *para*-positions exhibited opposite PSS conformations with different intensities. This result indicates that large chiral menthoxy groups have a significant effect on the interaction between the neighboring repeating units.



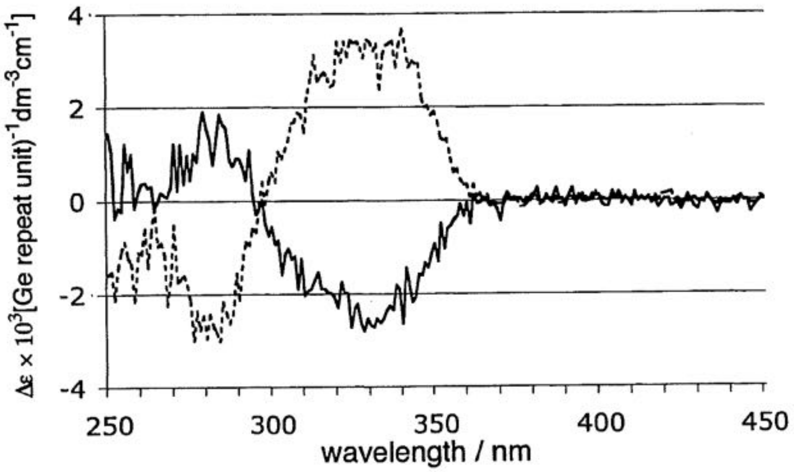
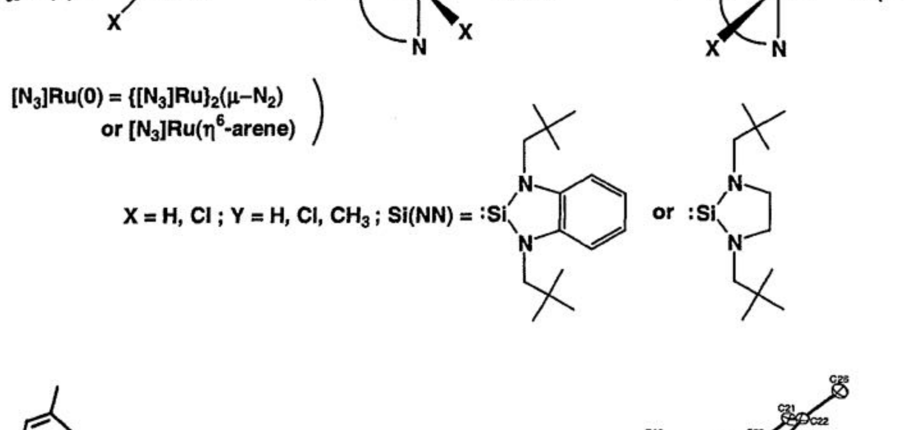


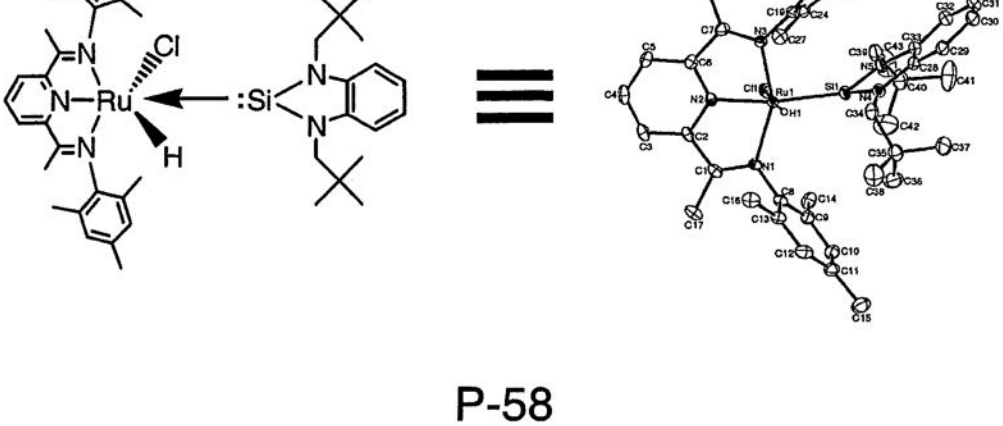
Fig. CD Spectra ------ 3-, substitution ——— 4-, substitution

SYNTHESIS AND STRUCTURE OF RUTHENIUM-SILYLENE COMPLEXES : TWO - STEP ACTIVATION OF N-HETEROCYCLIC SILANES

Hyojong Yoo, Patrick J. Carroll, and Donald H. Berry*
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323
hyojong@sas.upenn.edu

A new class of Ru(0) complexes, $[N_3]Ru(\eta^6\text{-}Ar)$ and $([N_3]Ru)_2(\mu\text{-}N_2)$, where Ar = C_6H_6 or C_6H_5Me, and $[N_3]$ = 2,6-$(MeslN{=}CMe)_2C_5H_3N$, react with N-heterocyclic silane compounds, which can be precursors to silylene complexes. A two-step activation of the silane substrates involving initial oxidative addition of the Si-X bond, followed by a 1,2-migration of the Y group gives various ruthenium silylene complexes of the type $[N_3]Ru(X)(Y){\leftarrow}Si(NN)$, (X = H, Cl; Y = H, Cl, CH_3, and Si(NN) = N,N'-bis(neopentyl)-1,2-phenylenedi(amino)silylene). For example, reaction of these Ru(0) complexes with (H)(Cl)Si(NN) yields the novel ruthenium silylene, $[N_3]Ru(H)(Cl){\leftarrow}Si(NN)$, which has been structurally characterized. These complexes may also prove to be useful in catalytic transformations in organosilicon reactions. Other N-heterocyclic silanes were also tried to yield various ruthenium silylene complexes and to gain knowledge of their stabilities and properties. The mechanism of formation and reaction chemistry of the silylene complexes will be discussed.

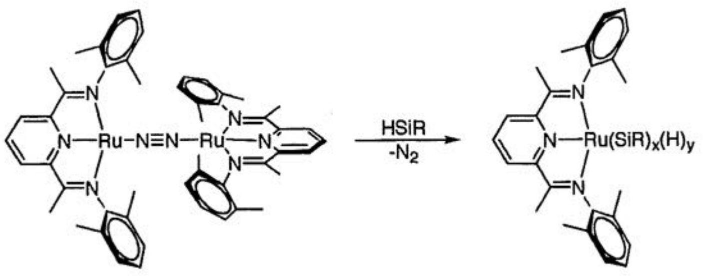




REACTIVITY OF ORGANOSILANES WITH LOW VALENT RUTHENIUM COMPLEXES BEARING TRIDENTATE PYRIDYL LIGANDS

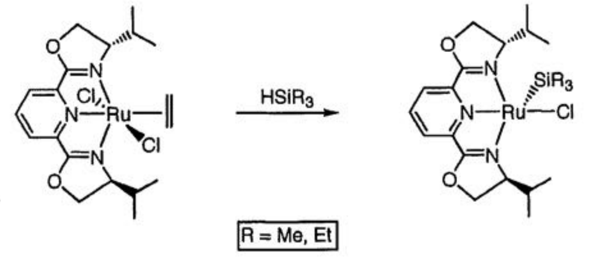
Michelle Gallagher, Noah Wieder, Patrick J. Carroll and Donald H. Berry*
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

A new class of low valent ruthenium complexes containing only nitrogen-based ligands has been developed. These complexes exhibit high reactivity towards a variety of organic and main group substrates. A series of ruthenium(0) complexes bearing 2,6-bis(imino)pyridyl ligands has been synthesized and characterized. Reduction of $[N_3^{xyl}]RuCl_2(C_2H_4)$ or $[{}^tBu\text{-}N_3^{mes}]RuCl_2(C_2H_4)$, where $[N_3^{xyl}] = [2,6\text{-}(XylN{=}CMe)_2C_5H_3N]$ and $[{}^tBu\text{-}N_3^{mes}] = [2,6\text{-}(MesN{=}CMe)_2\,p\text{-}{}^tBuC_5H_2N]$, with hydrido silanes in an arene solvent (toluene, benzene) yields new $[N_3]Ru(\eta^6\text{-arene})$ complexes, **1a – 1c** (**1a** = $[N_3^{xyl}]Ru(\eta^6\text{-}MeC_6H_5)$; **1b** = $[N_3^{xyl}]Ru(\eta^6\text{-}C_6H_6)$; **1c** = $[{}^tBu\text{-}N_3^{mes}]Ru(\eta^6\text{-}MeC_6H_5)$). The coordinated arene ligand can be displaced with dinitrogen to yield the dimeric Ru(0) complexes $\{[N_3]Ru\}_2(\mu\text{-}N_2)$, **2a** and **2b** (**2a** = $\{[N_3^{xyl}]Ru\}_2(\mu\text{-}N_2)$; **2b** = $\{[{}^tBu\text{-}N_3^{mes}]Ru\}_2(\mu\text{-}N_2)$). Reaction of these Ru(0) complexes with hydrido silanes leads to the formation of various oxidative addition products, as well as novel silylene dihydride complexes (eq 1). In contrast, reaction of hydrido silanes with a ruthenium complex bearing a chiral pybox ligand, $[N_3^{ip\text{-}pybox}]RuCl_2(C_2H_4)$ (**3**), where $[N_3^{ip\text{-}pybox}]$ = 2,6-Bis[4′-(S)-isopropyloxazolin-2′-yl]pyridine, leads to the formation of stable 16 electron ruthenium silyl chlorides (eq 2). Attempts to reduce complex **3** with dialkylsilanes produce silyl oligomers with concurrent formation of ethane and silyl redistribution products. The mechanisms of these transformations and the stoichiometric reactions of these complexes will be discussed.



(1)

R = Me₃, Et₃, Me₂H, Et₂H, ᵗBu₂H, ᵗBu₂Cl



(2)

R = Me, Et

BIOLOGICAL TEMPLATES FOR PATTERNING OF NOVEL METAL NANOPARTICLES

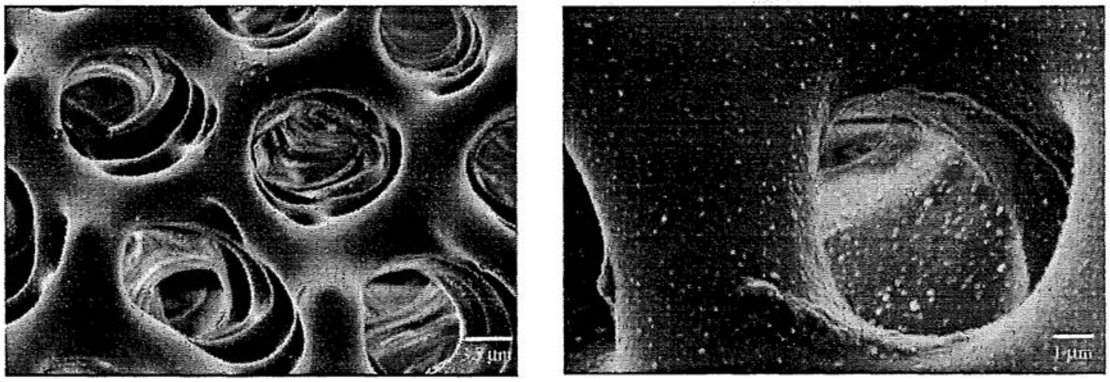
Bhanu P. S. Chauhan* and Adriana Vela

Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry, City University of New York at The College of Staten Island, 2800 Victory Boulevard, Staten Island, New York 10314

Templates of biological origins are known to affect the structure of the minerals formed therein. There are only a few examples in which templates of biological origin have been exploited for the preparation of nanostructured materials. To the best of our knowledge, no one has reported the effects of particle deposition and structure of nanoparticle formation in biological templates such as *sea urchins*. In this research we seek to provide much needed fundamental information on nanoparticle formation and self-assembly in naturally occurring biological templates and in their polymer replicas. The nanoparticles formed in biological templates and in their polymeric replicas may have unique electrical and photonic properties, which could be exploited for device and sensor construction.

In this presentation we will disclose our results on the structure of sea urchins and diatoms and their conjugation with metallic nano-particles. Gold, silver and platinum nano-particles were synthesized by different methods leading to particles of different size and morphology. The interaction of silver and platinum nano-particles with sea urchin shells has been analyzed and will be discussed in depth along with the preliminary results concerning the conjugation of gold nano-particles and diatoms. Our results indicate that agglomeration of the nano-structured particles is successfully prevented and stable under atmospheric conditions.

Sea Urchin Pores Nucleated with Silver Nanoparticles



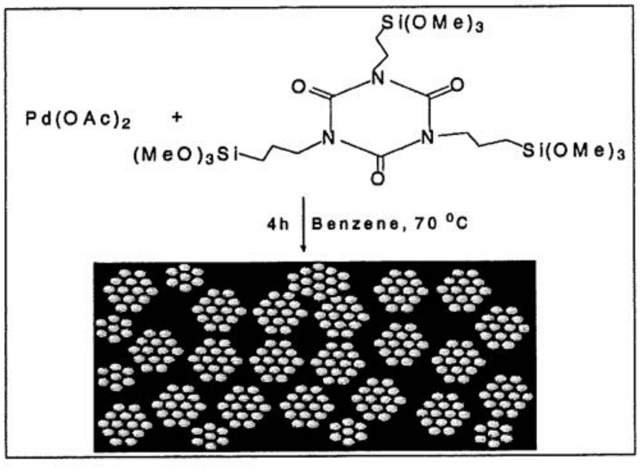
SILICON BASED TEMPLATES FOR SYNTHESIS AND STABILIZATION NANOSIZED NOVEL METAL PARTICLES

Moni Chauhan,*[a] Richard Pantano,[a] Jitendra S. Rathore[b] and Bhanu P. S. Chauhan*[b]

[a] *Department of Chemistry, City University of New York at the Queensborough Community College, Bayside, New York 11364*
[b] *Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry and Graduate Center, City University of New York at The College of Staten Island, 2800, Victory Boulevard, Staten Island, New York 10314*

Nanometer-sized particles of metals and semiconductors have been investigated intensively because of their size-dependent properties and the possibility of arranging them in micro assemblies (and nano assemblies). Nanosized metal particles possess unique chemical and physical properties that can be exploited in a wide variety of technological applications, including catalysis, nonlinear optics ultra-purification and microelectronics.

One of the design strategies that has shown tremendous potential as a viable route by which to produce metal nanoparticles with improved size control and colloidal stability is to employ polymeric matrixes as the form of growth media.[1] In this presentation, we will disclose a new approach to synthesis and stabilization of nanosized Pd particles. Our synthetic design is based on the need to generate catalytically active nonpassivated nanoparticles under mild reaction conditions and high yield. In this novel approach, cyclic siloxyisocynoureates are utilized to accomplish duel function of macromolecular stabilizing template as well as reducing agents. The details of synthetic design, nanoparticle properties and their catalytic activity will also be discussed.



Chauhan, B. P. S.; Rathore, J. S.; Chauhan, M.; Krawichz, A. *J. Am. Chem. Soc.* **2003**, *125*, 2876-2877.

POLY(METHYLHYDROSILOXANE) DIRECTED SYNTHESIS OF SELF-ASSEMBLED NANOSIZED SILVER NECKLACES

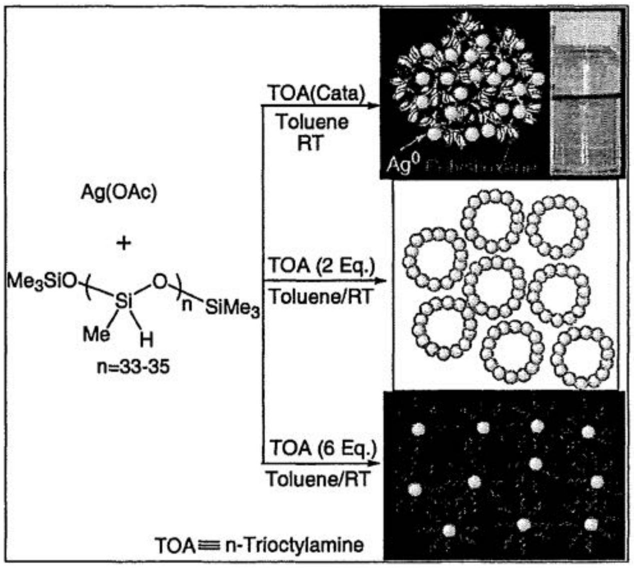
Bhanu P. S. Chauhan*, Rajesh Sardar and Prashant Sharma

Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry and Graduate Center, City University of New York at The College of Staten Island, 2800, Victory Boulevard, Staten Island, New York 10314

Silver nanoparticles are of great interest due to their role in photographic processes, their utility as substrates for surface-enhanced Raman spectroscopy (SERS) and also due to their application in catalysis. Silver nanocrystallites, mostly hydrosols, have been widely studied because of the ease of their preparation. On the other hand colloidal dispersions of silver in nonaqueous liquids (organosols) are rare and more difficult to prepare and stabilize. In this context it is desirable to develop synthetic strategies to fabricate nanoparticles, which provide flexibility to functionalize nanoparticles according to the need hence tailoring of nanoparticle surfaces. Moreover, for catalytic applications such conjugates may have superior activity and selectivity over the nanoparticles passivated by strong coordinating ligands.

Monomeric hydrosilanes are known reducing agents and have been used for the generation of Pt, Pd, and Rh nano-sized particles. On the other hand, investigations of polymeric analogous such as polyhydrosilanes as reducing agents for the generation and in-situ stabilization of nanosized metal particles have not been explored. Though, their property profile may provide the means of directing metallic particles into specific physicochemical environments in addition to their utility as reducing agents. Moreover, combining the ease of processability of polysiloxane polymers with the improved mechanical and optical properties of metal nanoparticles is of practical use for the fabrication of many new devices.[9b]

In this communication, we describe a versatile method and first example of polyhydrosiloxane induced generation and stabilization of functionalizable monodisperse silver sols (Scheme). This method enables routine formation of stable nanosilver reservoirs avoiding particle aggregation during the storage as well as nucleation and growth process. We also demonstrate the utility of such reservoirs in grafting the surface properties of nanosized silver particles by exchange reactions with trioctylamine.



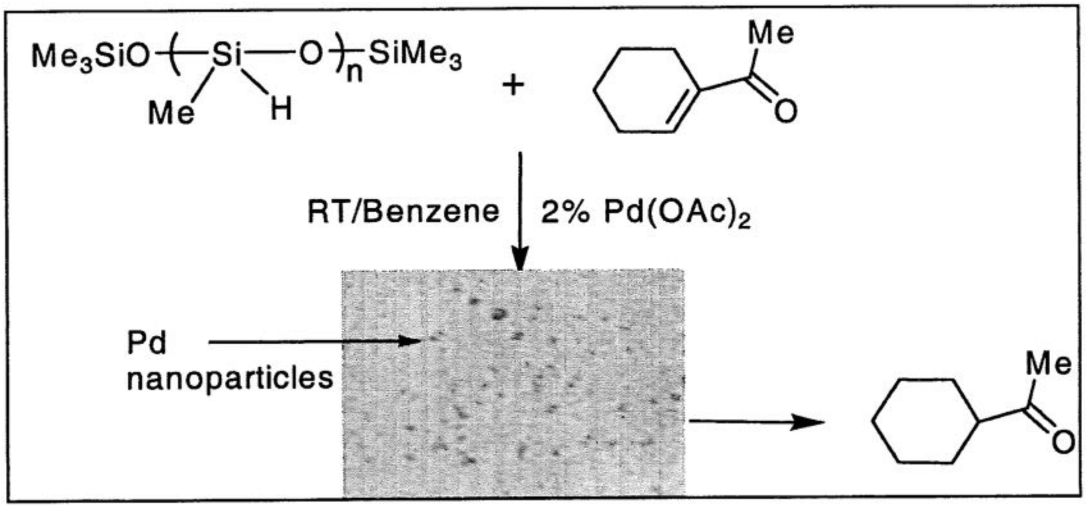
HIGHLY CHEMOSELECTIVE HYDROGENATION CATALYSTS BASED ON "SILICONES-Pd" NANOCONJUGATES

Bhanu P. S. Chauhan*, Jitendra Rathore and Tariq Bandoo

Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry and Graduate Center, City University of New York at The College of Staten Island, 2800, Victory Boulevard, Staten Island, New York 10314

The search for more efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis is one of the most exciting challenges of modern chemistry. Chemoselective hydrogenation of conjugated alkenes is an important class of reaction used extensively in petroleum and vegetable oil industry. In a recent report by our group, we evidenced Polysiloxane stabilized "Pd" colloids as potent catalyst for silaesterification of siloxane polymers.[2] These colloids display the advantage of better selectivity, activity and recyclability.

In this communication, we describe a new approach to one pot, highly efficient chemoselective hydrogenation of conjugated alkenes. This strategy involves polyhydrosiloxane as hydrogen source for reduction of alkenes as well as stablilizing agents for catalytically active "Pd" nanoclusters (See Scheme). Controlled poisoning experiment in conjunction with electron microscopy studies confirm "Pd" nanoclusters as the real catalytic species. "Pd-polysiloxane conjugates" offer selectivity of homogeneous catalyst and activity as well as recyclability of heterogeneous catalysts.



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[1] B. P. S. Chauhan, J. S. Rathore, and Tariq Bandoo, *J. Am. Chem. Soc.* **2004**, 000 (Submitted for Publication)

[2] B. P. S. Chauhan, J. S. Rathore, M. Chauhan and A. Krawicz *J. Am. Chem. Soc.* **2003**, *125*, 2876

NANOCLUSTER CATALYZED MACROMOLECULAR GRAFTING VIA HYDROSILYLATION REACTIONS

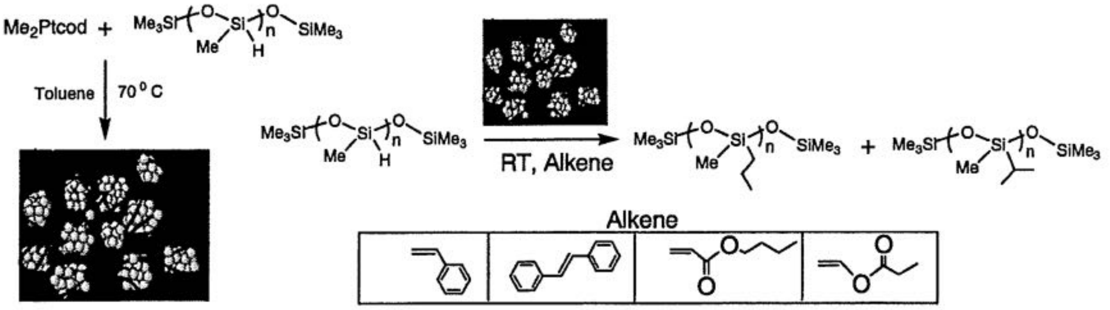
Bhanu P. S. Chauhan,* Jitendra S. Rathore, Alok Sarkar and Naim Galloxhani

Polymers and Engineered Nanomaterials Laboratory, Department of Chemistry and
Graduate Center, City University of New York at The College of Staten Island,
2800, Victory Boulevard, Staten Island, New York 10314

Metallic colloids find extensive application in the field of catalysis. Metal nanoparticles show enhanced efficiency and improved selectivity for various important conversions. Formation of silicon-carbon bond by the hydrosilylation of alkenes is an important synthetic tool for variety of useful carbo-silicon compounds. Establishing the exact nature of catalyst during hydrosilylation, has been the area of intensive study.

In this communication, we report polyhydrosilxane-induced generation and stabilization of Pt-nanoclusters and their utility in hydrosilylation catalysis. "Pt" colloids were generated by the polymethylhydrosiloxane (PMHS) reduction of platinumdimethylcyclooctadiene [Pt(COD)Me_2]. The reduction in presence of PMHS permits stabilization of Pt nanoparticles. "Pt" colloids supported on polysiloxane matrix were characterized by EM (electron microscopy) and NMR techniques. Our method enables routine formation of stable nanometallic pools avoiding particle aggregation during the storage as well as catalytic process. We also demonstrate the utility of Pt-reservoirs in hydrosilylation reactions of oligo- and polymeric siloxanes and present strong evidence of their participation in catalysis. We will address the questions related to the identity of real catalysts of hydrosilylation process in general.

Generation and catalytic application of "Pt"-Nanoclusters



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* Corresponding Author; Email: chauhan@postbox.csi.cuny.edu; Phone: (718)-982-3902; (718)-982-3910

TRANSIENT SPECTROSCOPY OF RADICAL CATIONS OF A VARIETY OF SUBSTITUTED POLYSILANES

S. Seki, Y. Koizumi, T. Kawaguchi, H. Habara, and S. Tagawa

ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Despite positive charge being the dominant charge carriers in the transport process, there have been few dynamics or quantitative analyses on the electronic state of positive charges on the Si chain other than by transient spectroscopy [1-3] or electron spin resonance [4]. Localization of the charge carriers was revealed to be suppressed in the polysilanes bearing bulky pendant groups, suggesting not only that the localization in typical dialkyl polysilanes arises from the flexibility of Si catenation, but also that delocalization occurs in polysilanes with stiff or rod-like Si skeletons. However, the quantitative correlation between the molecular stiffness and the degree of positive charge delocalization had not been elucidated to date.

The present paper reports on the direct observation of polysilane radical cations by pulse radiolysis. Pulse-radiolysis transient absorption spectroscopy (PR-TAS) is a very powerful and useful technique for achieving the selective formation of radical ions in matrices (solvents) and tracing reaction kinetics. To date, quantitative tracing of polysilane radical cations has been very difficult because of their very low ionization potentials (< 6 eV) and complicating side reactions. Recent improvements in our transient spectroscopy system have made it possible to probe dilute solutions of transient species with a very high signal-to-noise (S/N) ratio [3]. This paper reports the molar extinction coefficient and oscillator strength of polysilane radical cations determined by both spectroscopic techniques and an efficient charge transfer reaction between polysilane radical cations and *N,N,N',N'*-tetramethyl-*p*-phenylene-diamine (TMPD). Based on the molar extinction coefficient of the TMPD radical cation, the molar extinction coefficients for the radical cations of polysilanes are found to increase in the range $3.3 \times 10^4 - 2.0 \times 10^5$ M^{-1} cm^{-1} with increasing polymer segment length. The stepwise increase in the total oscillator strength with an increase in the number of phenyl rings directly bonded to the Si skeleton suggests the delocalization of the positive polaron state and/or the SOMO state over the phenyl rings, indicating the importance of phenyl rings in intermolecular hole transfer processes.

Reference: 1) S. Seki, et al., *J. Am Chem Soc.*, 2004, **126**, 3521, 2) T. Kawaguchi, et al, *Chem. Phys. Lett.* 2003, **374**, 353., 3) S. Seki, et al., *Macromolecules* 1999, **32**, 1080.

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