



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Volume 686, Issues 1–2, 21 November 2003

Journal
of Organo
metallic
Chemistry

www.elsevier.com/locate/jorgchem

Contents

Special Issue: What's New in Silicon Chemistry

Preface 1

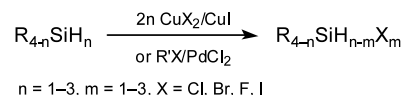
Accounts

Atsutaka Kunai, Joji Ohshita

J. Organomet. Chem. 686 (2003) 3

Selective synthesis of halosilanes from hydrosilanes and utilization for organic synthesis

Selective synthesis of halosilanes has been examined. Various types of halosilanes and halohydrosilanes, such as R_3SiX , R_2SiHX , R_2SiX_2 , $RSiH_2X$, $RSiHX_2$ ($X = Cl, Br, F$), were obtained by the reactions of the corresponding hydrosilanes with Cu(II)-based reagents selectively in high yields. Iodo- and bromosilanes and germanes were obtained by Pd- or Ni-catalyzed hydride–halogen exchange reactions of hydrosilanes with alkyl or allyl halides. Their synthetic applications have been demonstrated by using iodossilanes, bromosilanes, and chlorofluorosilanes.

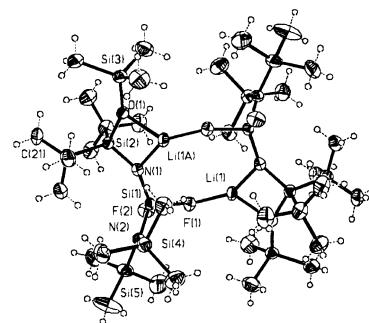


Susanne Kliem, Uwe Klingebiel, Stefan Schmatz

J. Organomet. Chem. 686 (2003) 16

Intramolecular rearrangement of organosilyl groups between oxygen and nitrogen in aminosiloxanes: A joint experimental–theoretical study

Lithium salts of 1-amino-siloxanes form, depending on the properties and bulkiness of the silyl groups, 1,3-disilylamino-1-olates or 1-amido-1,3-disiloxanes. The second case includes a 1,3-silyl group migration from oxygen to the nitrogen atom. In order to understand the driving force of the isomerization, we isolated single crystals of the lithium derivatives and calculated the energies of isomeric lithium salts of model compounds.

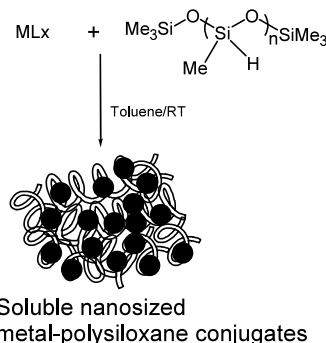


Bhanu P.S. Chauhan, Jitendra Rathore, Rajesh Sardar, Pankaj Tewari, Umar Latif

J. Organomet. Chem. 686 (2003) 24

Synthesis, stabilization, and applications of nanoscopic siloxane–metal particle conjugates

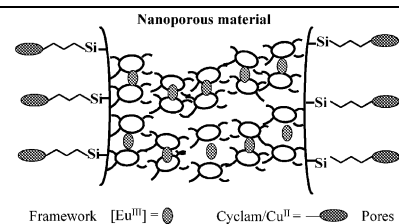
Facile conversion of metallic salts to stable nanosized metal particles is achieved under mild conditions in high yields. An examination of the effects of physicochemical and morphological property profile of polysiloxanes in controlling nucleation, growth, and stabilization of nanoparticles was undertaken. The results indicate the promise for new opportunities in nanoscale synthesis of metal particles, in addition, to possibilities of carrying out facile surface tailoring reactions.



Robert Corriu*J. Organomet. Chem.* 686 (2003) 32

Organosilicon chemistry and nanoscience

Nanosciences are opening a wide future to chemistry and particularly to organosilicon chemistry, the flexibility of which is particularly well adapted to the design of materials. However, in this scope the chemists have to 'think' their chemistry in terms of properties (physical, chemical, biological...).

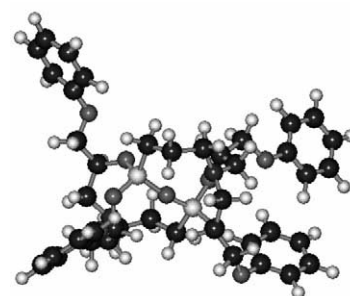
**Regular Papers**

Ignacio E. dell' Erba, Diana P. Fauce, Roberto J.J. Williams, Rosa Erra-Balsells, Yuko Fukuyama, Hiroshi Nonami

J. Organomet. Chem. 686 (2003) 42

Poly(silsesquioxanes) derived from the hydrolytic condensation of organotrialkoxysilanes containing hydroxyl groups

The hydrolytic condensation of organotrialkoxysilanes containing secondary hydroxyl groups led to a narrow distribution of OH-functionalized polyhedral oligomeric silsesquioxanes. The generation of closed structures was ascribed to the reversible formation of intramolecular cycles through Si–O–C bonds. Under appropriate conditions, structures containing these cycles were present in high concentrations.

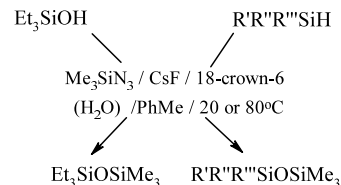


Ramona Abele, Edgars Abele, Mendel Fleisher, Solveiga Grimberga, Edmunds Lukevics

J. Organomet. Chem. 686 (2003) 52

Novel fluoride ion mediated synthesis of unsymmetrical siloxanes under phase transfer catalysis conditions

Unsymmetrical siloxanes have been prepared from silanols or hydrosilanes using phase transfer catalytic (PTC) systems Me_3SiN_3 –CsF–18-crown-6–toluene or Me_3SiN_3 –CsF–18-crown-6– H_2O –toluene, correspondingly. Quantum chemical calculations of mechanism have been performed.

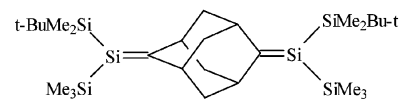


Dmitry Bravo-Zhivotovskii, Gady Korogodsky, Yitzhak Apeloig

J. Organomet. Chem. 686 (2003) 58

Synthesis of the first long-lived bis-silene

The first long-lived bis-silene *t*-BuMe₂Si(Me₃Si)Si=(2,6-Ad)=Si(SiMe₃)SiMe₂Bu-*t* (**1**) and the related transient bis-silene (Me₃Si)₂Si=(2,6-Ad)=Si(SiMe₃)₂ were synthesized by a sila-olefination reaction, i.e. by the reaction of the corresponding branch polysilyllithium compounds with adamantane-2,6-dione. The proposed structure of *t*-BuMe₂Si(Me₃Si)Si=(2,6-Ad)=Si(SiMe₃)SiMe₂Bu-*t* was secured by ¹H-, ¹³C-, and ²⁹Si-NMR spectroscopy and by isolation of the corresponding trapping products when **1** was reacted with methanol and 1-methoxy-1,3-butadiene.

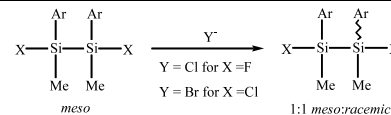


**Kevin A. Trankler, Joyce Y. Corey,
Nigam P. Rath**

J. Organomet. Chem. 686 (2003) 66

Halide induced epimerization of *meso*-1,2-dihalo-1,2-diaryl-1,2-dimethyldisilanes

The 1,2-difluorodisilane, *meso*-F[(*p*-CF₃C₆H₄)MeSi]₂F, was prepared and crystallographically characterized. Kinetic data were obtained for the halide induced epimerization of *meso*-X[(*p*-RC₆H₄)MeSi]₂X (halide = Cl⁻ where X = F, R = H, CH₃O, CH₃, F, CF₃; halide = Br⁻ where X = Cl, R = H) to a 1:1 *meso:racemic* mixture of diastereomers and possible mechanisms are discussed.

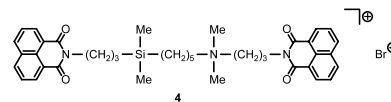


Seraina Duda-Johner, Jürgen O. Daif, Klaus Mohr, Reinhold Tacke

J. Organomet. Chem. 686 (2003) 75

Synthesis and pharmacological characterization of new silicon-based W84-type allosteric modulators for ligand binding to muscarinic M₂ receptors

The synthesis and pharmacological characterization of novel silicon-based allosteric modulators for ligand binding to muscarinic M₂ receptors is reported. These compounds bear one phthalimido and one 1,8-naphthalimido moiety (or two 1,8-naphthalimido moieties) as lateral residues, which form the termini of a 4-azonia-10-silatridecane backbone (such as compound **4**), which, together with the use of a silicon atom within this backbone, leads to unique pharmacological properties that are atypical of allosteric modulators of the W84-type.

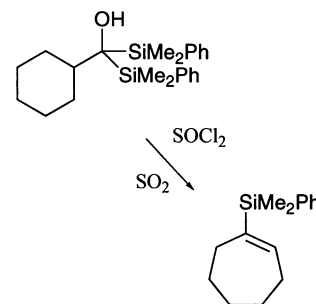


Alain Chénéde, Ian Fleming, Roger Salmon, Mark C. West

J. Organomet. Chem. 686 (2003) 84

Cationic rearrangements controlled by the presence of a silyl group

1,1-Disilylcarbinols having two alkyl groups on the adjacent carbon atom react with thionyl chloride in sulfur dioxide to give the product in which one of the alkyl groups has migrated towards the two silyl groups, and one of the silyl groups has been removed from the resultant cation.

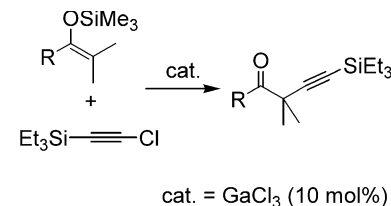


Ryo Amemiya, Akiko Fujii, Mieko Arisawa, Masahiko Yamaguchi

J. Organomet. Chem. 686 (2003) 94

GaCl₃-catalyzed α -ethynylation reaction of silyl enol ethers

10 mol.% of GaCl₃ catalyzes α -ethynylation reaction of silyl enol ethers with triethylsilylated chloroethyne. The reaction is considered to involve addition/elimination of gallium enolate to chloroacetylene.

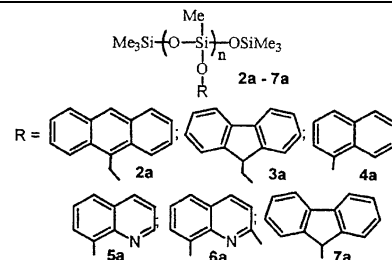


Irina Touloukhonova, Ben Bjerke-Kroll, Robert West

J. Organomet. Chem. 686 (2003) 101

Synthesis and photophysical properties of novel fluorescent silicones

Polymers **2a–7a** were prepared and their absorption and emission spectra were studied; emission from both monomer and excimer states appears to take place. The emission spectra of polymers **2a–7a** also show strong dependence from solvent and the excitation wavelength applied during recording.

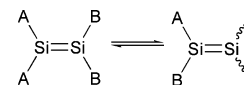


Takeaki Iwamoto, Junichiro Okita, Chizuko Kabuto, Mitsuo Kira

J. Organomet. Chem. 686 (2003) 105

Synthesis, structure and isomerization of $A_2Si=SiB_2$ -type tetrakis(trialkylsilyl)disilenes

Two novel $A_2Si=SiB_2$ -type tetrakis(trialkylsilyl)disilenes, which were synthesized applying a silametallation route, have a twisted $Si=Si$ double bond with a planar arrangement around each of the unsaturated silicon atoms in the solid state. The twist angle was $27.95(3)^\circ$ for a highly congested disilene. The facile formal dyotropic rearrangement of a tetrasilyl disilene was investigated NMR spectroscopically.



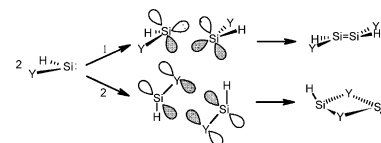
A = *t*-BuMe₂Si
B = *i*-Pr₂MeSi or *i*-Pr₃Si

Julianna Oláh, Tamás Veszprémi

J. Organomet. Chem. 686 (2003) 112

Relationship between stability and dimerization ability of silylenes

The dimerization energy for disilene formation correlates with the stabilization energy of silylenes. No correlation can be found, however, in the case of bridged dimer formation.

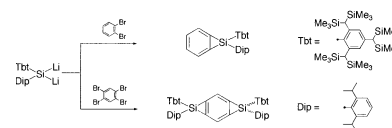


Tomoyuki Tajima, Ken Hatano, Takayo Sasaki, Takahiro Sasamori, Nobuhiro Takeda, Norihiro Tokitoh, Nozomi Takagi, Shigeru Nagase

J. Organomet. Chem. 686 (2003) 118

Syntheses and structures of silicon analogues of cyclopropabenzenes

The reaction of diaryldilithiosilane, Tbt-(Dip)SiLi₂ (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl; Dip = 2,6-diisopropylphenyl), with *o*-dibromobenzene and 1,2,4,5-tetrabromobenzene resulted in the synthesis and isolation of the first stable silacyclopropabenzene and bis(silacyclopropa)benzenes, respectively. The molecular structures of these silacyclopropabenzene derivatives were discussed on the basis of the X-ray structural analyses and theoretical calculations.

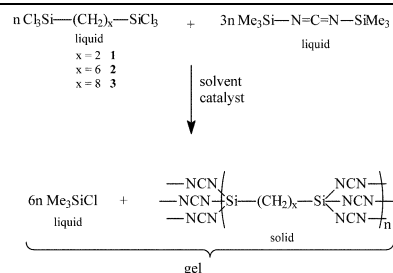


Saifun Nahar-Borchert, Edwin Kroke,
Ralf Riedel, Bruno Boury,
Robert J.P. Corriu

J. Organomet. Chem. 686 (2003) 127

Synthesis and characterization of alkylene-bridged silsesquicarbodiimide hybrid xerogels

Hybrid polymers consisting of flexible organic chains within an inorganic silsesquicarbodiimide network of the type $[(\text{NCN})_{1.5}\text{Si}(\text{CH}_2)_x\text{Si}(\text{NCN})_{1.5}]_n$ (where $x = 2, 6,$ and 8) were prepared by mild sol-gel polycondensation reactions of bis(trichlorosilyl)alkanes and bis(trimethylsilyl)carbodiimide. The presence of the NCN groups in xerogel structures was identified by FTIR spectra.

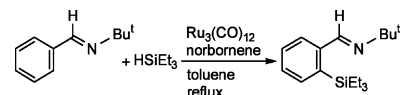


Fumitoshi Kakiuchi, Mitsutaka Matsumoto,
Kazuyuki Tsuchiya, Kimitaka Igi,
Tomoo Hayamizu, Naoto Chatani,
Shinji Murai

J. Organomet. Chem. 686 (2003) 134

The ruthenium-catalyzed silylation of aromatic C-H bonds with triethylsilane

The $\text{Ru}_3(\text{CO})_{12}$ -catalyzed silylation of aromatic and heteroaromatic compounds with triethylsilane gave the corresponding silylation products in good to excellent yields. The deuterium-labeling experiment using phenyloxazoline- d_5 indicates that C-H bond cleavage is not the rate-determining step and that a rapid equilibrium prior to C-Si bond formation occurs in this catalytic reaction.

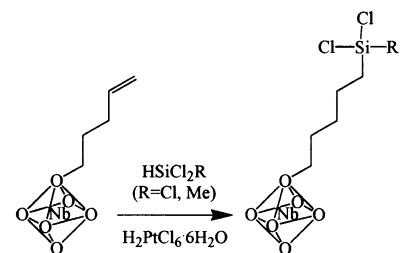


Satoru Yoshioka, Yosuke Takeda,
Yuko Uchimaru, Yoshiyuki Sugahara

J. Organomet. Chem. 686 (2003) 145

Hydrosilylation in the 2D interlayer space between inorganic layers: reaction between immobilized C=C groups on the interlayer surface of layered perovskite $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ and chlorohydrosilanes

The C=C bonds immobilized in the interlayer space of layered perovskite, $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, have undergone hydrosilylation reactions with chlorohydrosilanes, dichloromethylsilane or trichlorosilane. The treatment of the $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{O}$ -derivative of $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ with dichloromethylsilane or trichlorosilane leads to the interlayer distance increase to 2.41 (dichloromethylsilane) or 2.07 (trichlorosilane) nm. Solid-state ^{13}C -CP/MAS-NMR and IR spectroscopies reveal the occurrence of hydrosilylation.

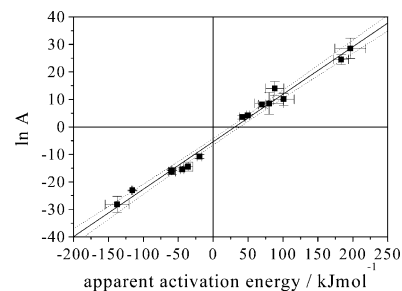


Jörg Acker, Klaus Bohmhammel

J. Organomet. Chem. 686 (2003) 151

Compensation effect in trichlorosilane synthesis

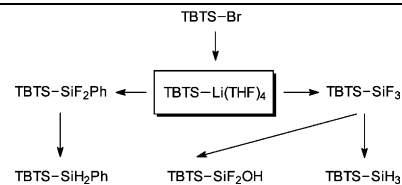
In a recent publication [J. Acker, K. Bohmhammel, *J. Phys. Chem. B* 106 (2002) 5105], the reactions between transition metal silicides and hydrogen chloride were studied by isothermal calorimetric measurements. The obtained apparent activation energies and pre-exponential factors show clearly a linear dependence that is attributed to the compensation effect.



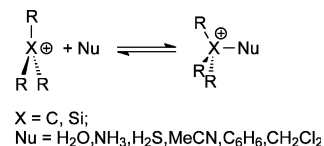
H. Reinke, C. Krempner*J. Organomet. Chem.* 686 (2003) 158

Synthesis and reactivity of a novel oligosilyl anion

TBTS–Li(THF)₄ {TBTS = Si[Si(SiMe₃)₂Me]₃} a novel sterically overcrowded oligosilyl anion has been prepared. This highly reactive compound can be used for the selective synthesis of a series of TBTS substituted silicon compounds in high yields. The controlled hydrolysis of TBTS–SiF₃ gave the first incompletely hydrolyzed stable silanol TBTS–SiF₂OH.

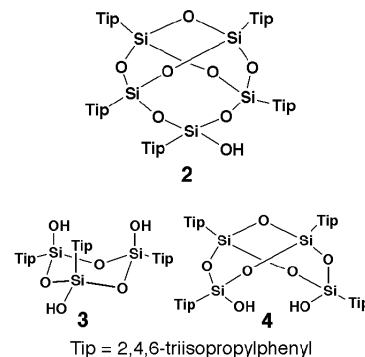
**Marek Cypryk***J. Organomet. Chem.* 686 (2003) 164Comparison of steric hindrance in silylenium and carbenium cations and their complexes
Natural steric analysis

Steric effect in the complexes of tri-coordinate silylenium and carbenium ions with model nucleophiles is discussed based on the calculated energies of complex formation and on the natural steric analysis (a part of the NBO theory).

**Masafumi Unno, Toshihiko Tanaka, Hideyuki Matsumoto***J. Organomet. Chem.* 686 (2003) 175

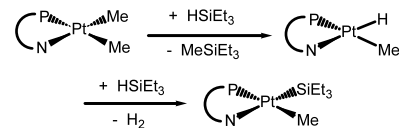
Tip-substituted cage and cyclic silanols

Novel silanols were obtained from Tip–Si(OH)₃ (**1**, Tip = 2,4,6-triisopropylphenyl). Condensation of **1** using 2-chloro-1,3-dimethylimidazolium chloride gave (TipSi)₅O₆OH. The reaction of **1** with (TipSiCl₂)₂O (**5**) gave *cis,trans*-cyclotrisiloxane-triol (TipSi(OH)O)₃ (**3**) and **4**. Dehydrochlorinative condensation of **5** and (TipSi(OH)₂)₂O afforded **4**. The packing diagram showed **3** composes a nano-size wire by intermolecular hydrogen bonding.

**Susan M. Thompson, Frank Stöhr, Dietmar Sturmayer, Guido Kickelbick, Ulrich Schubert***J. Organomet. Chem.* 686 (2003) 183

Reaction of hydrogenosilanes with dimethyl Pt(II) complexes promoted by hemilabile P,N-chelating ligands

Reaction of [(κ²-P,N)–Me₂N(CH₂)₃PPh₂]PtMe₂ [(P∩N)PtMe₂] with HSiEt₃ or HSiMePh₂ results in the formation of MeSiR₃ and the methyl silyl complexes (P∩N)Pt(Me)SiR₃ via the hydrido complex (P∩N)Pt(Me)H.

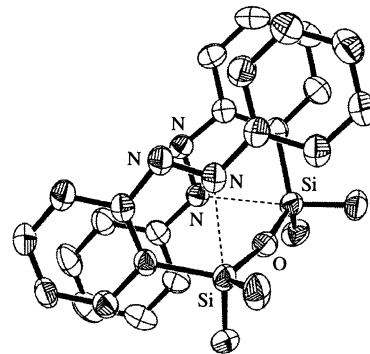


**Naokazu Kano, Masaki Yamamura,
Fuminori Komatsu, Takayuki Kawashima**

J. Organomet. Chem. 686 (2003) 192

Synthesis, crystal structure, and photoreaction of a disiloxane bearing two 2-(phenylazo)phenyl groups

An *E,E*-1,1,3,3-tetrafluoro-1,3-bis[2-(phenylazo)phenyl]-1,3-disiloxane (*E,E*-2) was synthesized by hydrolysis of *E*-trifluoro[2-(phenylazo)phenyl]silane (*E*-1) and characterized by X-ray crystallographic analysis showing Si–N interactions. Photoirradiation of *E,E*-2 caused both isomerization of the azo group and formation of *Z*-1 in a short time, while upon standing in the dark the *E*-1 was formed very slowly.

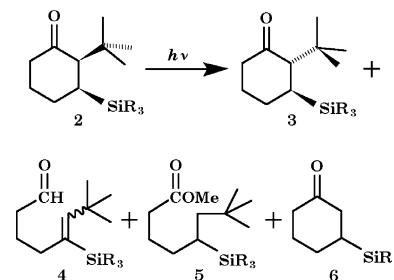


**Jih Ru Hwu, Buh-Luen Chen, Chien-Fu Lin,
Brown L. Murr**

J. Organomet. Chem. 686 (2003) 198

Electronic and steric effects of silyl groups in silicon-directed Norrish type cleavages

Sterically congested *cis*-2-*t*-butyl-3-silylcyclohexanones were irradiated with UV light to give a mixture of the Norrish type products and the corresponding *trans* isomers. The quantum yields and rate constants were greater for the *cis* than the *trans* isomers.

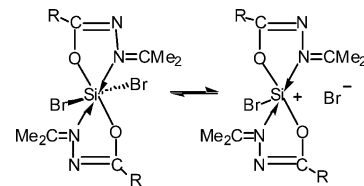


**Inna Kalikhman, Boris Gostevskii,
Olga Girshberg, Akella Sivaramakrishna,
Nikolaus Kocher, Dietmar Stalke,
Daniel Kost**

J. Organomet. Chem. 686 (2003) 202

Donor-stabilized silyl cations
Part 7: Neutral hexacoordinate and ionic pentacoordinate silicon chelates with *N*-isopropylideneimino-acylimidato ligands

Penta- and hexacoordinate silicon bis-chelates are described with a novel ligand group: isopropylideneimino. The latter is shown to have stronger donor properties than NMe_2 donors, judged by: N–Si and Si–halogen distances, ease of ionization, and ^{29}Si -NMR chemical shifts.

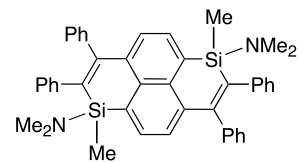


**Tomoyuki Saeki, Akio Toshimitsu,
Kohei Tamao**

J. Organomet. Chem. 686 (2003) 215

Thermolysis of bis(pentacoordinate) silicon compound bearing two 1-fluorodisilanyl units at 4- and 8-positions on 1,5-bis(dimethylamino)naphthalene ring: construction of disilapyrene skeleton and cyclophane-shaped siloxane dimer

Thermolysis of bis(pentacoordinate) silicon compound having two pentacoordinate silicon units at the 4- and 8-positions on the 1,5-bis(dimethylamino)naphthalene ring in the presence of diphenylacetylene affords a 1,6-dihydro-1,6-disilapyrene derivative through a two-site silylene trapping with acetylene molecule and the amino group migration from the naphthyl carbon atom to the silicon atom.

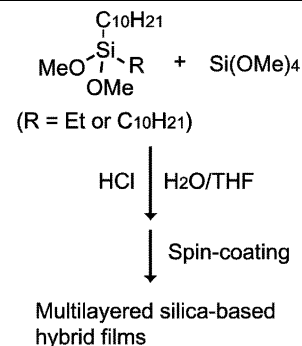


**Noritaka Umeda, Atsushi Shimojima,
Kazuyuki Kuroda**

J. Organomet. Chem. 686 (2003) 223

Synthesis of multilayered silica-based hybrid films from difunctional organosilanes by co-hydrolysis and polycondensation with tetraalkoxysilane

Multilayered silica-based hybrid films were prepared from decylethyldimethoxysilane and didecyldimethoxysilane by co-hydrolysis and polycondensation with tetramethoxysilane (TMOS) followed by spin-coating. The formation depends on the co-condensation between alkylmethoxysilanes and TMOS, and the reaction conditions should be controlled according to the length of the second organic groups.

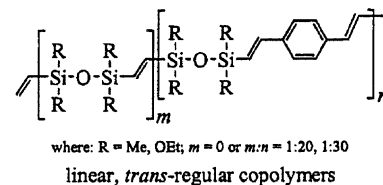


Bogdan Marciniec, Mariusz Majchrzak

J. Organomet. Chem. 686 (2003) 228

Synthesis and structural characterization of *trans*-tactic siloxylene-vinylene-*p*-phenylene polymers via ADMET copolymerization and silylative coupling (SC) polycondensation

The first *trans*-tactic stereo-regular vinylene-siloxylene-*p*-phenylene copolymer with perfect vinylsiloxane linkage has been obtained via ADMET copolymerization of divinyltetraethoxydisiloxane with 1,4-divinylbenzene in the presence of Grubbs catalyst. The similar *trans*-tactic copolymers but with no consecutive vinylsiloxane linkage have been also prepared by silylative coupling (SC) copolycondensation of 1,4-divinylbenzene with divinyltetra-(methyl,ethoxy)disiloxane catalyzed by [Ru(H)(Cl)(CO)(PCy₃)₂].

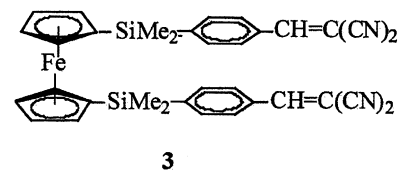


**Xiaoming Zhao, Hemant K. Sharma,
Francisco Cervantes-Lee, Keith H. Pannell,
Gary J. Long, Ahmed M. Shahin**

J. Organomet. Chem. 686 (2003) 235

Bis-silyl substituted ferrocenyls, including dicyanovinyl electron-withdrawing groups, as potential non-linear optical materials

The synthesis, structure, electrochemistry and non-linear properties of ferrocenylene (3) have been reported. Compound 3 crystallizes in a non-centrosymmetric space group *C*_c and forms chains via two types of unconventional C–H···N intermolecular hydrogen bonds. Hyperpolarizability measurements of 3 indicate moderate interactions between ferrocene and dicyanovinyl groups, which is not confirmed by the Mössbauer and EPR spectroscopy.

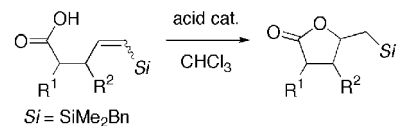


**Katsukiyo Miura, Joji Hayashida,
Tatsuyuki Takahashi, Hisashi Nishikori,
Akira Hosomi**

J. Organomet. Chem. 686 (2003) 242

Acid-catalyzed intramolecular addition of a carboxy group to vinylsilanes

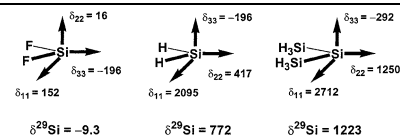
In the presence of a catalytic amount of TsOH·H₂O or TiCl₄, 5-silyl-4-pentenoic acids (1) were smoothly cyclized to γ -lactones in good to high yields. The TiCl₄-catalyzed cyclization of the substrates bearing a phenyl or alkyl group at the homoallylic position showed moderate *cis*-selectivity, while introduction of a substituent into the allylic position led to high *trans*-selectivity.



Thomas Müller*J. Organomet. Chem.* 686 (2003) 251

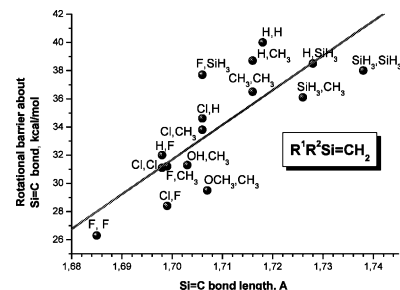
The chemical shift tensor of silylenes

^{29}Si -NMR chemical shift tensors of singlet silylenes are studied at the GIAO/MP2/6-311+G(2df,p) level of theory. The NMR chemical shift tensor for all silylenes is highly anisotropic, with a dominant paramagnetic eigenvalue δ_{11} in the plane of the central R_2Si unit and perpendicular to its C_2 axis. The calculations reveal an exceptional large substituent effect on the ^{29}Si NMR chemical shift. The high anisotropy as well as the huge substituent effects are direct consequences of the small energy difference between the singlet ground state $S_0(^1A)$ and the first excited singlet state $S_1(^1B)$.

**Vitaly G. Avakyan, Stephan L. Gusel'nikov, Leonid E. Gusel'nikov***J. Organomet. Chem.* 686 (2003) 257

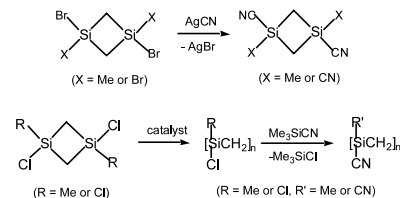
Classical planar doubly bonded Si-substituted silenes—a boundary system between olefins and heavier Group 14 analogs
Geometric and electronic structures, rotational barriers about the Si=C double bond, and comparison with the analogs and iso-electronic phosphenes, further evidence against C-ylides of silicon

Silenes, $\text{R}^1\text{R}^2\text{Si}=\text{CH}_2$, are a boundary system between olefins and heavier Group 14 analogs. Like in olefins, the more electronegative substituents shorten Si=C and weaken the π -bond and do not disturb a planar geometry. The values of rotational barriers about the double bonds and their potential energy profiles provide evidence against silenes to be C-ylides of silicon.

**M. Lienhard, C. Wiegand, T. Apple, L.V. Interrante***J. Organomet. Chem.* 686 (2003) 272

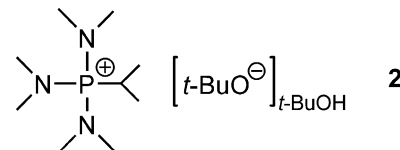
Synthesis and characterization of cyano-substituted disilacyclobutane rings and poly(silylenemethylene) polymers

The synthesis, and characterization by nuclear magnetic resonance spectroscopy, of the cyano-substituted 1,3-disilacyclobutanes, 1,3-dicyano-1,3-dimethyl-1,3-disilacyclobutane, $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_2$, and 1,1,3,3-tetracyano-1,3-disilacyclobutane, $[\text{Si}(\text{CN})_2\text{CH}_2]_2$, and the corresponding $[\text{Si}(\text{CN})(\text{Me})\text{CH}_2]_n$ and $[\text{Si}(\text{CN})_2\text{CH}_2]_n$ polymers are reported.

**Alla Bessmertnykh, Frédéric Ben, Antoine Baceiredo, Gérard Mignani***J. Organomet. Chem.* 686 (2003) 281

Anionic ring-opening polymerization of cyclic organosiloxanes using phosphorus ylides as strong non-ionic bases

Phosphonium alcoholates (**2**) obtained by the treatment of a phosphonium ylide with three to five equivalents of *t*-BuOH are stable in the presence of an excess of alcohol, and are efficient initiators for the polymerization of D_4 at room temperature.

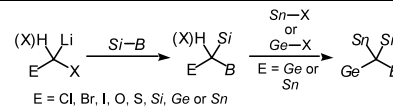


Masaki Shimizu, Takuya Kurahashi,
Hirotaka Kitagawa, Katsuhiko Shimono,
Tamejiro Hiyama

J. Organomet. Chem. 686 (2003) 286

gem-Silylborylation approach for tri- and tetrametalmethanes: the first synthesis of boryl(germyl)(silyl)(stannyl)methanes

Novel synthesis of functionalized boryl(silyl)methanes via *gem*-silylborylation of halomethylolithiums is described. Furthermore, the first synthesis and X-ray analysis of boron-, germane-, silicon-, and tin-substituted methanes are also reported.

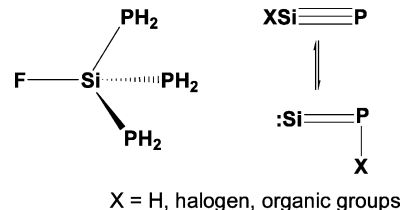


Matthias Driess, Christian Monsé,
Dieter Bläser, Roland Boese,
Holger Bornemann, Arvid Kuhn,
Wolfram Sander

J. Organomet. Chem. 686 (2003) 294

Synthesis and molecular structure of fluoro-(triphosphanyl)silane and attempts to synthesize a silylidyne-phosphane

The fluoro(triphosphanyl)silane $\text{FSi}(\text{PH}_2)_3$ is a potential silylidynephosphane-precursor which has been prepared by F/ PH_2 ligand exchange reaction between $\text{Si}(\text{PH}_2)_4$ and F_2SnIs_2 (Is = 2,4,6-triisopropylphenyl). The structure of the silane has been determined by NMR and Ar-matrix IR spectroscopy and confirmed by single-crystal X-ray diffraction analysis. Flash and pulsed thermolysis experiments of $\text{FSi}(\text{PH}_2)_3$ and the related silanes $\text{RSi}(\text{PH}_2)_3$ (R = Me, Et) have been investigated and ab initio calculations of possible products with Si-P double or triple bonds have been performed.

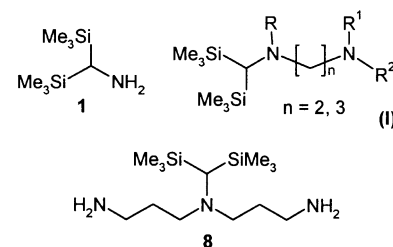


Jean-Paul Picard, Frédéric Fortis,
Stéphane Grelier

J. Organomet. Chem. 686 (2003) 306

Syntheses of novel *N*-[bis(trimethylsilyl)methyl]-1,2- and 1,3-diamines

Original *N*-[bis(trimethylsilyl)methyl]-1,2- and 1,3-diamines of type I were prepared either from bis-iminination reaction of 1,2-dicarbonyl compounds with BSMA (**1**) followed by reduction or from cyanoethylation of BSMA followed by reduction of the nitrile group. By varying the conditions of the cyanoethylation reaction bisaddition was obtained allowing to access to 5-[bis(trimethylsilyl)methyl]caldine (**8**).

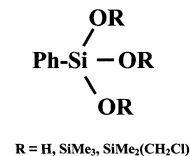


S.D. Korkin, M.I. Buzin, E.V. Matukhina,
L.N. Zherlitsyna, N. Auner,
O.I. Shegolikhina

J. Organomet. Chem. 686 (2003) 313

Phenylsilanetriol — synthesis, stability, and reactivity

Crystalline phenylsilanetriol, $\text{PhSi}(\text{OH})_3$, was obtained by smooth hydrolysis of phenyltrimethoxysilane and characterised by different analytical methods (wide angle X-ray powder diffractions, NMR, IR, thermogravimetric analysis). The compound is surprisingly stable in the solid state but slowly condenses in acetone solution. Reaction of the silanol with Me_3SiCl and $\text{Me}_2(\text{CH}_2\text{Cl})\text{SiCl}$ gave the corresponding tris-triorganysiloxy substituted derivatives in high yields.

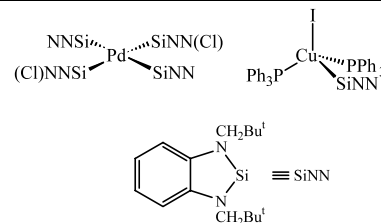


**Anthony G. Avent, Barbara Gehrhus,
Peter B. Hitchcock, Michael F. Lappert,
Hieronim Maciejewski**

J. Organomet. Chem. 686 (2003) 321

Synthesis and characterisation of bis(amino)silylene–nickel(0), –palladium(II), –platinum(0), –platinum(II) and copper(I) complexes

$\text{Si}[(\text{NCH}_2\text{Bu})_2\text{C}_6\text{H}_4\text{-1,2}]$ ($\equiv \text{SiNN}$) behaves as a source of the silylene ligand, but also may function as an unsaturated substrate by inserting into an M–Cl bond or as a reducing agent, as illustrated by the isolation of the crystalline complexes $[\text{Ni}(\text{PPh}_3)_{4-n}(\text{SiNN})_n]$ ($n = 4$ or 3), $[\text{Pt}(\text{PPh}_3)(\text{SiNN})_3]$, *trans*- $[\text{M}\{\text{SiNN}(\text{Cl})\}_2(\text{SiNN})_2]$ ($\text{M} = \text{Pt}$ or Pd) and $[\text{CuI}(\text{PPh}_3)_2(\text{SiNN})]$.

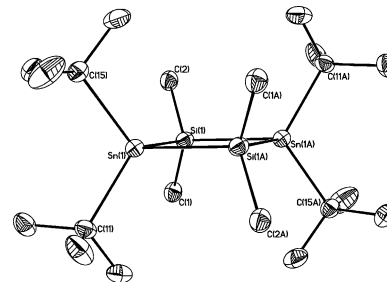


**P. Bleckmann, T. Brüggemann,
S.V. Maslennikov, T. Schollmeier,
M. Schürmann, I.V. Spirina, M.V. Tsarev,
F. Uhlig**

J. Organomet. Chem. 686 (2003) 332

Magnesium and chlorostannanes—building blocks for novel tinmodified silanes

Cyclic stannasilanes with alternating Si–Sn sequences ($[\text{Ph}_2\text{Sn}-\text{Me}_2\text{Si}]_3$, **1**; $[t\text{-Bu}_2\text{Sn}-\text{Me}_2\text{Si}]_2$, **2**) were synthesized by the reaction of dimethyldichlorosilane with diorganodichlorostannanes (R_2SnCl_2 , $\text{R} = \text{Ph}$, *t*-Bu) in the presence of magnesium. The reaction pathway towards **2** via the unexpected intermediate product $\text{Cl}-\text{SiMe}_2-(t\text{-Bu}_2\text{Sn})_2-\text{SiMe}_2-\text{Cl}$ (**5**) is discussed.

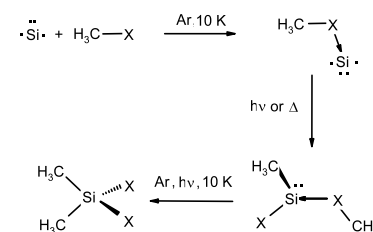


**Günther Maier, Jörg Glatthaar,
Hans Peter Reisenauer**

J. Organomet. Chem. 686 (2003) 341

Dihalodimethylsilanes from silicon atoms and methyl halides: a combined matrix-spectroscopic and density functional theory study

The reaction of silicon atoms with methyl halides ($\text{X} = \text{F}$, Cl , Br , I) has been studied in an argon matrix at 10 K. It is shown that the product formation depends on the relative methyl halide/argon ratio. In the initial step triplet *n*-adducts between the methyl halide and a silicon atom are formed. The next step can be induced photochemically. The primary photoproducts are halomethylsilylenes, which in the presence of an excess of the substrate exist as methyl halide complexes. Longer irradiation transforms these adducts into dihalodimethylsilanes.

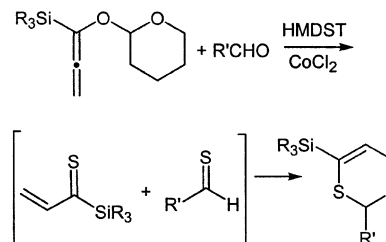


**Antonella Capperucci,
Alessandro Degl'Innocenti,
Tiziano Nocentini, Simona Biondi,
Francesca Dini**

J. Organomet. Chem. 686 (2003) 363

α,β -Unsaturated thioacylsilanes as efficient dienes in hetero Diels–Alder reactions

Reaction of several α,β -unsaturated thioacylsilanes with in situ generated thioaldehydes and thioacylsilanes affords a clean and regioselective access to 2-substituted 4-silyl-1,3-dithia-4-cyclohexene derivatives.

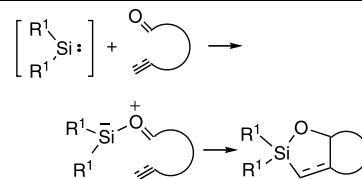


**Norio Sakai, Tsuyoshi Fukushima,
Aoi Okada, Seishi Ohashi,
Satoshi Minakata, Mitsuo Komatsu**

J. Organomet. Chem. 686 (2003) 368

Intramolecular cycloadditions of silacarbonyl ylides tethered to unactivated dipolarophiles: a new route to bicyclosilaoxolanes

The intramolecular 1,3-dipolar cycloaddition of silacarbonyl ylides derived from a silylene and unsaturated aldehydes tethered to unactivated olefinic or acetylenic dipolarophiles successfully proceeded to directly afford bicyclosilaoxolane derivatives in good yields.

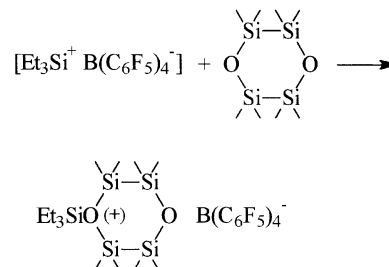


M. Cypryk, J. Kurjata, J. Chojnowski

J. Organomet. Chem. 686 (2003) 373

Tertiary trisilyloxonium ion in cationic ring-opening polymerisation of a model cyclic siloxane, octamethyl-1,4-dioxatetrasilacyclohexane

The formation of the cyclic trisilyloxonium ion is observed by the ^{29}Si -NMR spectroscopy as a result of hydride transfer reaction between triethylsilane and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in the presence of octamethyl-1,4-dioxatetrasilacyclohexane, $^2\text{D}_2$.

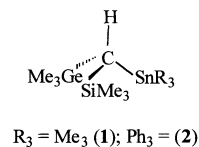


**Francisco Cervantes-Lee,
Hemant K. Sharma, Adrian M. Haiduc,
Keith H. Pannell**

J. Organomet. Chem. 686 (2003) 379

Silylgermylstannylmethanes

Silylgermylstannylmethanes **1** and **2** were synthesized by the deprotonation of trimethylgermyltrimethylsilyl methane with *t*-butyllithium in THF–HMPA solvent mixture at -78°C followed by stannylation with R_3SnCl .



Author Index of Volume 686	383
Subject Index of Volume 686	385
Contents of Volume 686	391

The Publisher encourages the submission of articles in electronic form thus saving time and avoiding rekeying errors. Please refer to the online version of the Guide for Authors at <http://www.elsevier.com/locate/jorganchem>



Full text of this journal is available, on-line from **ScienceDirect**. Visit www.sciencedirect.com for more information.



This journal is part of **ContentsDirect**, the *free* alerting service which sends tables of contents by e-mail for Elsevier Science books and journals. You can register for **ContentsDirect** online at: www.elsevier.com/locate/contentsdirect



<http://chemweb.com/gateways/elsevier.html>