Chemistry of Heterocyclic Compounds, Vol. 44, No. 11, 2008

CHRONICLE

SILA-HETEROCYCLES IN 2008*

E. Lukevics

The 15th International Symposium on Organosilicon Chemistry was held from 1 to 6 June on the South-Korean island Jeju (chairman of the organizing committee Prof. M. E. Lee, Wonju, Korea). The Second Asian Symposium on Silicon and the 13th Symposium of the Japanese Society of Silicon Chemistry took place at the same time.

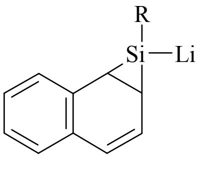
A total of 486 scientists from 25 countries took part in the symposium. The organizing country Korea was represented by the largest number of participants (172). Large delegations came from Japan (130), the People's Republic of China (40), Germany (37), USA (35), and Poland (12). Organosilicon chemists from Austria, Canada, Denmark, Estonia, Finland, France, Great Britain, Hungary, Iceland, India, Iran, Israel, Latvia, Mexico, Netherlands, Russia, Sweden, Switzerland, and Taiwan, also took part.

The main sponsors of the symposium on Organosilicon Chemistry were the KCC Corporation, the Society of Silicon Chemistry of Japan, and the silicone producers Dow Corning, Evonik Degussa, and Wacker Chemie.

The main subjects discussed at the symposium related to the theoretical and industrial aspects of silicon chemistry; the synthesis and study of the properties of organosilicon compounds with a silicon atom of reduced or enhanced valence, silicon compounds containing a silicon–element multiple bond; the production and study of the properties of new organosilicon polymers; nanostructures and supramolecules based on silicon.

A prominent position in the program of the symposium was taken up by reports on the synthesis of new silicon-containing heterocycles and study of their properties. They include heterocycles containing a silicon–element multiple bond, new silacyclanes, cyclosilanes, cyclosiloxanes, and a series of new heterocyclic systems containing a coordination bond between silicon and an electron-donating heteroatom.

Recently the first stable dilithiosilanes $RSiXLi_2$ containing functional atoms at the silicon atom were obtained by the reaction of $RSiX_3$ [R = $(Me_3Si)_3C$, X = Cl, Br] with NpLi in tetrahydrofuran at -78°C. The compounds (X = Br) enter into 1,2-addition with naphthalene and 1,4-addition with anthracene. In the first case the cyclic compound **1** with a silicon atom in a three-membered ring is formed, while in the second compounds **2** and **3** containing a bridging silicon atom are formed (Young Mook Lim, Yonsei University, Wonju, Korea).



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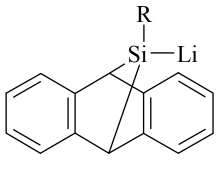

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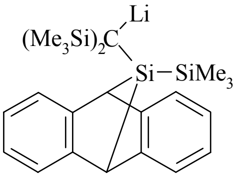

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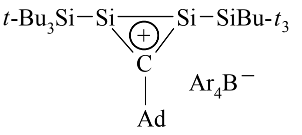
* The 15th International Symposium on Organosilicon Chemistry, June 1-6, 2008, Jeju, Korea.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1744-1752, November, 2008.

Dilithiosilanes were also used for the synthesis of disilacyclopropene and cyclotrisilene. For this purpose in the first case 2,2-dilithiotrisilane was brought into reaction with 1-adamantoyl chloride and in the second with 2,2,3,3-tetrabromotetrasilane. Subsequent treatment of the silacyclopropenes with triphenylmethylium tetraarylborate in toluene led to disilacyclopropenylium **4** and cyclotrisilenium **5** cations. Investigation of their NMR spectra and X-ray diffraction analysis showed that these cations are 2π-aromatic systems (A. Sekiguchi, Tsukuba University, Japan).



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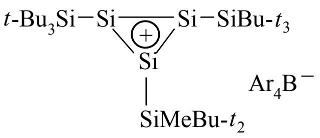
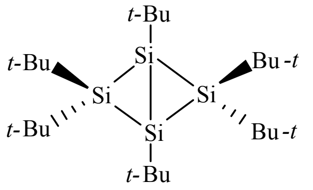


5

While studying the structure and properties of bicyclo[1.1.0]tetrasilane **6** the authors came to the conclusion that the Si–Si bridging bond in these compounds is an ordinary π-bond. Such a bond is formed from two sp^2-silicon atoms and, unlike a carbon–carbon double bond, is not accompanied by the formation of a σ-bond (S. Kyushin, Gunma University, Kiryu, Japan). A short Si–Si bridging bond is observed in other sila analogs of bicyclo[1.1.0]butane **7** (V. Y. Lee, Tsukuba University, Japan).



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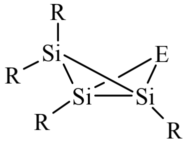
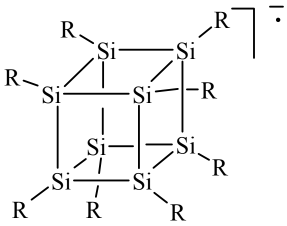


7

R = Me(*t*-Bu)2Si; E = CH2, S, Se, Te

The radical-anion of octasilacubane **8** was obtained by the reduction of tetra-*tert*-butyltetrachlorocyclotetrasilane with 5.2 equiv. of metallic potassium. If this reaction is carried out with 6.2 equiv. of potassium the dianion **9** is formed (S. Ishida, Gunma University, Kiryu, Japan).



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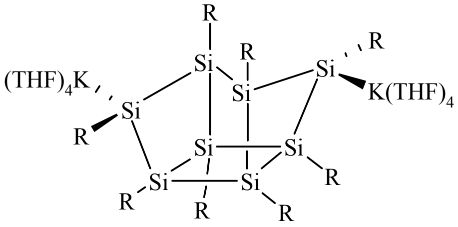
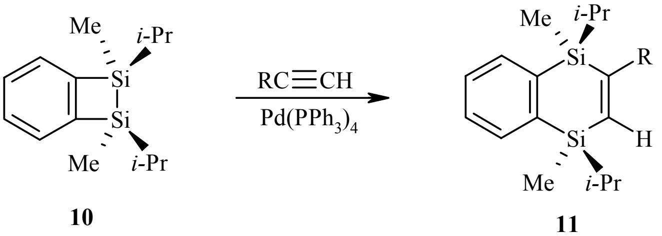


9

R = *t*-Bu

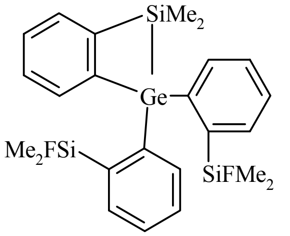
It was shown that 1,2-disilacyclobutenes **10** are extremely reactive compounds that enter into insertion reactions at the Si–Si bond. Thus, their reaction with alkynes in the presence of palladium catalysts leads to the formation of 1,4-disilacyclohexa-2,5-dienes **11** (A. Naka, University of Science and Arts of Kurashiki, Japan).



10 **11**

R = n-Bu, *t*-Bu, Ph, Me_3Si

The formation of the germanium analog **12** of benzo-1,2-disilacyclobutenes **10** was unexpectedly observed in the reaction of *o*-(fluorosilyl)phenyllithium with the dioxane complex of $GeCl_2$. In reaction with divalent germanium chloride this lithium derivative, which reacted normally with halosilanes and haloboranes, formed an intermediate derivative of triarylgermyllithium, which then gave benzosilagermacyclobutene **12** during intramolecular cyclization (A. Kawachi, Hiroshima University, Japan).



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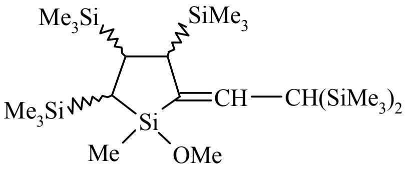
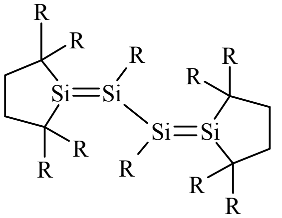


13

An unexpected reaction, taking place with transformation of the six-membered aromatic ring into a five-membered ring and insertion of a silicon atom, was observed during the reaction of methylphenyldimethoxysilane with lithium in the presence of an excess of trimethylchlorosilane. Here the phenyl group was easily reduced to cyclohexene substituted with four trimethylsilyl groups at positions 3, 4, 5, and 6 (yield 45%), but at the same time the ring was contracted with the formation of two diastereomeric silolanes **13** (20 and 8%) (Myong Euy Lee, Yonsei University, Wonju, Korea).

Investigation of the characteristics of tetrasila-1,3-dienes **14** confirmed that there is considerable conjugation in the two π(Si=i) systems. Their thermolysis and photolysis in benzene led to the formation of the silylene **15** and cyclotrisilene **16** with high yields (T. Iwamoto, M. Kira, Tohoku University, Sendai, Japan).



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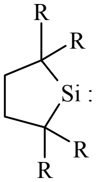

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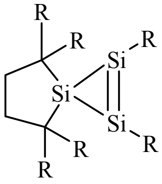
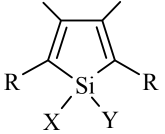


16

R = Me_3Si

On account of the discovery of valuable electrooptical characteristics in the siloles researches on the synthesis of their functionally substituted derivatives **17** are being vigorously pursued. Chemosensors were created on the basis of 1-amino-1-methyl-2,3,4,5-tetraphenylsilole and 1-(3-aminopropyl)-1-methyl-2,3,4,5-tetraphenylsilole for the determination of inorganic acids (Honglae Sohn, Choson University, Kwangju, Korea), fluorescent siloles were combined with biotin for the production of biosensors (Youngde Koh, Choson University, Kwangju, Korea), and various polysiloles were synthesized to increase the intensity of the photoluminescence (Myong-Hee Kim, Chonnam National University, Kwangju, Korea; In-Sook Lee, Kyungpook National University, Taegu, Korea; Honglae Sohn, Choson University, Kwangju, Korea).



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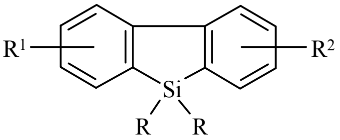
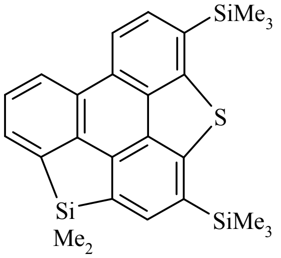


18

Two new methods were developed for the synthesis of dibenzosiloles **18** (9-silafluorenes). They are usually obtained from 2,2′-dilithium derivatives of biphenyl by silylation with dihalosilanes, which does not always give good results if the molecule also contains other functional groups. The new methods are based on intramolecular cyclizations of (2-arylsilyl)phenyltriflates in the presence of palladium catalysts (K. Mochida, Kyoto University, Japan) and 2-biphenylylhydrosilanes under the conditions of a sila Friedel–Crafts reaction (S. Furukawa, Tokyo University, Japan).

It was established that sumanene can be metallated with butyllithium and cyclized to the silole **19** in reaction with diorganyldichlorosilane. During subsequent reaction of the obtained hexacyclic compound **19** with butyllithium and dimethyldichlorosilane the methyl groups at the silicon atom in the silole ring are exchanged for butyl groups, metallation occurs, and a second silole ring is closed with the formation of compound **20** (M. Saito, Saitama University, Japan).



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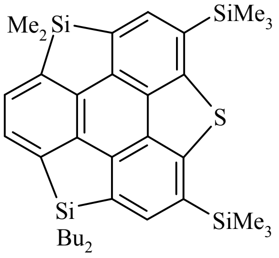
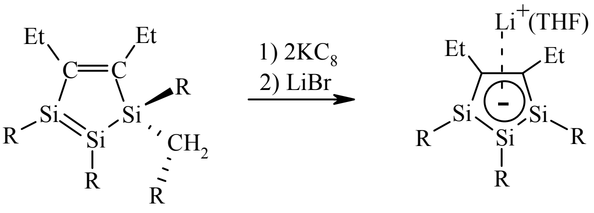


20

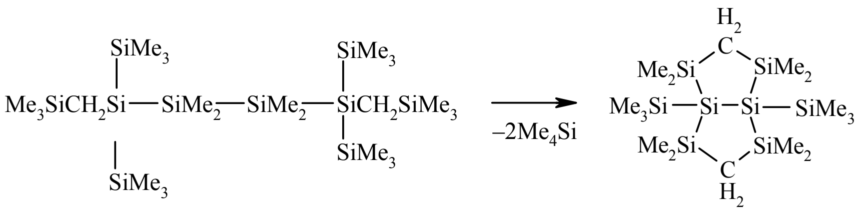
The first lithium cyclopentadienylide, containing three silicon atoms in the ring **22**, was obtained by the reduction of 1,2,3-trisilacyclopenta-1,4-diene **21** with two equivalents of KC_8 in tetrahydrofuran followed by treatment with an excess of LiBr (H.Yasuda, Tsukuba University, Japan).



21 **22**

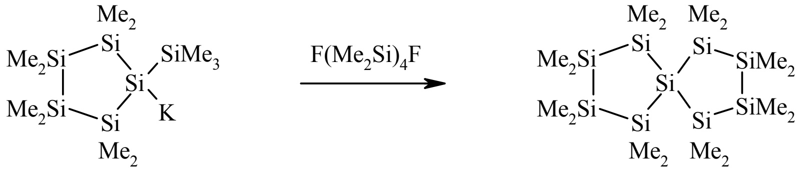
R = Me(*t*-Bu)$_2$Si

A series of new transformations leading to the formation of five-membered organosilicon bicycles and spirocycles was discovered in oligosilanes and cyclopentasilanes. Thus, the cyclization of octasilane **23** by the action of $AlCl_3$ takes place with the elimination of tetramethylsilane and the formation of the bicyclic compound **24**.



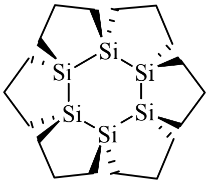
23 **24**

The reaction of the potassium derivative of cyclopentasilanes **25** with 1,4-difluorooctamethyltetrasilane takes place not only with the release of KF but also with cleavage of the Si─Si bond and the formation of the spirocycle **26** (C. Marschner, Graz Technical University, Austria).



25 **26**

During the reductive condensation of 1,1-dichloro-1-silacyclobutane with KC_8 in THF at −78°C the hexasila[6.5]coronane **27** is formed with a low yield (0.1%). Unlike the [6.5]coronane, which exists in the *chair* conformation, it has a planar cyclohexasilane ring (M. Kira, Tohoku University, Sendai, Japan). The reduction of bis(2-bromophenyl)hydrosilane with magnesium gives 9-phenyl-9,10-disilatriptycene **28** with a yield of 31%. In contrast to the carbon analog the crystals of **28** phosphoresce at room temperature (T. Kuribara, Gunma University, Kiryu, Japan).



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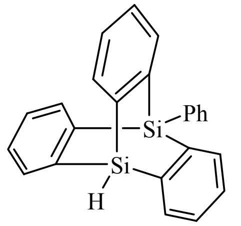
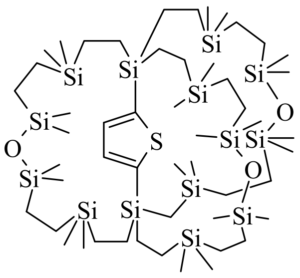


28

The first silicon-containing macrocyclic rotors **29** and rotaxanes **30** were also synthesized (M. Kira, W. Setaka, Tohoku University, Sendai, Japan).



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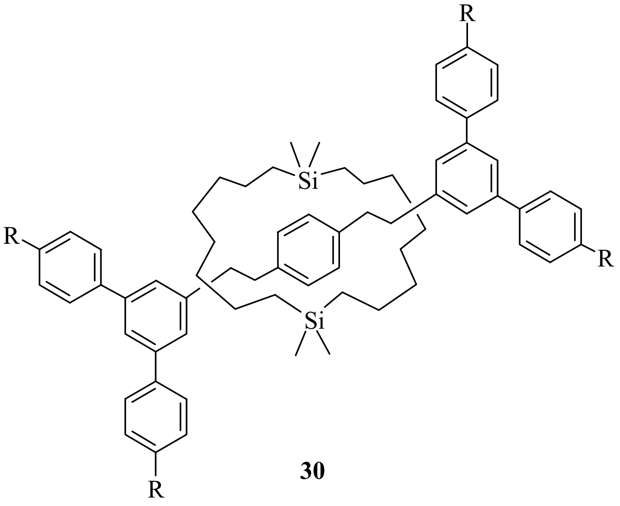
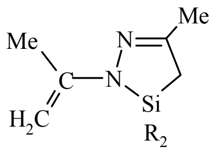


30

New sila-heterocycles containing nitrogen as well as silicon atoms in the ring were obtained by the cyclocondensation of N-lithium compounds with halosilanes and by addition reactions to stable nitrogen-containing silylenes and compounds containing silicon–silicon multiple bonds.

Thus, derivatives of 1,2-diazasilacyclopentene **30** were obtained by the reaction of lithiated hydrazones with fluorosilanes (U. Klingebiel, University of Göttingen, Germany), and the previously synthesized unusually stable silylene **31** was transformed into the first silacyclopropenium betaine **32** (M. Driess, Berlin Technical University, Germany).



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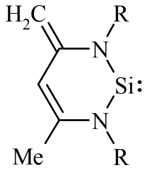

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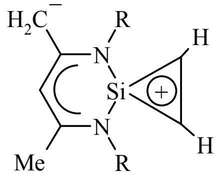
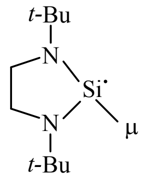


32

R = 2,6-*i*-$Pr_2C_6H_3$

Muon-containing silicon and germanium radicals were produced for the first time by using spin-polarized muons suitable for muon–spin resonance, generated in a TRIUMF cyclotron (Vancouver, Canada). Muonium (μ·), formed during capture of an electron by a muon, adds to stable N-heterocyclic silylenes and germylenes, which transform to muonated silylenes **33** and **34** (hyperfine coupling constants 154.9 and 286.4 MHz smaller than for the unsaturated carbon analog – 694.3 MHz) and germylene **35** with a very large HFCC – 694.3 MHz (P. West, Wisconsin University, Madison, USA).



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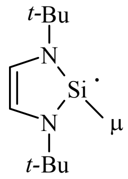

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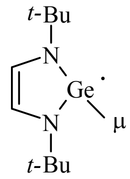

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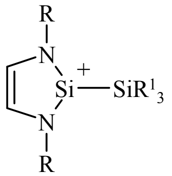
Whereas the addition of free radicals to these diazasilylenes leads to new silyl radicals their reaction with silyl cations gives silaimidazolium ions **36** (T. Müller, Carl von Ossietzky University, Oldenburg, Germany).

At Tsukuba University it was shown that the first stable disilyns containing an Si≡Si triple bond obtained in 2004 enters into numerous addition reactions with the formation of new cyclic sila compounds. Their reactions with acetonitrile and benzonitrile, leading to the formation of derivatives of the new heterocyclic system of 2,6,7-triaza-1,4-disilabicyclo[2.2.2]octa-2,5,7-triene **37**, take place in a distinctive manner (A. Sekiguchi, K. Takeuchi).



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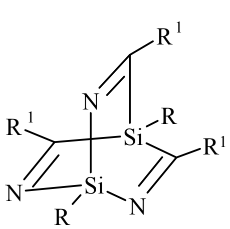


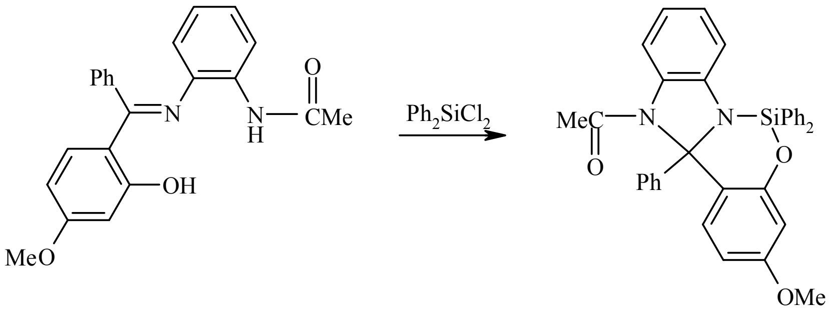
37

36 R = *t*-Bu, 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$, $R^1{}_3$ = Et_3, *i*-Pr_3, $MeMes_2$, Cy_3;
37 R = $[(Me_3Si)_2CH]_2SiPr$-*i*, R^1 = Me, Ph

Investigations in the region of cyclosiloxanes were concentrated on the production of functional compounds with various numbers of functional groups in the molecule and study of their structure and reactivity. Hydrolysis of the alkoxy derivatives in the presence of Bu_4NF (A. Kowalewska, Center of Molecular Investigations, Polish Academy of Sciences, Łódź, Poland), condensation with cyclosilanols in the presence of Et_2NOH (H. Seki, Tokyo University of Science, Japan), dehydrocondension of cyclohydrosiloxanes with silanols (T. Shioda, Tokyo University of Science, Japan), and hydrosilylation of vinylcyclosiloxanes with hydrosilanes (K. Yoshida, Chisso Petrochemical Corporation, Ichihara, Japan) were used for this purpose. For the production of photopolymerizing cyclosiloxanes unsaturated groups and mostly groups containing fragments of unsaturated carboxylic acids are inserted into their molecules (T. Hanada, University of Osaka Prefecture, Japan; R. M. Laine, University of Michigan, Ann Arbor, USA; H. Maciejewski, Adam Mickiewicz University, Poznań, Poland). Cyclometallosiloxanes containing a Si–O–Ti (E. Eyjolfsdottir, Science Institute, Reykjavík, Iceland), Si–O–Ru (T. Tanabe, Kyoto University, Japan), and Si–O–Pd bond (K. Osakada, Laboratory of Chemical Resources, Yokohama, Japan) were also synthesized.

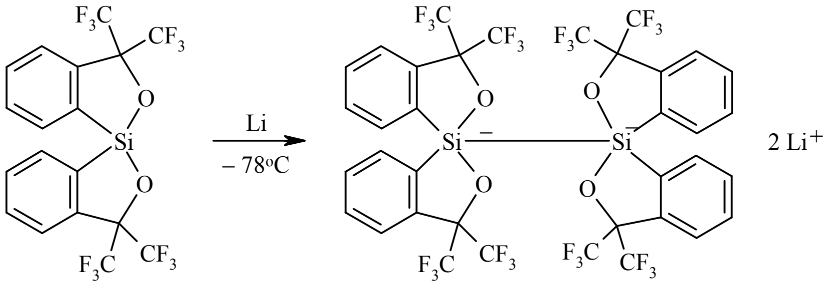
The formation of a O→Si or N→Si donor–acceptor bond was used for the synthesis of a series of new heterocycles containing a penta- or hexacoordinated silicon atom. The ligands were dibenzoylmethane (G. Gonzàlez-García, Guanajuato University, Mexico), pyrocatechol (F. Riedel, Chemnitz Technological University, Germany), a mixture of amides with pyrocatechol (Yu. I. Baukov, Russian State Medical Institute, Moscow, Russia), amino alcohols (Jee Min Yu, Yonsei University, Wonju, Korea), 2-hydroxyamides (S. Yu. Bylikin, Russian State Medical Institute, Moscow, Russia), hydrazides (D. Kost, Ben Gurion University of the Negev, Beersheva, Israel), and azobenzene (N. Kano, Tokyo University, Japan).

It was shown that the O, N, N-chelating ligand **38**, which can form cyclic derivatives of pentacoordinated silicon in result of O- and N-silylation in reaction with chlorosilanes, can react with diphenyldichlorosilane with closure of the ring **39**, containing a tetracoordinated silicon atom (J. Wagler, Technical University of Freiburg Mountain Academy, Germany).



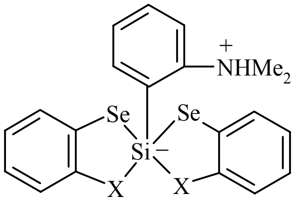
38 **39**

The reaction of the spirocyclic silane **40** with 1.2 equiv. of finely dispersed lithium at -78°C in dimethoxyethane gave the disilane dianion **41** containing two pentacoordinated silicon atoms (δ^{29} Si -58.9 ppm) (T. Kawashima, Tokyo University, Japan).



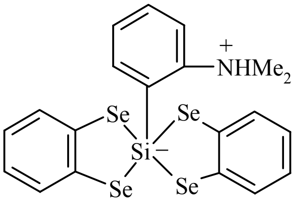
40 **41**

The first representatives of compounds of pentacoordinated silicon (analogs of pyrocatechol derivatives) containing between two (compound **42**) and four (compound **43**) selenium atoms were synthesized (B. Theis, Wurzburg University, Germany).



42

X = O, S



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The next International Symposium on Organosilicon Chemistry will be held in 2011 in Hamilton (Ontario, Canada).