

SILA HETEROCYCLES IN 2005*

E. Lukevics

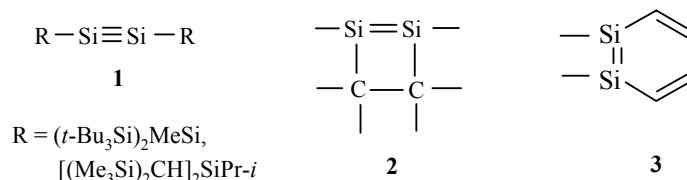
The 14th International Symposium on Organosilicon Chemistry (chairman of the organizing committee: Professor R. Tacke, Würzburg) was held from July 31 through August 5 at the University of Würzburg (Germany). The 3rd European Organosilicon Days were held at the same time.

546 scientists from 33 countries participated in the symposium. The organizing country, Germany, was represented by the largest number of participants (281). The largest delegations came from Japan (63), the USA (35), Russia (26), Poland (23), Austria (22), France (15), the UK (12), Israel (12), and South Korea (11).

The major topics discussed at the symposium concerned the theoretical and industrial aspects of silicon chemistry, the application of organosilicon compounds in organic synthesis and medicinal chemistry, the synthesis and study of the properties of organosilicon compounds with a low-valent or high valent silicon atom and silicon—transition metal compounds, synthesis of new organosilicon polymers, and also silicon-based nanostructures and supramolecules.

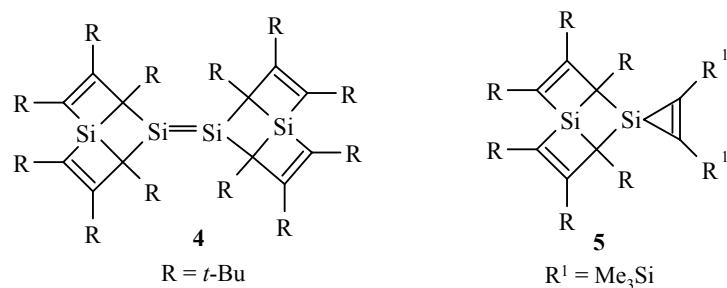
Reports devoted to synthesis of new organosilicon heterocycles and study of their properties were a substantial part of the symposium.

The most outstanding achievement of organosilicon chemistry in recent years has been synthesis of the first stable organosilicon compounds containing an Si≡Si triple bond (**1**). This turned out to be possible as a result of introducing bulky substituents on the silicon atoms forming the triple bond: (*t*-Bu₃Si)₂MeSi (**N. Wiberg**, University of Munich, Germany) and [(Me₃Si)₂CH]₂SiPr-*i* (**A. Sekiguchi**, University of Tsukuba, Japan). In the first case, the Si≡Si bond length is 2.072 Å (δ ²⁹Si 91.5 ppm), in the second case it is 2.062 Å (δ ²⁹Si 89.5 ppm). These compounds have proven to be quite reactive in cycloaddition reactions with olefins and acetylenes, leading to formation of novel types of unsaturated sila heterocycles **2** and **3**.

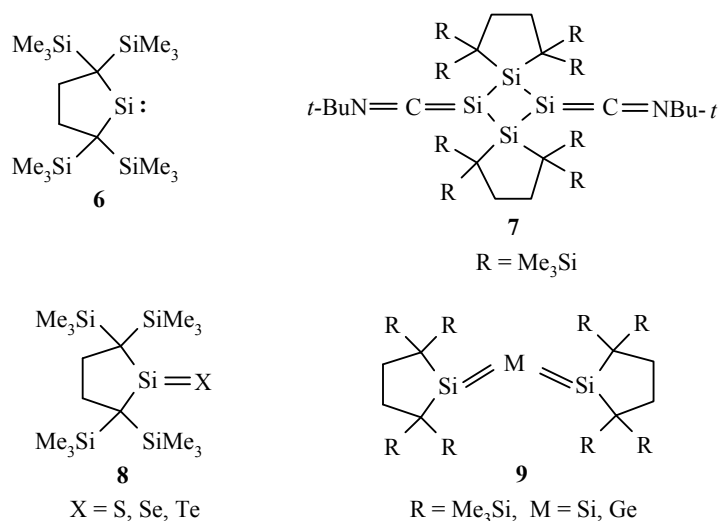


Another type of unsaturated sila heterocycles were synthesized at the Photodynamic Research Center of the Institute of Physical and Chemical Research (RIKEN) and at Tohoku University (**K. Sakamoto, Sh. Tsutsui**, Sendai, Japan). When tri(*tert*-butyl)cyclopropenyltribromosilane is reduced by KC₈ at -130°C in methyltetrahydrofuran, the disilene **4** is obtained which is formally a tetramer of tri(*tert*-butyl)cyclopropenylsilylyne. This disilene is in equilibrium with silylene, which is formed upon thermal or photochemical dissociation of the Si=Si bond and enters into a cycloaddition reaction with acetylene to form a novel tetracyclic system **5**, containing a spirosilacyclopropenoic moiety.

* The 14th International Symposium on Organosilicon Chemistry and the 3rd European Organosilicon Days, July 31 - August 5, 2005, Würzburg, Germany.

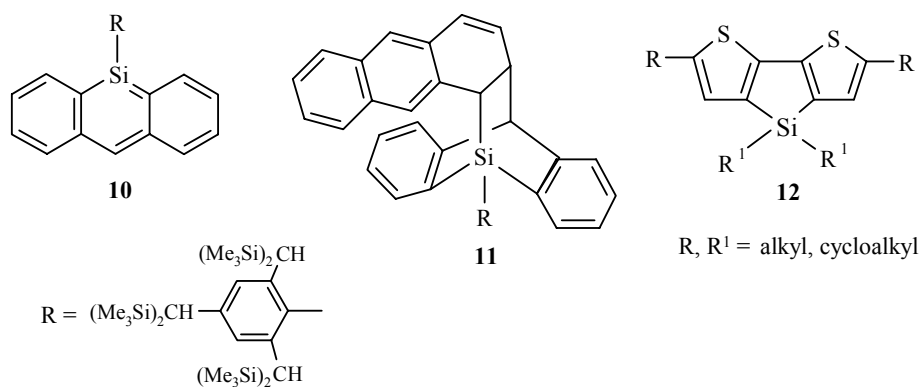


Using stable cyclic silylenes **6**, the 2005 laureate of the Wacker Silicone Award (Wacker-Chemie GmbH), **M. Kira** (Tohoku University, Sendai, Japan) obtained a series of compounds in which the silicon atom of the heterocycle is bonded *via* an exocyclic double bond to carbon (**7**), sulfur, selenium, tellurium (**8**), silicon or germanium atoms (**9**).

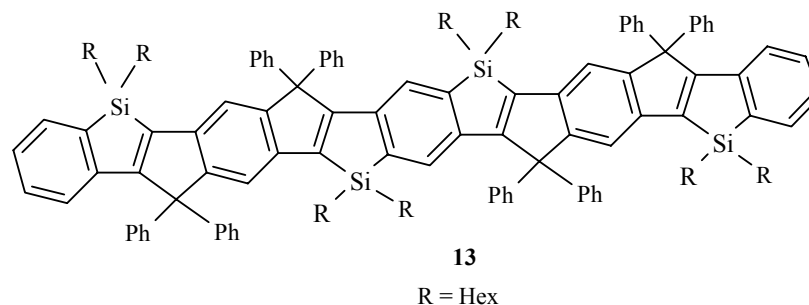


In the latter, in contrast to carbon analogs, the cumulene moiety is not linear but rather is bent. For $M = \text{Si}$, for example, the $\text{Si}=\text{Si}=\text{Si}$ angle is 136° .

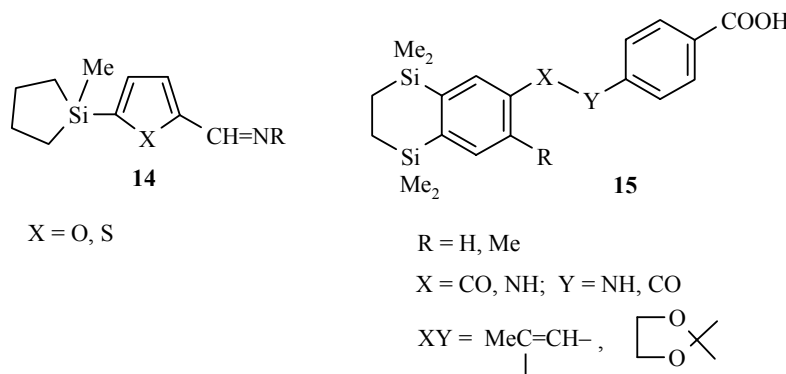
9-Silaanthracene **10**, stabilized by the bulky 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl substituent, stereoselectively adds CCl_4 to form 9-SiCl, 10- CCl_3 adducts. 9-Silaanthracene **10** enters into a [4+2] cycloaddition reaction with naphthalene and anthracene to form adducts of type **11**, while with tetracene and pentacene the products of more conventional [4+4] cycloaddition are formed (**N. Tokitoh**, Kyoto University, Japan).



A number of silaheterocycles have attracted attention because of their properties which are of practical value. This is especially so for siloles and their derivatives (for example, compounds of type **12** and **13**), which have luminescent properties with high quantum yield (**M. Tanaka**, Tokyo Institute of Technology; **Sh. Yamaguchi**, Nagoya University; **J. Oshita**, Hiroshima University, Japan; **Sang Ook Kang**, Korea University, South Korea).



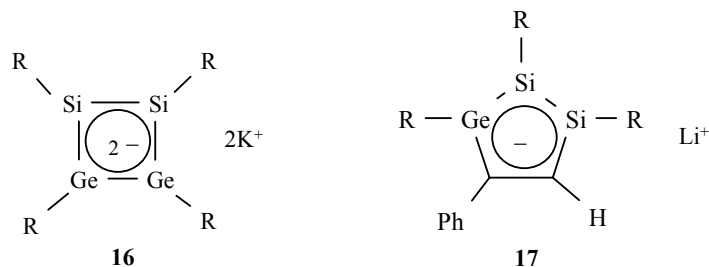
Sila heterocycles having pronounced biological activity make up another group. Thus silacycloalkyl-substituted derivatives of furan and thiophene aldehydes **14** have high cytotoxicity with respect to a number of tumor cells (**L. Ignatovich**, Latvian Institute of Organic Synthesis, Riga), while disila analogs of benzoretinoids **15** are stronger agonists of retinoid X receptors than their carbon analogs (**R. Tacke**, University of Würzburg, Germany).



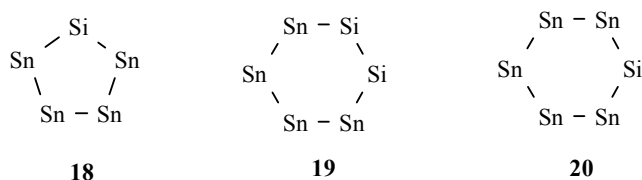
Phthalocyanine derivative Pc-4, $\text{HOSiPcOSiMe}_2(\text{CH}_2)_3\text{NMe}_2$, containing a six-coordinate silicon in the ring, is undergoing clinical testing as an agent for photodynamic therapy of tumors (**M. E. Kenney**, Case Western Reserve University, Cleveland, USA).

Many metallaheterocycles have been synthesized that contain one or more other heteroatoms besides silicon in the ring.

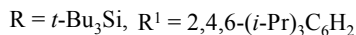
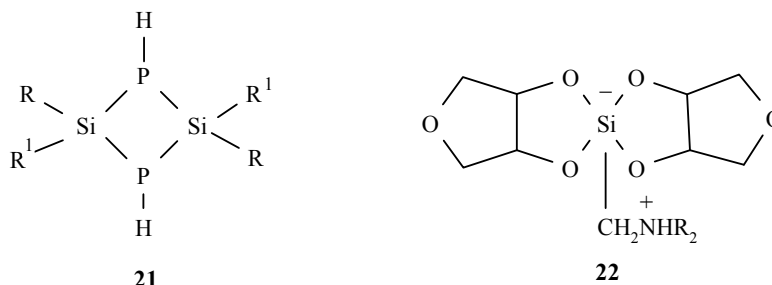
Reduction of the corresponding precursors by alkali metals has been used to obtain the 1,2-disila-3,4-digermacyclobutadiene anion **16** (analog of the cyclobutadiene dianion) and 1,2-disila-3-germacyclopentadienyllithium **17** (analog of the cyclopentadienyl anion Cp^-). Compound **17** is aromatic like its carbon analog Cp^- , while dianion **16** does not have such properties (**V. Y. Lee**, Tsukuba University, Japan).



Four-membered and six-membered sila-stanna heterocycles were obtained earlier with the same numbers of silicon and tin atoms in the ring. In continuing these studies at Graz University of Technology (Austria), reactions of α,ω -dichloropolystannanes with dichlorosilanes have been used to synthesize a number of new heterocycles of type **18-20** in which the Sn:Si ratio is greater than unity (**F. Uhlig**).

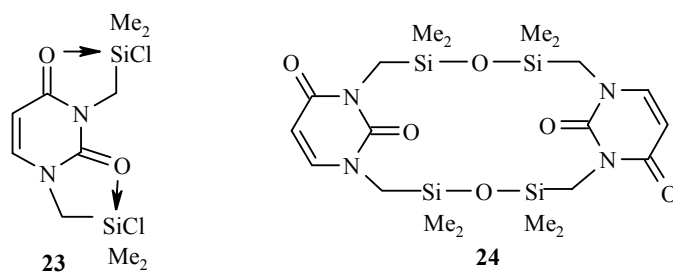


Calculations have shown that of the poorly studied heteronuclear conjugated silicon systems such as systems with an Si=P–P=Si moiety, 1,4-disila-2,3-diphosphabutadiene is the most stable. However, an attempt to synthesize it from 1,4-disila-2,3-diphosphabutane resulted in a novel four-membered Si₂P₂ heterocyclic system **21** (**M. Driess**, Technical University of Berlin, Germany).

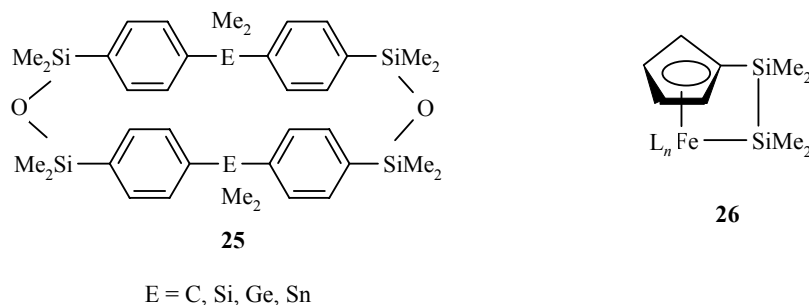


A number of novel siloxacyclanes have been synthesized that contain a five-coordinate silicon atom. Thus when aminomethyltrialkoxysilanes are reacted with *meso*-oxolane-3,4-diol, the zwitterionic complexes **22** are obtained which contain two bidentate *meso*-oxolane-3,4-diolato(2⁻) ligands. These compounds, in contrast to conventional alkoxy silanes containing an Si–OR group, are stable in aqueous solutions at pH 7.0-8.0 and can even be synthesized in water (**A. Dragota**, University of Würzburg, Germany).

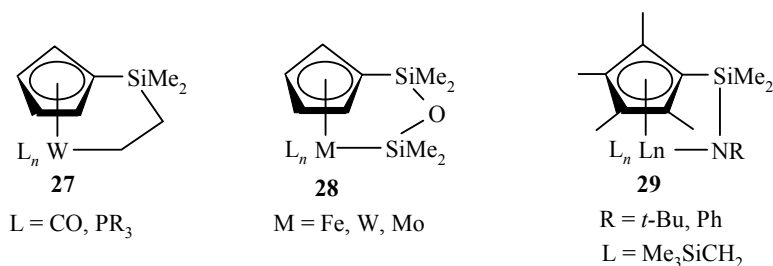
When 1,3-bis(trimethylsilyl)uracil reacts with dimethyl(chloromethyl)chlorosilane, a cyclic complex of five-coordinate silicon (**23**) is formed. Its hydrolysis yielded macrocycle **24**, containing two disiloxane groups (**D. Kost**, Ben Gurion University, Israel).



Paracyclophanes of Group 14 elements have also been obtained (**25**) that contain disiloxane bridges (**A. Duthie**, Deakin University, Australia).



Another series of silametallacycles **26-29** have been synthesized based on cyclopentadienyl derivatives of metals. Besides a silicon atom, these heterocycles contain another iron atom (**K. H. Pannel**, University of Texas at El Paso, USA), a molybdenum or tungsten atom (**W. Malisch**, University of Würzburg, Germany), or a lanthanide atom (**D. Robert**, University of Aachen, Germany). The latter are active catalysts for hydrosilylation of olefins and acetylenes.



The Fifteenth Symposium on Organosilicon Chemistry will be held in 2008 in South Korea.