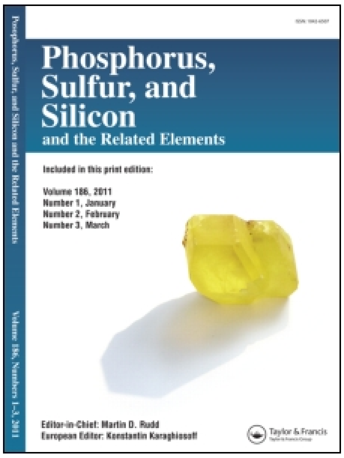

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Strained Cage Molecules Constructing with Chalcogen and Silicon Atoms

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STRAINED CAGE MOLECULES CONSTRUCTING WITH CHALCOGEN AND SILICON ATOMS

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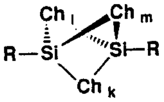
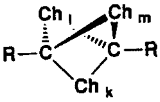
ABSTRUCT A new type of cage molecule which consists of two silyne units and three chalcogen bridges (containing four S or Se atoms) was prepared. Its notable stabilities and structure are discussed.

Some trifunctional silanes react with chalcogen-containing molecules under appropriate conditions to give silsesquioxanes[1], adamantane-type silthianes[2] or silselenanes.[2a] These cage molecules consist of chalcogens and four or more silyne units. However, such a molecule consisting of only two silyne moieties and three chalcogen bridges, (general form, **1**) was not known. Moreover, the carbon analog, **2** (Ch = a chalcogen atom; k, l, m = 1, 2, 3...) also is not known so far. In this paper, we report the first preparations of novel cage molecules, **1** (Ch = S or Se).[3]

While, concept of chemical bonding is an essential subject in chemistry, and it involves most interesting and profound problems. Propellane is the very molecule of this interest, because a conventional bond can not form between its bridgeheads. For examples, in [1.1.1]propellane, a back-lobe bond was proposed at first, but according to ab-initio calculation, this HOMO orbital is not bonding orbital.[4] Recently Nagase predicted notable structures of trioxadisilabicyclo[1.1.1]pentanes using ab-initio calculation.[5] The Si-Si non-bonded distance equals Si-Si triple bond distance, alkthough between Si atoms no conventional bond exists. This type of molecule has been just a hypothetical molecule, so far. In this work we wish to report a first preparation of selenium containing molecule, **1-*Se3***.



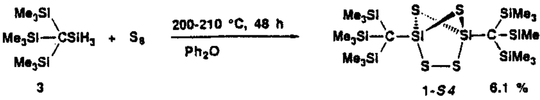
1



2

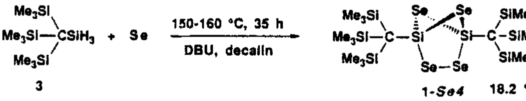
The trisyl group (trisyl- = tris(trimethylsilyl)methyl-) was introduced on the Si atom as a very bulky substituents in order to prevent polymerization or oligomelization of the silyne unit.[6]

A mixture of trisylsilane, **3**, elemental sulfur, and diphenyl ether was heated at 200-210 °C for 48 h under a nitrogen atmosphere. 1,4-Bis{tris(trimethylsilyl)methyl}-2,3,5,6-tetrathia-1,4-disilabicyclo[2.1.1]hexane, (**1-*S4***) was isolated from the reaction mixture by silica gel column chromatography, TLC, and GPC in a 6.1% yield as odorless, pale yellow crystals (eq. 1). The structure was determined on the basis of spectral data (TABLE I).[7]



(1)

The compound **3** did not react with elemental Se in decalin (or Ph$_2$O) under the same reaction conditions described above, so that DBU (1,8-diazabicyclo[5.4.0]-7-undecene) was added to the reaction mixture as an activator of elemental Se (eq. 2).[8] A mixture of trisylsilane, **3**, metallic Se, DBU, and decalin was heated at 150-160 °C for 35 h under a nitrogen atmosphere. 1,4-Bis{tris(trimethylsilyl)methyl}-2,3,5,6-tetraselena-1,4-disila-bicyclo[2.1.1]hexane, (**1-*Se4***) was isolated by silica gel column chromatography and GPC in 18.2% yield as reddish orange crystals (TABLE I).[9] The electronic absorption spectrum of **1-*Se4*** showed nearly the same absorption maximum (450 nm) as observed for five-membered cyclic diselenides (ca. 440 nm) which in the case of the latter depends on the dihedral angle between the lone pair orbitals.[10]



(2)

Compounds **1-*S4*** and **1-*Se4*** had nearly the same physical properties and spectral features. They are extremely stable to solvolysis even in boiling MeOH or EtOH. The steric protection of the trisyl group must be effective because normal silthianes and silselenanes easily react with alcohol or atmospheric moisture.[2, 11] Silsesquioxanes are expected to be used for new materials displaying a high heat resistance and thermo-oxidative resistance,[1] the **1-*S4*** and **-*Se4*** also showed high thermal stability (TABLE I).

The structure of **1-*Se4*** was confirmed by X-ray crystal analysis (FIGURE 1).[12] The Si-Se-Si angle of **1-*Se4*** was very sharp, compared with a normal Si-Se-Si angle (ca. 96 °).[13] One of the angle 74.8 ° is almost the same value as Si-O-Si angle of 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]hexane (74.7 °).[3, 14]

Irradiation to **1-*Se4*** afforded **1-*Se3*** in a good yield. On the basis of the X-ray structure and the NMR data, the surprising feature of the inter-bridgehead bonding in **1-**

Se3 was discussed in the presentation.

TABLE I. Spectral Data of **1-*S4*** and **1-*Se4***

	1-*S4*	**1-*Se4***
color and habit	pale yellow needles	reddish orange plates
mp / °C	330-334[a]	342-345[a]
sublimation point / °C	250	280
absorption spectra / λ_{max} nm (ε)[b]	227(s)(1600) 251(s)(730) 319(s)(130)	243(s)(2400) 280(s)(620) 450(60) 500(s)(30)
^{1}H NMR[c] / δ	0.418(s)	0.441(s)
^{13}C NMR[d] / δ	5.00(q), 6.43(s)	5.10(q), 6.04(s)
^{29}Si NMR[e] / δ	0.5 (SiMe)[f]	13.1(Se-Si), 0.9(SiMe)

[a] In sealed tube. [b] In n-hexane. [c] In $CDCl_3$, 500 MHz. [d] In $CDCl_3$, 125 MHz. [e] In $CDCl_3$, 18 MHz. [f] The measurement of ^{29}Si NMR of bridge head silicon was unsuccessful by routine method.

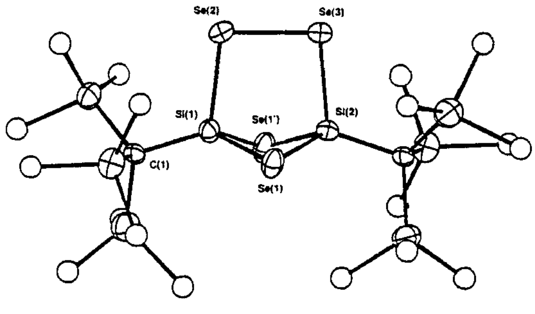


FIGURE 1.
X-ray structure of **1-*Se4*** Selected bond lengths (Å) and angles (deg): Si(1)-Se(1), 2.252; Si(2)-Se(1), 2.234; Si(1)-Se(3), 2.325; Si(1)-Se(1′), 2.331; Si(2)-Se(1′), 2.312; Si(2)-Se(2), 2.294; Se(2)-Se(3), 2.353; Si(1)-C(1), 1.855; Si(1)-Si(2), 2.820; Si(1)-Se(1)-Si(2), 77.9; Si(1)-Se(1′)-Si(2), 74.8; Se(1)-Si(1)-Se(1′), 95.9; Se(1)-Si(1)-Se(3), 100.9; Si(1)-Se(3)-Se(2), 95.7; Si(2)-Se(2)-Se(3), 95.9; Se(1)-Si(2)-Se(2), 100.9.

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(7) **1-*S4***: MS m/e 646 (M^+); Anal. Calcd for $C_{20}H_{54}Si_8S_4$: C, 37.10; H, 8.41. Found: C, 37.07; H, 8.51. The measurement of ^{29}Si NMR of **1-*S4*** was unsuccessful by routine method. The X-ray crystal structure of **1-*S4*** could not be analysed because of its internal twin structure.

(8) **1-*Se4***: MS m/e 838 (M^+); Anal. Calcd for $C_{20}H_{54}Si_8Se_4$: C, 28.76; H, 6.52. Found: C, 28.53; H, 6.20.

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(11) Compound **1-*Se4***: $C_{20}H_{54}Se_4Si_8$, F.W. 835.18, orthorombic, a=23.321(3), b=13.510(4), c=11.488(14) Å, V=3619.5 Å^3, Z=4, space group Pbca, $\rho=1.53$ g/cm^3, $\mu=42.9$ cm. The 1364 independent observed reflections [$2\theta \leq 50$ °; $|F_o2| > 3\sigma|F_o2|$] were measured on an Enraf-Nonius CAD4 diffractometer using MoKα irradiation and ω−θ scan. No absorptions correction was made. The structure were solved by direct methods and only silicon and selenium atoms were refined anisotropically to R=0.061 and Rw=0.079.

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(13) Masamune reported that some cyclic or cage molecules have structurally required NBD/BL values (NBD is the non-bonded distance; BL is the bond length).[14] NBD/BL of **1-*Se4*** is 1.23, so that **1-*Se4*** may be belong to the same class as 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane.

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