General Introduction

Organosilicon Chemistry

The organosilicon chemistry has been widely opened since the establishment of the convenient preparation for organosilicon compound by the reaction of silicon tetrachloride with various Grignard reagents by F. S. Kipping in early 20th century.[1] That is the reason why he is called as a great pioneer of silicon chemistry. The discovery of direct process for preparation of halogenated organosilane derivatives by the reaction of methyl chloride with alloy of silicon and copper by E. G. Rochow in the latter half of 1940's[2,3] made a rapid progress of not only silicone industry but also fundamental organosilicon chemistry.[4]

Silicon is classified into Group 14 element right under carbon in the Periodic Table, and electronic configuration of its outer shell is $3s^23p^2$ that is isoelectronic structure of carbon ($2s^22p^2$). For this reason, silicon is expected to have a similar character of carbon. Actually, silicon gives numerous stable compounds, which have a tetrahedral structure, such as $SiMe_4$ and $SiCl_4$. However, according to the progress of organosilicon chemistry, the points of difference between silicon and carbon have been also made clear. For example, although unsaturated compounds in carbon system such as ethylene and acetylene are generally stable and play an important role in organic chemistry, unsaturated species consisting of silicon atoms are highly reactive. This difference can be applicable between carbon and other heavier Group 14 elements (Ge, Sn, and Pb). What is the origin for the difference between cabon and heavier Group 14 elements? As shown Table 0-1, there are some distinctions in the atomic properties of Group 14 elements.[5-9] It is noteworthy that the size and energies of the two valence atomic orbital show different tends for *n*s and *n*p orbitals (n = 2,3,4,5 and 6 for C, Si, Ge, Sn, and Pb). In contrast to the alternative arrangement of the *n*s energy with increasing atom size, the *n*p energy decreases steadily until Pb. On the other hand, the difference of the *n*s–*n*p atomic radius increase steadily with atomic number, with a particularly large change between carbon and silicon. Therefore

hybridization between *n*s and *n*p obitals for heavier atoms are unfavorable to affect their chemical behavior. Such a disadvantage to hybridization in the heavier Group 14 elements can be an important idea to understanding of the difference between carbon compounds and their heavier analogues.

Table 0-1. Atomic Properties of the Group 14 Elements

Atom	C	Si	Ge	Sn	Pb	ref.
n	2	3	4	5	6	
Orbital energy (eV)						5)
*n*s	-19.39	-14.84	-15.52	-13.88	-15.41	
*n*p	-11.07	-7.57	-7.29	-6.71	-6.48	
Electronegativity						
Mülliken	1.92	1.46	1.40	1.30	1.21	6)
Pauling	2.55	1.90	2.01	1.96	2.33	7)
Allen	2.28	1.76	1.81	1.68	1.91	8)
Atomic radius (<*r*> in au)						5)
*n*s	1.58	2.20	2.19	2.48	2.39	
*n*p	1.74	2.79	2.88	3.22	3.22	

Chemistry of Small Ring Systems Consisting of Silicon Atoms

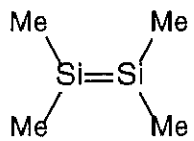
Cyclotetrasilane derivatives, that are silicon analogue of cyclobutane, have been known since the fundamental work of Kipping in 1921.[10] Kipping synthesized octaphenylcyclotetrasilane along with five- and six-membered ring perphenylcyclopolysilanes from dichlorodiphenylsilane and sodium. Since then numerous cyclotetrasilane derivatives bearing organic substituents have been synthesized.[11] In contrast to the cyclotetrasilane, cyclotrisilane that is silicon analogue of cyclopropane is relatively a new compound, and the first known stable cyclotrisilane was prepared in 1982 by Masamune and co-workers from dichlorobis(2,6-dimethylphenyl)silane by the reductive dehalogenation with lithium naphthalenide.[12] Other cyclotrisilanes bearing substituents of comparable steric bulk have been synthesized analogously, and the chemistry of cyclotrisilane presently known has been reviewed in 1995 by Weidenbruch.[13] Quite recently, trialkylsilyl-substituted cyclotrisilanes were also synthesized by the reductive dehalogenation of the corresponding

dihalosilanes by Kira and co-workers.[14]

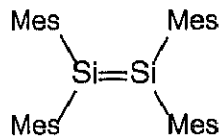
Cyclotrisilane shows unique chemical behavior due to the presence of high strain energy in the three-membered ring. The chemical reactions of the cyclotrisilane initiated generally by Si-Si bond cleavage to relieve the ring strain. There are three fundamental pathways for the degradation of the cyclotrisilane ring; (i) cleavage of one Si-Si bond affording linear trisilanes, (ii) cleavage of two Si-Si bonds leading to the formation of a disilene and a silylene, and (iii) breaking of all Si-Si bonds affording monosilanes. Chemical reactivity and physical properties of the cyclotrisilane derivatives were widely investigated at the present.[11,13]

Chemistry of Doubly-Bonded Species Consisting of Silicon Atoms

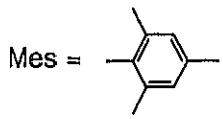
Disilene, that is silicon analogue of ethylene, had been regarded as one of the most important reactive intermediate in the organosilicon chemistry since the first generation of tetramethyldisilene, $Me_2Si{=}SiMe_2$, by Roark and Peddle in 1972.[15] Since then, it was of major interest to examine the double bond character of these reactive disilenes.[16] Such disilenes bearing sterically small substituents are generally highly reactive, and easy to polymerize in the absence of trapping reagent. After 10 years of the first generation of disilene, introducing bulky substituents in order to take advantage of kinetic stabilization brought a break through for the study on the chemistry of doubly-bonded compounds consisting of silicon atoms. Thus, West et al. successfully synthesized the first isolable disilene, tetramesityldisilene (mesityl = 2,4,6-trimethylphenyl), by the photolysis of 1,1,1,3,3,3-hexamethyl-2,2-dimesityltrisilane.[17] Since then, there has been explosive growth in the area of unsaturated compounds of heavier Group 14 elements, and many stable disilenes have been synthesized and characterized in the last two decades.[16]



D. N. Roark and G. J. Peddle (1972)



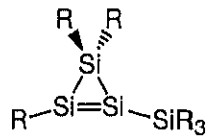
R. West (1981)



Chemistry of Unsaturated Small Ring Systems Consisting of Heavier Group 14 Elements

In contrast to the chemistry of cyclotrisilane and disilenes, the study of unsaturated compounds consisting of heavier Group 14 elements comparatively new field. The first cyclotrigermenes $(^tBu_3E)_4Ge_3$, (E = Si, Ge), which are germanium analogue of cyclopropene, were synthesized by Sekiguchi et al. in 1995, by the reaction of $^tBu_3ENa$ with $GeCl_2$ dioxane in THF.[18] Sekiguchi et al. have demonstrated the formation of cyclotrigermenylium ion $(^tBu_3E)_3Ge_3$ that are germanium analogue of cyclopropenylium ion by the oxidation of the corresponding cyclotrigermenes with trityl tetraarylborates (trityl = triphenylmethyl)[19] and also shown that cyclotrigermenylium ion is a good precursor of asymmetrically substituted cyclotrigermenes.[20] In 1996, Kira et al. reported the synthesis of the first cyclic disilenes, hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene $(^tBuMe_2Si)_6Si_4$, which photochemically isomerized to tetrasilabicyclo[1.1.0]butane derivative, by the reductive condensation of the corresponding dibromosilane and tetrabromodisilane.[21] In 1999, Wiberg and co-workers reported the isolation of cyclotristannene $(^tBu_3Si)_4Sn_3$ that is a tin analogue of cyclopropene by the isomerization of 1,1,3,3-tetrakis(tri-*tert*-butylsilyl)-tristannaallene which initially generated from the reaction of $^tBu_3SiNa$ with $SnCl_2$.[22] In 2000, Sekiguchi et al. synthesized disilagermirene $(^tBu_2MeSi)_4Si_2Ge$ which are the first 'mixed' cyclotrimetallenes consisting of heavier Group 14 elements.[23] Cyclotrisilene that is silicon analogue of cyclopropene were independently reported by Kira et al. and this work in 1999. Kira and co-workers had prepared asymmetrically substituted cyclotrisilene, 1-tris(*tert*-butyldimethylsilyl)silyl-2,2,3-tris(*tert*-butyldimethylsilyl)cyclotrisilene, by the reduction of 1,1-dibromo-3-*tert*-butyl-2,2-bis(*tert*-butyldimethylsilyl)-1-chloro-3,3-dimethyltrisilane with KC_8.[24] Very recently, structural analysis of the asymmetrically substituted cyclotrisilene was finally reported.[24b] Kira et al. have also found an interesting compound, spiropentasiladiene derivative, as a minor product of the same reaction system.[25]

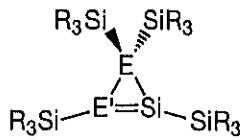
Cyclotrimetallenes consisting of heavier Group 14 elements exhibited an enhanced reactivity arising from the combination of highly reactive metal-metal double bond and highly strained three-membered ring in one molecule, which gives an access to the novel cyclic and bicyclic compounds by the addition and cycloaddition reactions. The unique reactivities of these compounds have been also investigated up to date.[26]



Cyclotrisilene

R = ^{t}BuMe$_2$Si

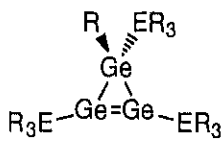
R = R$_3$Si = ^{t}Bu$_2$MeSi



Disilagermirene

R$_3$Si = ^{t}Bu$_2$MeSi

E = Si, E' = Ge; E = Ge E' = Si

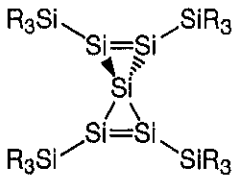


Cyclotrigermene

R = R$_3$E = ^{t}Bu$_3$Si, ^{t}Bu$_3$Ge

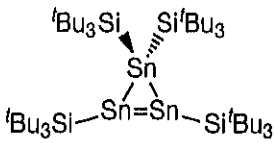
R$_3$E = ^{t}Bu$_3$Si, R = Mes, (Me$_3$Si)$_3$Si, etc..

R$_3$E = ^{t}Bu$_3$Si, R = Cl, Br, I

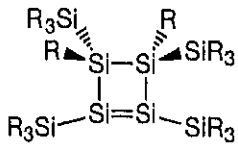


Spiropentasiladiene

R$_3$Si = (^{t}BuMe$_2$Si)$_3$Si



Cyclotristannene



Cyclotetrasilene

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

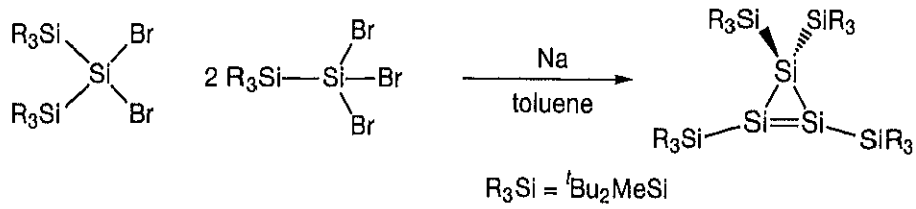
R$_3$Si = ^{t}Bu$_3$Si, R = I

Purpose of the Present Study

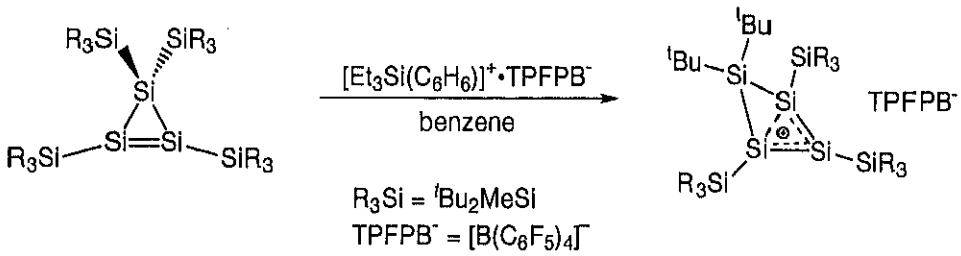
As memtioned above, the chemistry of unsaturated small ring systems consisting of heavier Group 14 elements is comparatively new field in the histry of organosilicon chemistry. The author believe that it is very important for development of organosilicon chemistry to investigate these compounds more widely and deeply. The results of these reserch will spread the horizons of organic chemistry. In this doctor's thesis, cyclotrisilene that is a silicon analogue of cyclopropene, is regarded as a key compound and the chemical properties of the cyclotrisilene such as molecular structure and reactivity are examined.

In Chapter 1, synthesis, characterization, and the first crystal structure of cyclotrisilene, which has an endocyclic Si=Si double bond in the three-membered ring

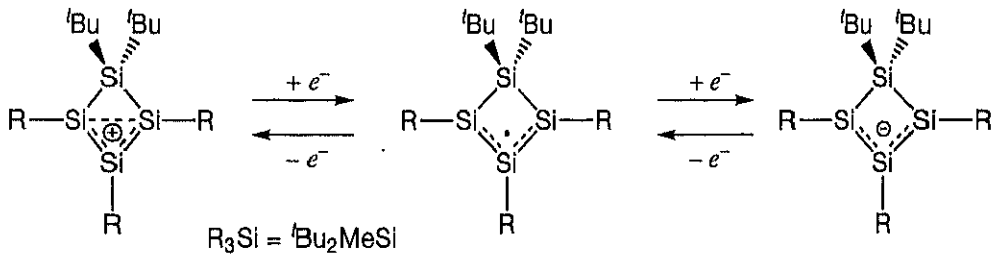
skeleton, are described. The reactivity of the cyclotrisilene toward haloalkanes, phenylacetylene, and $GeCl_2$ dioxane, are also described.



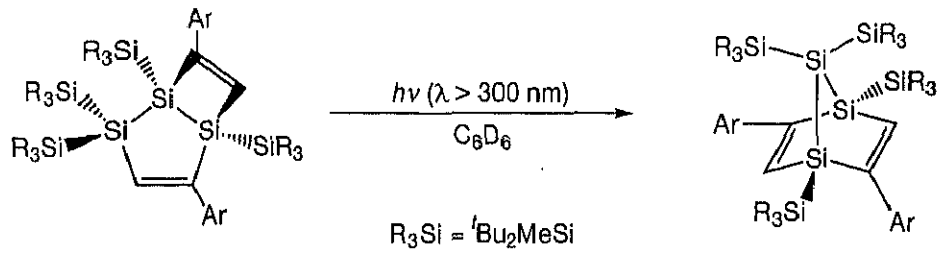
In chapter 2, synthesis of cyclotetrasilenylium ion that is the homocyclotrisilenylium ion by the reaction of the cyclotrisilene with $[Et_3Si(C_6H_6)]^+$ is described, along with mechanistic discussion. Homoaromaticity of the cyclotetrasilenylium ion is also discussed.



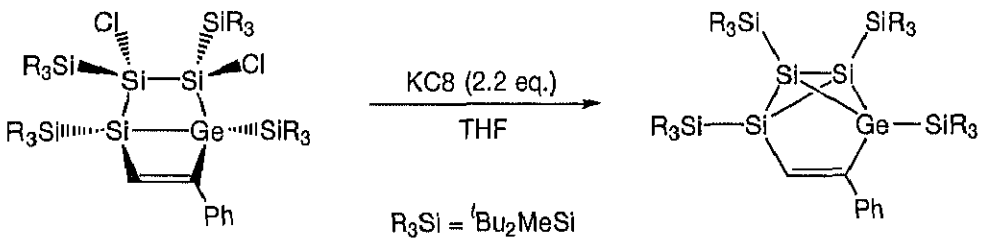
In chapter 3, synthesis and structure of cyclotetrasilenyl and cyclotetrasilenide which are produced by the reduction of cyclotetrasilenylium ion are described. Moreover, a reversible redox system of cyclotetrasilenyl cation, radical, and anion is reported.



In chapter 4, photochemical isomerization of 1,2,5-trisilabicyclo[3.2.0]hepta-3,5-diene to 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene is described, along with the mechsanistic discussion.



In chapter 5, synthesis of the first 1,2,6-trisila-5-germabenzvalene by the reaction of 2,3-dichloro-1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene with KC_8 is described. Molecular structure of 1,2,6-trisila-5-germabenzvalene derivative and its isomerization to 1,2,5-trisila-6-germabenzvalene is also described, along with the mechanistic discussion.



In chapter 6, synthesis and structure of the first 'heavy' cyclobutadiene dianion consisting of silicon and germanium atoms are described.

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