Isolable silylene, disilenes, trisilaallene, and related compounds

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Abstract

Our recent studies of synthesis, structure, and reactions of an isolable silylene, stable novel cyclic and conjugated disilenes, a trisilaallene are summarized. Due to the distinctive electronic and steric effects of trialkylsilyl substituents, tetrakis(trialkylsilyl)disilenes showed interesting structural features around Si=Si bonds, electronic spectra, and reactions. The tetrasilyldisilenes were useful reagents for the synthesis of novel types of organosilicon compounds such as η^2-disilene transition metal complexes and a 1,3-disilabicyclo[1.1.0]butane. Photochemical and thermal interconversion among Si_4R_6 isomers including a cyclotetrasilene, a silylcyclotrisilene, and a bicyclo[1.1.0]tetrasilane occured without apparent participation of the corresponding tetrasila-1,3-diene. The first spiropentasiladiene was thermally very stable and showed remarkable spiroconjugation between the two ring π systems. An isolable dialkylsilylene was found to be well-protected sterically from dimerization but least perturbed electronically. Using the silylene, a trisilaallene, the first stable compound with formal sp-hybridized silicon atom, was synthesized. In contrast to carbon allenes, the skeleton of the trisilaallene was significantly bent and remarkably fluxional.
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1. Prologue

In 1965, when I was a third-year student of Kyoto University, Professor Makoto Kumada said us proudly on the first day of his class of Organometallic Chemistry, "A new journal specialized to organometallic chemistry started last year." The new journal, *The Journal of Organometallic Chemistry*, was a symbol of the rise of the new chemistry field, and since then, the journal has played a role of a major information base of this field. Since I was very much interested in both organosilicon chemistry and physical organic chemistry at that time, I chose to start my research career in Prof. Kumada's laboratory without hesitation and I was guided directly by associate Prof. Hideki Sakurai. It was not long before that I realized there was no Si=X doubly bonded com-

pounds (X = Si, C, and O) mysteriously. I asked neighboring senier students the reason but nobody had an answer. The absence of the silicon doubly bonded compounds had been taken as a matter of course. In 1970, I moved to Sendai to join newly established Prof. Sakurai's laboratory at Tohoku University. There, I have had an opportunity to dedicate myself to the studies of organosilicon chemistry as a research associate, an associate professor, and a full professor for more than 30 years. During these earier days, I had been attracted by the electronic structure and properties of organosilicon reactive intermediates such as silyl radicals, silyl anions, silylium ions, silylenes, radical ions of silicon containing π electron systems, excited states of aryldisilanes, and hyper-coordinate silicon compounds, under the strong influence of Prof. Sakurai. My attitude to the chemistry was furthered during my stay in Prof. H. Bock's labolatory in Frankfurt as an Alexander von Homboldt Research Fellow.

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In 1981, West et al. [1] and Brook et al. [2] succeeded to synthesize the first isolable disilene and silene, respectively (Eqs. (1) and (2)). Since these stimulative discoveries, much attention has been focused on the chemistry of unsaturated bonds of heavier group-14 elements [3].

$$(Me_3Si)_2SiMes_2 \xrightarrow[-Me_3SiSiMe_3]{h\nu} [Mes_2Si:] \xrightarrow{X2} Mes_2Si=SiMes_2$$

(1)

(2)
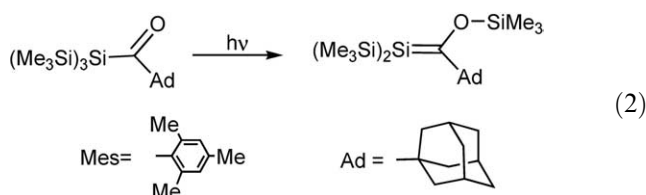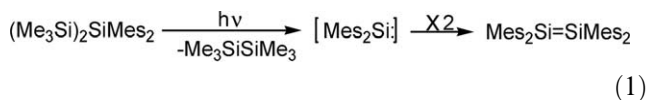
Although these discoveries did not move me immediately to participate in this interesting research field, I have been guided there quite naturally by fortunate accidental findings, brilliant coworkers, the great intellectual curiosity, and my earnest wishes to contribute toward the development of the basic silicon chemistry. In this account, I wish to summarize some of our results obtained during the last 10 years together with my personal reminiscences.

2. Attempted generation of triplet silylenes and synthesis of stable acyclic and cyclic tetrakis(trialkylsilyl)disilenes

In their theoretical paper published in 1991 [4], Grev et al. stated "*a winning strategy for the experimental design of a triplet ground state silylene is to produce, by whatever means, a bis(trialkylsilyl)silylene, with alkyl being something larger than methyl*". As an associate professor of Sakurai's laboratory, I had many discussions with a PhD student, T. Maruyama, how to generate a triplet silylene, during the course of our studies of substituent effects on the UV–Vis spectra of silylene [5]. We thought that bis(trialkylsilyl)silylenes would be generated by the photolysis of the corresponding cyclotrisilanes, because Matsumoto et al. [6] had already succeeded a couple of years ago to prepare bis(triethylsilyl)silylene by the photolysis of hexakis(triethylsilyl)cyclotrisilane, while the final product was the corresponding disilene, which was persistent in solution.

In the hope of generating triplet silylenes in low-temperature matrices by the photolysis of the corresponding cyclotrisilanes, we started investigating the synthesis of cyclotrisilanes with diisopropylmethylsilyl, *t*-butyldimethylsilyl, and triisopropylsilyl substituents. However, the products of the reduction of the corresponding dibrom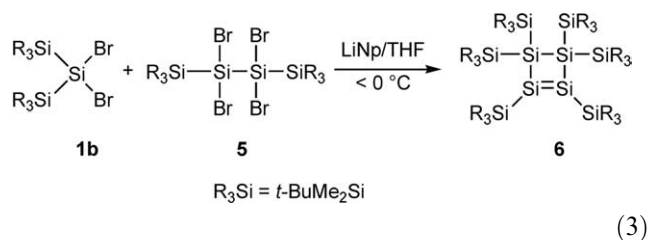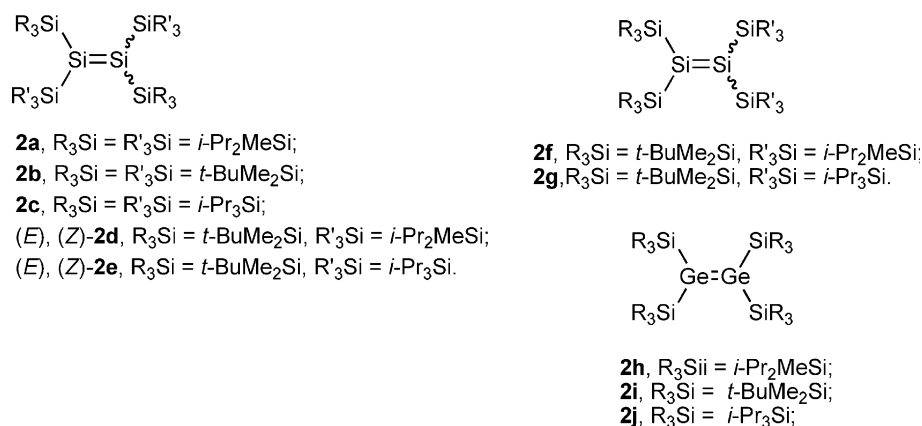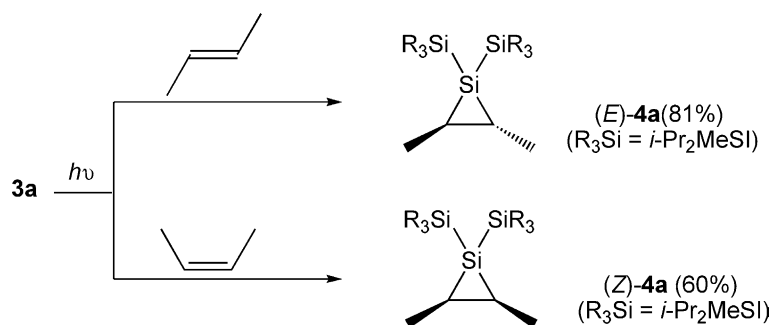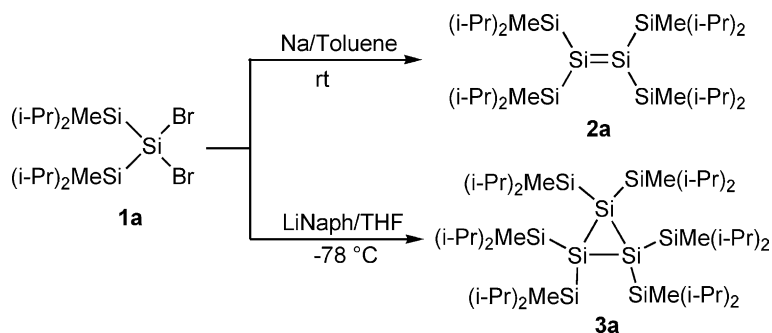osilanes were strongly dependent on the reducing reagents and steric bulkiness of the silyl substituents. The corresponding tetrakis(trialkylsilyl)disilenes were obtained often as major products.

Typically, the reduction of bis(diisopropylmethylsilyl)dibromosilane **1a** with lithium naphthalenide in THF afforded the corresponding cyclotrisilane **3a** as the major product, while the reduction of **1a** with sodium in toluene gave disilene **2a** (Scheme 1).

I had the appointment of a full professor at Tohoku Universty in 1995, as the successor of Sakurai. We quitted a study of triplet silylenes after confirming that the bis(trialkylsilyl)silylenes generated by the photolysis of the corresponding cyclotrisilanes behaved as singlet silylene in solution as evidenced by the stereospecific *syn* addition of the silylenes to (*E*)- and (*Z*)-2-butenes (Scheme 2) and that the silylenes did not form during similar photolysis in a low-temperature matrix [7]. Very recently, bis(tri-*t*-butylsilyl)silylene and a similar bis(trialkylsilyl)silylene were evidenced to be a triplet silylene by the reactivity, theoretical calculations, and ESR spectroscopy [8].

I was delighted, however, with those accidental findings that the formation of stable disilenes was performed by the simple reduction of the corresponding dihalosilanes [9], i.e., by the same method used by Kipping in 1922 for his unsuccessful approach to tetraphenyldisilene [10]. In addition, Liang and Allen [11a] and Karni and Apeloig [11b] had found theoretically that the geometry of disilene was very much influenced by the substituents; electron-donating silyl substituents were expected to change the geometry around disilene from usual *trans*-bent to planar. We synthesized various stable tetrakis(trialkylsilyl)disilenes [9,12a,12b] and tetrakis(trialkylsilyl)digermenes [12c] by this and other routes (Chart 1). Whereas the theoretical prediction [11] was not confirmed by the X-ray analysis of these disilenes because the geometry around Si=Si bond was very flexible and strongly influenced by the steric bulkiness of the substituents and crystal packing force. The ^{29}Si resonances for the unsaturated silicons in **2a**–**2e** appeared at 140–150 ppm. These unusually low-field resonaces were understood by the significantly large deshielding along one principal axis related to the $\sigma \rightarrow \pi^*$ transition in tetrasilyldisilenes [13].

As a natural extention of our studies, I had planned to synthesize a tetrasila-1,3-butadiene derivative and asked a Ph.D. student, T. Iwamoto, to investigate the reduction of a mixture of a 2,2,3,3-tetrabromotetrasilane **5** and dibromosilane **1b**. In reality, the reduction using lithium naphthalenide at −78 °C and then warming up afforded the corresponding cyclotetrasilene **6** instead of the desired tetrasila-1,3-diene derivative (Eq. (3)) [14]. We succeeded again accidentally to synthesize the first cyclic disilene. A tetrasila-1,3-diene was synthesized soon by Weidenburch et al. [15].

Scheme 1.

Scheme 2.

2a, $R_3Si = R'_3Si = i\text{-}Pr_2MeSi$;
2b, $R_3Si = R'_3Si = t\text{-}BuMe_2Si$;
2c, $R_3Si = R'_3Si = i\text{-}Pr_3Si$;
(E), (Z)-**2d**, $R_3Si = t\text{-}BuMe_2Si$, $R'_3Si = i\text{-}Pr_2MeSi$;
(E), (Z)-**2e**, $R_3Si = t\text{-}BuMe_2Si$, $R'_3Si = i\text{-}Pr_3Si$.

2f, $R_3Si = t\text{-}BuMe_2Si$, $R'_3Si = i\text{-}Pr_2MeSi$;
2g, $R_3Si = t\text{-}BuMe_2Si$, $R'_3Si = i\text{-}Pr_3Si$.

2h, $R_3Sii = i\text{-}Pr_2MeSi$;
2i, $R_3Si = t\text{-}BuMe_2Si$;
2j, $R_3Si = i\text{-}Pr_3Si$;

Chart 1.

$R_3Si = t\text{-}BuMe_2Si$

(3)

Because the yield of cyclotetrasilene **6** was very low, we searched for another route. Trihalosilane **7** was designed as a new interesting precursor for the cyclotetrasilene by Iwamoto, who has been a research associate of my group since 1998. Actually, cyclotetrasilene **6**

formed rather in high yield, when the reduction of **7** was carried out using sodium in toluene. However, the reduction of **7** with pottasium graphite in THF at low temperature gave an isomeric cyclotrisilene **8** as the first cyclotrisilene (Scheme 3) [16]. Another cyclotrisilene was synthesized and analyzed by X-ray crystallography soon by Sekiguchi et al. [17].
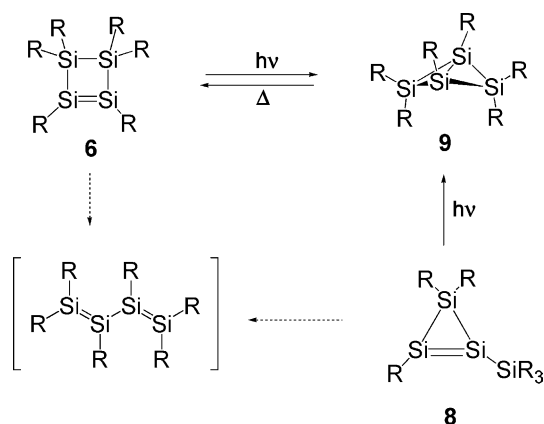
During the course of our studies on the reactions of these cyclic disilenes, we found interesting interconversion among **6**, **8**, and the corresponding bicyclo[1.1.0]tetrasilane **9** [14,18]. When cyclotetrasilene **6** in 3-methylpentane was irradiated with a high-pressure Hg arc lamp ($\lambda > 420$ nm), the solution turned from
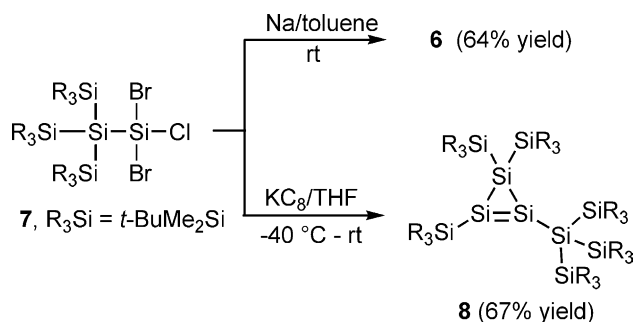
Scheme 3.

the original bright orange to red brown; the absorbance at 465 nm decreased with two clear isosbestic points at 424 and 515 nm. Leaving the photolysate for 12 h in the dark at room temperature, **6** was reproduced quantitatively. The structure of the photoproduct was characterized as the corresponding tetrasilabicyclo-[1.1.0]butane **9** by ^{1}H NMR spectroscopy and by the product analysis of hydrolysis of the photoproduct of **6**. The photochemical conversion of **6** to **9** and the thermal reversion were repeated more than ten times without appreciable side reactions. Both the thermal and photochemical isomerizations were confirmed using substituent-labeling experiments to proceed via 1,2-silyl-migration instead of skeletal isomerization [14b]. Cyclotrisilene **8** isomerized photochemically to bicyclo[1.1.0]tetrasilane **9**, which converted thermally to cyclotetrasilene **6** (Scheme 4). However, no evidence was found for the intervention of the corresponding tetrasila-1,3-diene in the present Si_4R_6 interconversion.

In later years, Müller [19] searched theoretically for energy surfaces of a set of Si_4H_6 isomers involving cyclotetrasilene, bicyclo[1.1.0]tetrasilane, tetrasila-1,3-diene, silylcyclotrisilene, etc. and found the most stable isomer should be bicyclo[1.1.0]tetrasilane, while the second stable cyclotetrasilene was only 3.0 kcal/mol higher in energy; tetrasila-1,3-diene and 1-silylcyclotrisilene were more than 33 and 22 kcal/mol less stable than the bicy-

clotetrasilane, respectively. It was reasonable we did not get the tetrasila-1,3-diene but we had the fortune to get the cyclic disilene rather than the bicyclotetrasilane probably due to the electronic effects of silyl-substituents.

I asked an undergraduate student, M. Tamura, to investigate the addition mode of alcohols to cyclotrisilene because I had been very much interested in the mechanisms of the reactions of disilenes with alcohols [20]. He investigated the reactions of **8** with various alcohols such as methanol, ethanol, *t*-butyl alcohol, and phenols with Iwamoto, and found all these reactions afforded the coresspanding *anti*-adduct regio- and stereospecifically (Eq. (4)) [21].

$$(4)$$
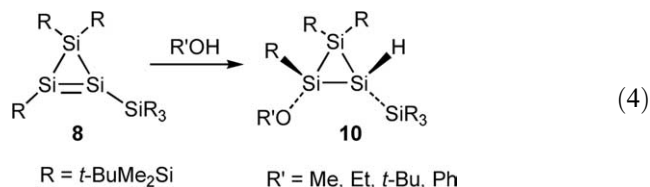
One day, when Tamura was tracing the reaction of red cyclotrisilene **8** with ethanol, he noticed that although the NMR spectra showed the complete consumption of **8**, the solution remained red. Careful recrystallization from hexane gave crystals of the first spiropentasiladiene **11** in addition to the crystals of ethanol adduct of **8**. Reinspection of the starting cyclotrisilene **8** by NMR spectroscopies revealed contamination of a small amount of **11**. Spiropentasiladiene **11** was found finally to form during the reaction of trihalosilane **7** with KC_8 in 3.5% yield together with **8** (Eq. (5)) [22]. Spiropentasiladiene **11** was sensitive to air but thermally very stable and melted at 216–218 °C without decomposition. Fortunately, spiropentasiladiene **11** was less reactive toward alcohols than **8**, less soluble in organic solvents, and higher in crystallinity than **8** and its ethanol adduct.

$$(5)$$
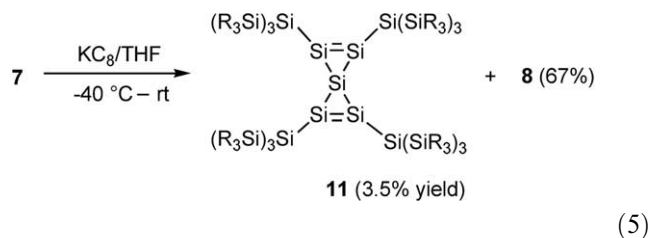
Carbonic spiropentadiene is a fascinating compound because of the possible through-space interaction between the two perpendicular double bonds (spiroconjugation). Whereas the spiro-conjugation in spiropentadiene and other related systems has been discussed extensively [23], no spiropentadiene derivatives have been isolated so far; Billups et al. [24] generated parent spiropentadiene and 1,1′-dichlorinated spiropentadiene in solution but they were very unstable in solution to decompose within a few minutes even below 100 °C. Spiropentasiladiene **11** was synthesized

Scheme 4.

as the first stable spiropentadiene comprising of group-14 elements. In the X-ray structure of **11**, the two three-membered rings were not perpendicular to each other with a dihedral angle of 78.3° and the two vicinal silyl-substituents were significantly up and down from the cyclotrisilene ring plane. The spiropentasiladiene ring of **11** had local D_2 symmetry rather than D_{2d} symmetry for theoretically optimized parent spiropentasiladiene, which had two Si=Si double bonds arranged perpendiculary. Four major $\pi \rightarrow \pi^*$ bands were observed in the UV–Vis spectrum of **11**, indicating significant spiro-conjugation between the two Si=Si double bonds; λ_{max}/nm ($\varepsilon/10^4$) 560 (0.253), 500 (0.364), 428 (1.17), 383 (1.81). The complicated spectral pattern did not meet with the simple spiroconjugation theory for the D_{2d} spiropentadiene, which allowed only the splitting of the two π^* orbitals. In the distorted D_2 spiropentasiladiene, the through-space interaction between the π orbitals was also allowed (Fig. 1). The significant through-space interactions between π orbitals as well as between π^* orbitals were concluded to be the origin of the splitting of the low-energy transition bands and the red-shift of the longest wavelength band observed in **11**. Spiropentasiladiene **11** not only served

as a probe to support the theoretical consequence of the spirocojugation in spiropentadiene but also afforded an opportunity to consider how the theory should be modified by the distortion of the geometry in a spiroconjugation system.

3. Reactions of tetrasilyldisilenes and their application to the synthesis of novel silicon systems

The facile intramolecular isomerization between (*E*)-**2d** and (*Z*)-**2d** was observed by temperature-dependent ^{29}Si NMR spectroscopy to occur with the free energy of activation less than 15 kcal/mol at 300 K [12a]. The activation energy was ca. 10 kcal/mol smaller than those of *E,Z*-isomerization of other known stable disilenes with aryl and alkyl substituents [3h]. The origin of the low barrier for the silyl-substituted disilenes was ascribed to the effective σ–π interaction at the transition state of the isomerization (Eq. (6)). In addition to the rotational isomerization, apparent dyotropic rearrangement of **2d** to **2f** was observed to be accompanied at higher temperatures.
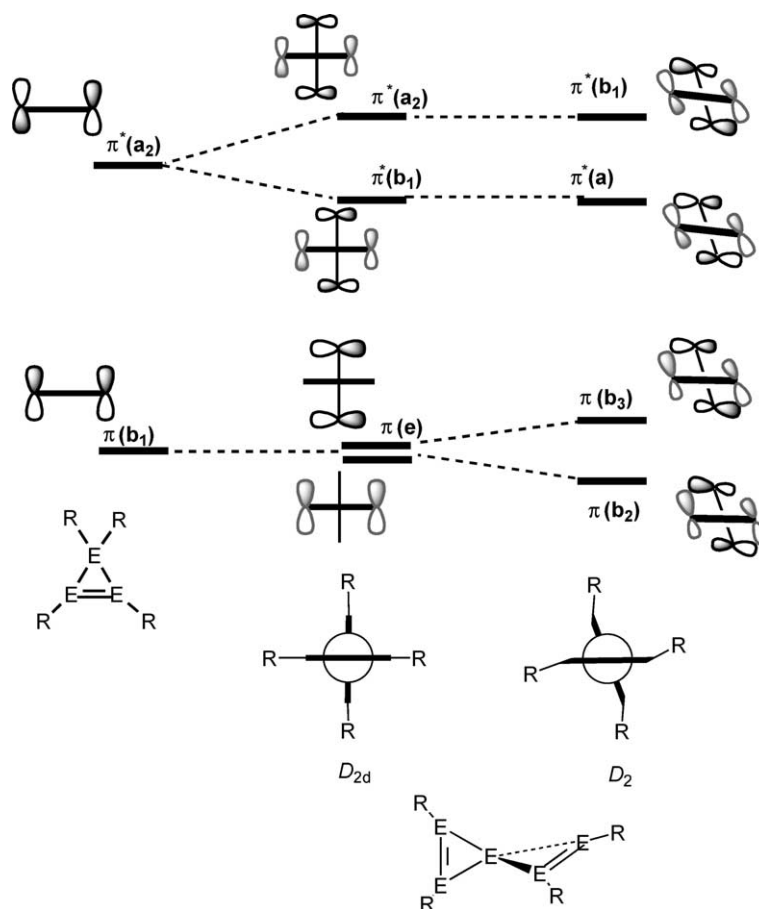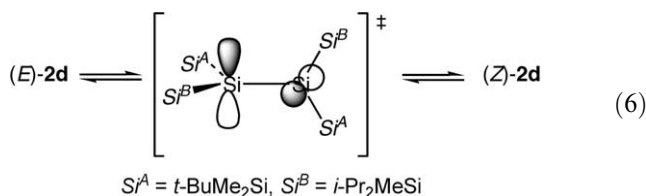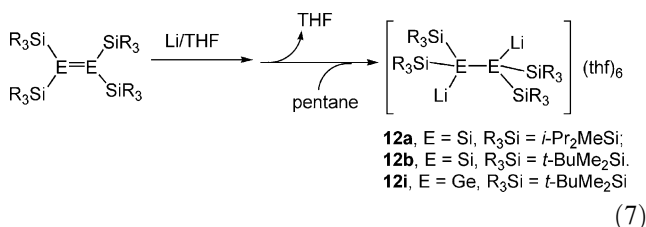

Fig. 1. Schematic MO diagram for spiroconjugation applied for D_{2d} and D_2 spiropentadienes.

$$(E)\text{-}2d \; \Longrightarrow \; \left[\begin{array}{c} Si^A \\ Si^B \end{array} \!\! Si \cdots Si \!\! \begin{array}{c} Si^B \\ Si^A \end{array} \right]^{\ddagger} \; \Longrightarrow \; (Z)\text{-}2d \qquad (6)$$

$$Si^A = t\text{-}BuMe_2Si, \; Si^B = i\text{-}Pr_2MeSi$$

Tetrakis(trialkylsilyl)disilenes reacted with various reagents [25]. Some reactions were similar to those found for tetramesityldisilene and other tetraaryldisilenes [3] but several reactions were unique to tetrasilyldisilenes. Typical examples are summarized in Scheme 5. A mechanistic study of the smooth reactions of these disilenes with various haloalkanes revealed the biradical character of disilenes [26].

The reactions of tetrasilyldisilenes and tetrasilyldigermenes with lithium gave uniquely the corresponding 1,2-dilithiodisilanes and 1,2-dilithiodigermane as off-white solids (Eq. (7)) [27].

$$R_3Si \!\! \underset{R_3Si}{\overset{\displaystyle SiR_3}{\diagdown}} \!\! E\!\!=\!\!E \!\! \underset{SiR_3}{\overset{\displaystyle SiR_3}{\diagup}} \; \xrightarrow[\text{pentane}]{\text{Li/THF}} \; \xrightarrow{\text{THF}} \; \left[\begin{array}{c} R_3Si \\ R_3Si \end{array} \!\! E\!\!-\!\!E \!\! \begin{array}{c} Li \\ SiR_3 \\ SiR_3 \end{array} \right] (\text{thf})_6 \qquad (7)$$

12a, E = Si, R_3Si = i-Pr_2MeSi;
12b, E = Si, R_3Si = t-$BuMe_2Si$.
**12i**, E = Ge, R_3Si = t-$BuMe_2Si$

The 1,2-dilithiodisilanes served as synthetic reagents for new types of organosilicon compounds. As the first stable 1,3-disilabicyclo[1.1.0]butane derivative, **13b** was synthesized as air- and moisture-sensitive bright yellow crystals in 70% yield using the reaction of 1,2-dilithiodisilane **12b** with 2-adamantanone (Eq. (8)) [28].

$$\text{12b} \; + \; \overset{\displaystyle }{\bigominus}\!\!=\!\!O \; \xrightarrow{\text{benzene}} \; \text{[structure]} \qquad (8)$$

13b, 70%
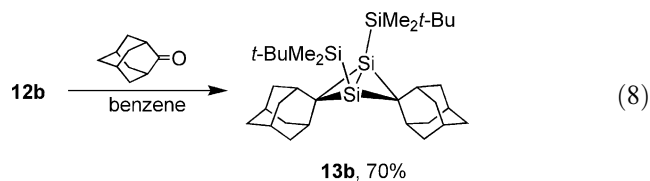
We noticed immediately the importance of the structural issue of 1,3-disilabicyclo[1.1.0]butane **13b** because we were aware of the theoretical papers on metallabicyclo[1.1.0]butanes reported by Schleyer et al. [29] during our study of Si_4R_6 isomers. The theoretical papers showed that two isomers, long-bond (LB) and short-bond isomers (SB), exsisted in metallabicyclo[1.1.0]butanes. As shown in Chart 2, the SB isomers are characterized by not only the short bridge-bond distance (r), but the small interflap angle (ϕ) and the large R–M–M angle (θ), while the long-bond (LB) isomers have long r, large ϕ, and small θ. The bridge bond in an SB isomer is a normal bent σ bond, while the bond in an LB isomer should be ascribed to an inverted σ bond with significant singlet biradical character.

The bridge Si–Si bond distance, the interflap angle between two three-membered ring planes, and the Si–Si–Si angles of **13b** determined by X-ray analysis were 2.412(1) Å, 140.78(2)°, and 118.8(3)°, respectively. DFT calculations of 1,3-bis(trihydrosilyl)-1,3-disilabicyclo[1.1.0]butane as a model of **13b** showed the existence of LB and SB isomers. Comparison of the structural characteristics as well as ^{13}C and ^{29}Si resonances of **13b** with those of the model compound indicated the LB nature of **13b**. Interestingly, **13b** showed a distinct band maximum at 420 nm (ε 6500) due to the σ → σ* transition of the bridge Si–Si bond, in good agreement with the high-lying HOMO and low-lying LUMO found theoretically for the LB isomer of the model disilabicyclobutane. Biradical nature of the Si–Si bond in **13b**
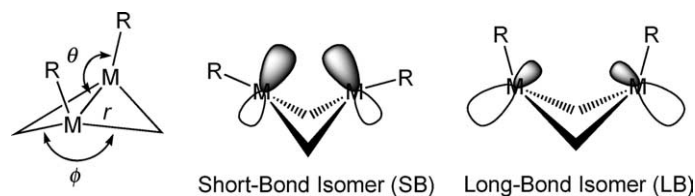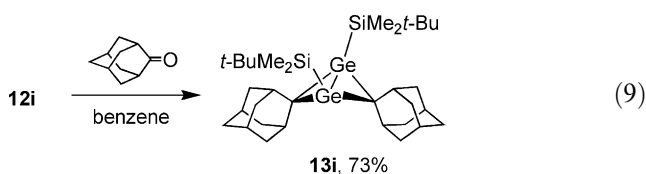

Scheme 5.
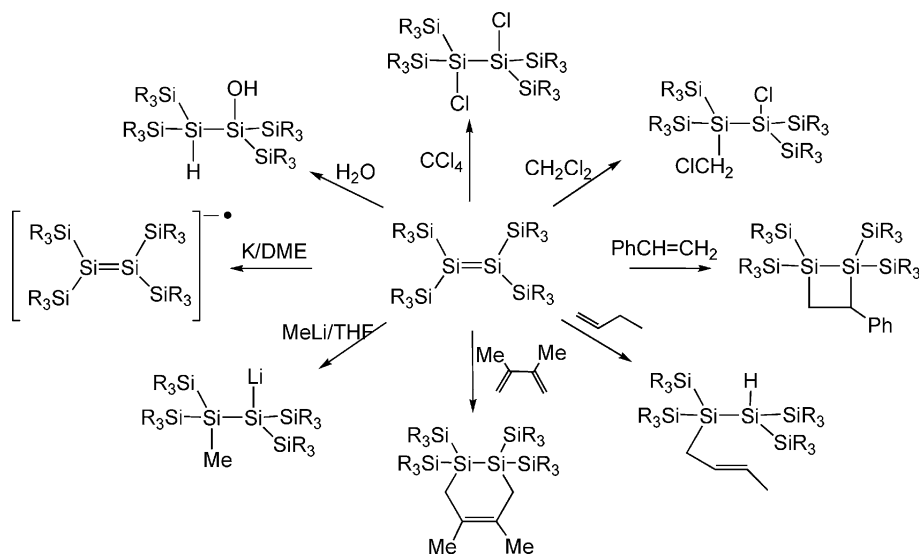
Chart 2.

was evidenced by the facile reactions of **13b** with halo-alkanes, phenylacetylene, and ketones.

Using a similar method, 1,3-digermabicyclobutane **13i** was synthesized and characterized as a long-bond isomer (Eq. (9)); the UV absorption maximum was found at 440 nm with ε of 9800 [30].


$$(9)$$

Another application of dilithiodisilane **12b** was found in the synthesis of stable η^2-disilene transition metal complexes. At that time, there had been few reports on the synthesis and properties of mononuclear transition-metal complexes with η^2-disilene ligands [31].

The bonding of a disilene to a metal center would be understood in terms of "ligand-to-metal σ-donation" and "metal-to-ligand π-back donation", similarly to that of an olefin (Dewar–Chatt–Duncanson model). According to this model, the η^2-disilene transition-metal complexes can be described using two resonance structures of a π-complex and a metallacycle (Scheme 6). The π-complex character will increase with decreasing the π-back donation. One of our interests in this study was how the π-character of a disilene ligand in a complex was increased by changing cental trnasition metals, ligands except the disilene, and substituents on the disilene.

Platinum (**14**) and palladium η^2-disilene complexes **15** were synthesized by the reactions of cis-(Me₃P)₂MCl₂ (M = Pt, Pd) with 1,2-dilithiodisilane **12b** in THF at 50 °C (Eq. (10)) [32,33]. Complexes **14** and **15** were stable to air and moisture in the solid state as well as in solution at room temperature.

$$(10)$$
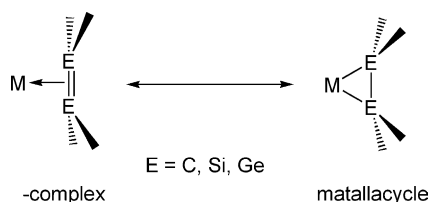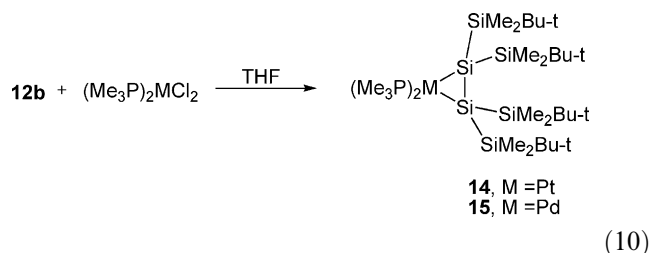
The X-ray structural analysis revealed that the central Si1–Si2 bond length in **14** and **15** [2.401(1) and 2.3027(8) Å, respectively] were between the known values for Si–Si single and double bonds. The bent angles (δ) of **14** (28.4°) and **15** (27.2°), which were defined as an angle between the Si3–Si1–Si4 plane and the Si1–Si2 bond, were far larger than that of free disilene **2b** (0.1°), indicative of the significant bending around the silicon atom in the complexes (Chart 3). In accord with the theoretical calculations by Sakaki et al. [34], these complexes were characterized as metallacycle, while the π-complex character for **15** was suggested to be somewhat stronger than that for **14**.

At the 13th International Symposium on Organosilicon Chemistry in Mexico in 2002, Prof. Apeloig informed in his lecture that the 14-electron platinum complex of stable silene was prepared by the reaction of bis(tricyclohexylphosphine)platinum with a stable silene [35]. In search of a disilene-transition metal π complex, the reaction of bis(tricyclohexylphosphine)palladium dichloride with dilithiodisilane **12b** was investigated. Expectedly, the reaction gave the first 14-electron disilene-palladium complex **16** as red crystals (Eq. (11)) [30]. In the 14-electron disilene-palladium complex, the bent angle around the Si=Si bond was less than 10° with the Si=Si bond length of 2.273(1) Å. The 14-electron disilene palladium complex with the least π-back donation was regarded as a π-disilene complex [36].

Scheme 6.

Chart 3.

$$(11)$$

4. Stable dialkylmetallenes and trimetallaallenes

The road to a stable dialkylsilylene started with a small accidental discovery. In 1985, I investigated with an undergraduate student, N. Matsuyama, the generation of radical anions of 1,1-bis(trimethylsilyl)ethylene **17** and related silylalkenes to compare their ESR spectra with those of the corresponding radical cations generated by the γ-irradiation of the olefins in CFCl$_3$ matrices [37]. She never succeeded in the observation of the corresponding radical anion of **17** by ESR, while anion radicals of 2-methyl- and 2-*t*-butyl-substituted 1,1-bis(trimethylsilyl)ethylenes were easily geneareted. Instead, she found the reduction of **17** by pottassium in THF afforded the dimeric 1,4-dianion **18** (Eq. (12)). Soon after the discovery, we were aware somewhat disappointedly that a similar dimerization of the radical anion of triphenylsilylethylene had been reported by Eisch et al. [38] long time ago. To turn the results into the publishable, we improved the method for the preparation of **18** using lithium as a reducing reagent and investigated several reactions of **18**. Peterson ractions of **18** with various aldehydes gave the corresponding 1,5-hexadienes and the reactions of **18** with some dichlorosilanes afforded the corresponding silacyclopentanes [39].

$$(12)$$

I noticed shortly that 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl bidentate ligand was able to replace two bis(trimethylsilyl)methyl groups, which had been used by Lappert and co-workers [40] as good sterically protecting groups of divalent germanium and tin compounds and their dimers. The cyclic bidentate ligand was thought to protect the divalent compounds from the dimerization much more effectively than the two Januslike bis(trimethylsilyl)methyl groups that are more conformationally flexible.

The reaction of dianion **18** (M = Li) with anhydrous SnCl$_2$ was investigated by an undergraduate student, R. Hirano since April of 1989. He graduated without any positive results at the end of March of 1990 and

had to commence a master course study at another laboratory of the department since the next April. We, most of all faculty members and students of Sakurai's lab, left Sendai immediately after the graduation ceremony to attend the annual meeting of the Chemical Society of Japan in Tokyo. At the beginning of April, when I returned from the meeting, I found he was still working at the bench in our laboratory. He held a Shlenck tube up high and asked me, "Could you see several dark red particles on the wall?" Like this, he prepared finally the first stable cyclic stannylene **19** that was monomeric even in the solid state (Eq. (13)). I believe the key to success was the use of ether as a solvent instead of highly solvating THF, but the procedure was intricate and often unsuccessful. The work was continued by R. Yauchihara, who repeated the experiments and confirmed the structure by X-ray crystallography and NMR spectroscopies [41].

$$(13)$$

The results encouraged us to investigate the synthesis of the corresponding germylene and silylene. However, the synthesis of the germylene by the reaction of dilithium compound **18** with GeCl$_2$/dioxane, GeI$_2$, and Ge[N-(SiMe$_3$)$_2$]$_2$ never gave the desired germylene despite our long efforts. Although we had already recognized the reduction of the corresponding dichlorogermane as an alternative method for the germylene but had never investigated at that time because of the low-yield synthesis of the dichlorogermane.

Meanwhile, West et al. and then Lappert et al. succeeded to isolate stable silylenes **20–23** (Chart 4) [42]. They were the first dicoordinate silylenes, while decamethylsilicocene with η^5-cyclopentadienyl ligands (**24**) had been known as stable divalent silicon species [43]. We noticed, however, that these silylenes as well as related *N*-heterocyclic carbenes [44] were stabilized by the strong interaction between the vacant pπ-orbital at the divalent atom and filled π-type orbitals of nitrogen, and hence, their electronic nature was strongly modified from the parent divalent species.
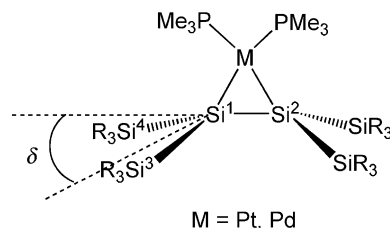

Chart 4.

We decided to continue our study of the synthesis of the silicon analog of **19** because it was expected to be isolable and least perturbed electronically. I asked a new graduate student, S. Ishida in 1996 to continue the synthesis of the germanium and silicon analogues of stannylene **19**. After the unsuccessful investigations of the reactions of **18** with various GeX$_2$-type compounds for almost a year, he found finally that desired germylene **26** was obtained as a stable compound by the reduction of the corresponding dichlorogermane **25** with sodium in toluene at room temperature (Eq. (14)) [45].

$$\text{(14)}$$
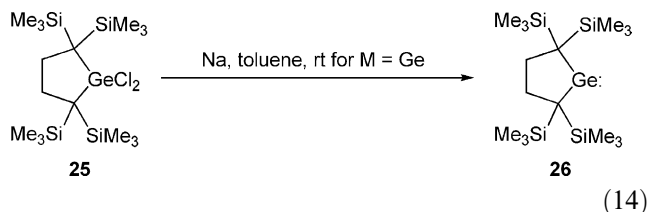
Although a similar reduction of dibromosilane **27** with sodium in toluene gave a mixture of the corresponding silylene **28** and its isomer **29**, **28** was obtained purely using pottasium graphite as a reducing reagent at low temperature in THF (Scheme 7) [46]. A similar procedure was recently applied to the improved synthesis of stannylene **19** [47].

The first isolable dialkylsilylene **28** was monomeric both in solution and in the solid state. The ^{29}Si resonance of the divalent silicon in **28** appeared at the extraordinarily low magnetic field (+567.4 ppm) and the absorption maximum due to n → p transition was observed at 440 nm (ε 500), indicating that **28** was well-protected sterically from dimerization but least perturbed electronically.

The bidentate ligand named helmet-like ligand protected silylene **28** effectively from the dimerization (Fig. 2) but still afforded enough space for the silylene to react with sterically compact reagents. Actually, silylene **28** reacted with various known trapping reagents for silylenes such as methanol, triethylsilane, ethylene, 2,3-dimethylbutadiene, and bis(trimethylsilyl)acetylene, giving the expected products. As a defect of this ligand, slow isomerzation of **28** to **29** occurred with the first-order rate constant of 1.82×10^{-6} s^{-1} in hexane, while no similar isomerization was found in germylene **26** and stannylene **19**.
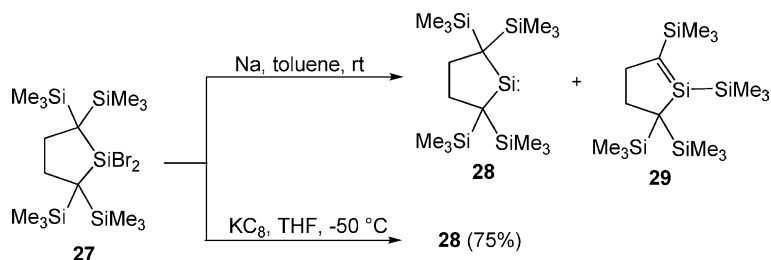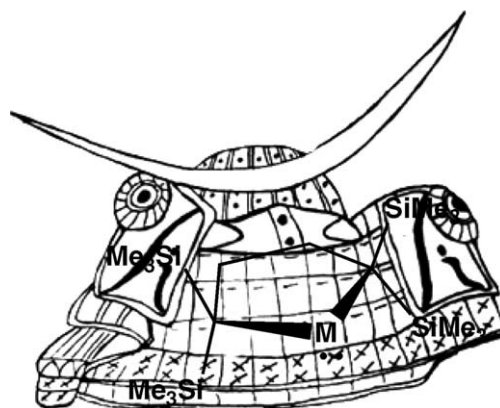

Fig. 2. 1,1,4,4-Tetrakis(trimethylsilyl) butane-1,4-diyl protects sterically the divalent metal center like a Japanese helmet (Kabuto).

The first intermolecular reactions of the excited state of silylene with benzene derivatives were discovered [48]. Typically, when a benzene solution of **28** was irradiated using longer wavelength light than 420 nm at room temperature, the corresponding silepin was obtained in quantitative yield; only the isomerization of **28** to **29** was observed in benzene in the dark. The photochemical insertion of silylene **28** toward substituted benzenes occurred generally to give the corresponding substituted silepins (Eq. (15)). The insertion reaction was highly sensitive to the steric hindrance at a reacting C–C double bond in a benzene; only unsubstituted C–C double bonds in the benzene ring reacted selectively. The excited state responsible for the photoreactions were established to be the singlet excited state with 1,1-biradical nature by laser flash photolysis and chemical trapping experiments [49].

Quantitatively

30a, X = H; **30b**, X = CH$_3$; **30c**, X = CH$_3$O; **30d**, X = F; **30e**, X = CF$_3$

$$\text{(15)}$$
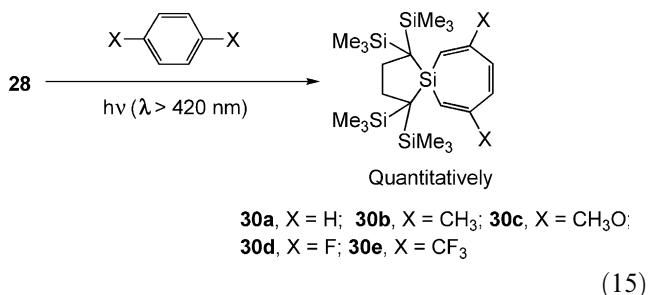
Since silylenes as well as germylenes and stannylenes had low-lying vacant pπ orbitals, the corresponding radical anions were expected to be generated as a unique

Scheme 7.

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class of reactive intermediates by one-electron reduction. By the reduction of silylene **28** with potassium, sodium, and lithium 4,4′-di(*tert*-butyl)biphenylide in DME at low temperatures, the corresponding silylene radical anion **31** was generated as the first persistent silylene radical anion in solution and characterized by ESR spectroscopy (Eq. (16)) [50]. The *g*-factor and ^{29}Si hyperfine splitting constants (hfs's) of **31** were almost independent of the countercations, indicating that **31** existed as a free ion or a solvent-separated ion pair in a polar DME solution. A very small hfs due to the ^{29}Si nucleus of the divalent silicon (30 G) as well as a very large *g*-factor (2.0077) indicated that an unpaired electron was accommodated in the vacant 3pπ orbital of silylene **28**.

$$ (16) $$
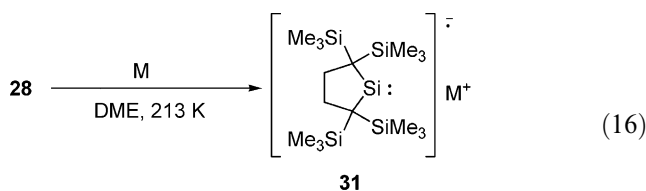
M = Cs, Rb, K, Na, Li/4,4′-di-*tert*-butylbiphenylide

Despite the fundamental importance, the reactions between doublet radicals and heavier group-14 divalent species with singlet electronic configuration had never been investigated until our study. The reactions of stable cyclic dialkylgermylene **26** and dialkylstannylene **19** with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, $R_2'NO^\bullet$) radical (2 equiv) to give the corresponding 1:2 adducts **32** and **33**, respectively (Eq. (17)). The kinetics of the stepwise addition of two TEMPO molecules to germylene **26** revealed that the initial addition of TEMPO to **26** was 10^{10} times slower than the second TEMPO addition to the resulted germyl radical **32** [47b,51].

$$ (17) $$
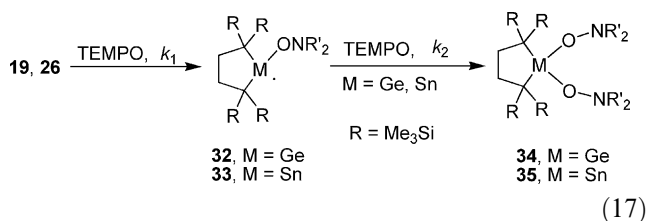
In contrast, the reaction of dialkylsilylene **28** with TEMPO gave an interesting 1,3-dioxadisiletane derivative **36** (Eq. (18)) [51]. In the reaction of **28**, the NO bond fission from the intermediate aminoxysilyl radical was concluded to be too fast to compete with the addition of extra TEMPO.

$$ (18) $$
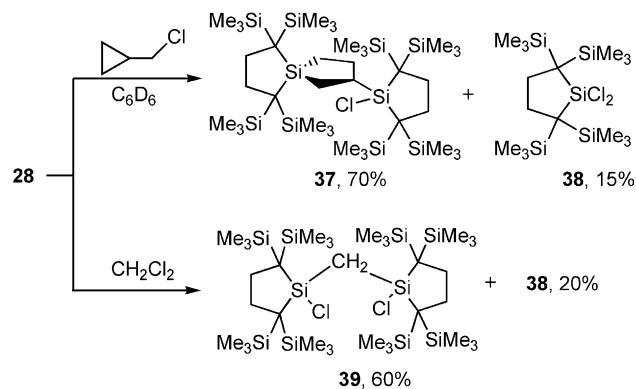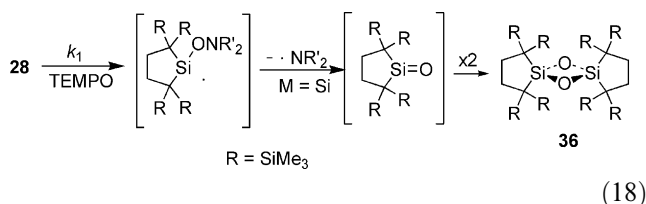
Scheme 8.

The reactions of silylene **28** with chloroalkanes, like dichloromethane and cyclopropylmethyl chloride afforded unusual products (Scheme 8) [52]. The results were understood not only by the dependence of the reaction modes on the silylene concentrations but the often unrecognized ambiphilic nature of silylenes.

The reactions of silylene **28** with chlorosilanes such as tetrachlorosilane, dimethyldichlorosilane, and dichlorosilane occurred smoothly at room temperature in hydrocarbon solvents to give the corresponding SiCl bond insertion products (Eq. (19)) [53]. In the reaction of **28** with H_2SiCl_2, only the SiCl bond insertion products were obtained, while a similar reaction with Me_2H-SiCl gave only the SiH insertion product, suggesting the remarkable difference in the steric requirements between these two insertion reactions. No reaction took place during the treatment of **28** with trimethylchlorosilane.

$$ (19) $$

40a, $SiR_3 = Me_2SiCl$;
40b, $SiR_3 = SiCl_3$;
40c, $SiR_3 = SiH_2Cl$
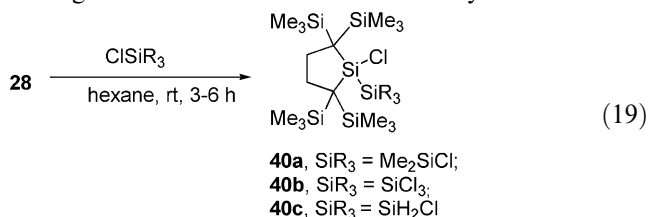
We expected that polychlorodisilanes thus obtained were applicable to the synthesis of novel unsaturated organosilicon frameworks. During studies in line with this idea, the reduction of 1,2,2,2-tetrachlorodisilane **40b** with potassium graphite was investigated in the hope of the formation of a tetrasilatriene. In reality, a fascinating trisilaallene derivative **41** was obtained as a dark green solid, while the mechanism remains open (Eq. (20)) [54]. Trisilaallene **41** was sensitive to air but thermally stable with a melting point of 198–200 °C.

$$ (20) $$
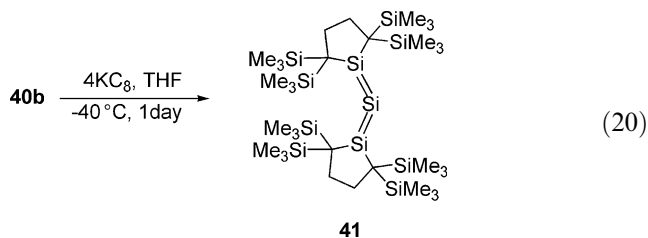
Although the sp-hybridized carbon atoms (sp-carbons) were commonly found in acetylene, allene, ketene, and carbon dioxide, heavy group-14 element analogs of these compounds have been very limited. Stable germanium, tin, and lead analogs of acetylene derivatives [55] as well as a marginally stable tristannaallene [56] were synthesized recently. However, no stable compounds with formal sp-silicon atoms had been isolated. Trisilaallene **41** was synthesized as the first isolable silicon compoundwith formally sp-hybridized silicon atom.

X-ray single-crystal analysis showed a very unusual structural feature of trisilaallene **41** (Fig. 3). In contrast to carbon allenes, the trisilaallene skeleton is not linear but bent. Remarkably, the central silicon atom (Si^2) of **41** in the crystal was found at four positions labeled Si^{2A}–Si^{2D} in Fig. 3, indicating that four structurally similar isomers existed, **A**–**D**. The occupancy factors for **A** through **D** were independent of crystals but significantly temperature dependent; 53%, 22%, 19% and 7% at −50 °C and 76%, 18%, 7% and 0% at −150 °C for crystal 1; 46%, 23%, 22% and 10% at 0 °C, 52%, 22%, 19% and 7% at −50 °C, 61%, 21%, 15% and 4% at −100 °C, and 72%, 19%, 10% and 0% at −146 °C for crystal 2. The energy differences between isomers **A**–**D** were estimated to be within 1 kcal/mol, suggesting a dynamic disorder mediated by a rotation of the Si^2 atom around the Si^1–Si^3 axis. The unusual bonding nature of **41** in the solid state
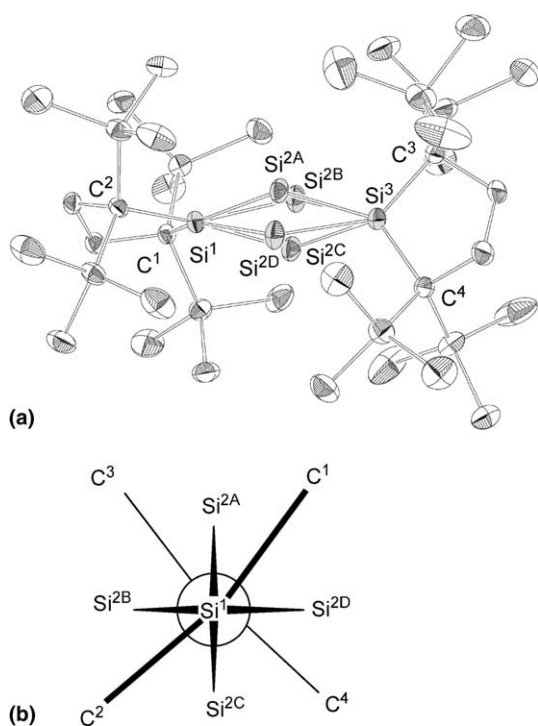
was also applicable to that in solution on the basis of the NMR spectroscopy.

The detailed analysis of the molecular structure of the most preferred isomer **A** of trisilaallene **41** revealed the bent-allenic nature with two *trans*-bent Si=Si double bonds that shared a silicon atom; at −150 °C, the Si^1–Si^2–Si^3 bond angle, the two Si=Si bond lengths, the dihedral angle between the C^1–Si^1–C^2 and C^3–Si^3–C^4 planes, the sums of the bond angles around Si^1 and Si^3 atoms were 136.49 (6)°, [2.177(1) and 2.188(1) Å], 92.5°, [354.1° and 354.9°], respectively. The UV–Vis absorption maxima were found at 390 nm (ε 21,300) and 584 nm (ε 700) in hexane. The remarkable red shift of the longest absorption band as well as the two-splitting band feature for **41** were consistent with significant conjugation between the two Si=Si double bonds.

The observed skeletal structure for **41** was not reproduced by the ab initio MO calculations for a model trisilaallene $Me_2Si=Si=SiMe_2$ (**42**). The optimized structure of **42** (**42[opt]**) was characterized to be neither linear nor bent allenic but zwitterionic (Fig. 4). The reason for the discrepancy between the experimental and theoretical structures was ascribed to the severe steric hindrance between two bulky silacyclopentane rings in **41**,which prevented **41** taking a zwitterionic structure. Calculations for **42[exp]**, where the coordinates of four carbon and three silicon atoms in **42** were fixed to those observed for **41**, revealed **42[exp]** was only 8.8 kcal/mol higher in energy than **41[opt]**. Trisilaallene **41** was found to have fluxional bent framework and to exhibit an effective conjugation between the two *trans*-bent Si=Si double bonds, in remarkable contrast to a carbon allene having rigid linear framework whose C=C π bonds are orthogonal to each other.

Recently, a germanium analogue of allene, trigermaallene **44** was synthesized using a similar method to that applied for trisilaallene **41** (Eq. (21)). In contrast to **41**, no disorder of central germanium atom was observed for **44** in the solid state [57].
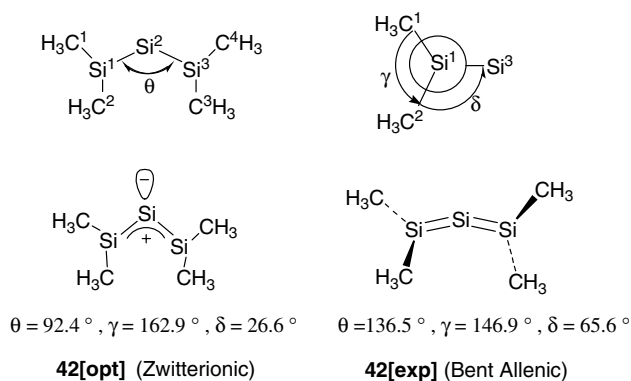

(a)

(b)

Fig. 3. Molecular structure of trisilaallene **41** at −50 °C: (a) a top view (hydrogen atoms were omitted for clarity) and (b) projection of the molecular frame to the plane perpendicular to Si^1–Si^3 axis.

$\theta = 92.4°$, $\gamma = 162.9°$, $\delta = 26.6°$ $\theta = 136.5°$, $\gamma = 146.9°$, $\delta = 65.6°$

42[opt] (Zwitterionic)   **42[exp]** (Bent Allenic)

Fig. 4. Schematic structural descriptions of trisilaallene **42[opt]** and **42[exp]** calculated at the B3LYP/6-31+G(d,p) level.

$$\text{(21)}$$
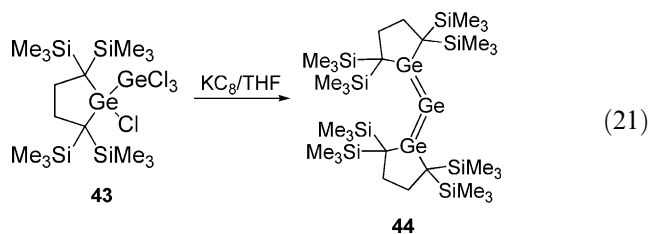
5. Epilogue

While our studies on some other unsaturated compounds such as silatriafulvenes [58], diaminosilylenes [59], and a stannaacetylene [60] were not included in this article, I have really enjoyed research in the wide and fruitful field of organosilicon chemistry. Not only our works but many other recent studies performed by other research groups have shown unusual bonding and structural characteristics of unsaturated compounds of heavier group-14 elements. First, the issue seems to be encouraging to build the modern systematic view in bonding, structure, and reactions covering the chemistries of all the main group elements. Second, the stable unsaturated compounds of heavier group-14 elements have the unique electronic properties that cannot be easily obtained, and hence, may be considered as new carriers of optoelectronic functions in organic–inorganic hybrid materials in the near future.

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