Reactions of a stable dialkylsilylene and their mechanisms

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Abstract. Various reactions for a stable dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl (**1**), are summarized and their mechanisms are discussed. Silylene **1** isomerizes to the corresponding silaethene via the 1,2-trimethylsilyl migration. Reduction of **1** with alkali metals affords the corresponding radical anion **1**[·−] with a relatively small ^{29}Si hfs constant (2.99 mT) and a large g-factor (g = 2.0077) compared with those for trivalent silyl radicals. Photo-excitation of **1** generates the corresponding singlet excited state (**1**[1*]) with the lifetime of 80.5 ns. The excited state reacts with C=C double bond compounds including benzene, naphthalene, and (*E*)- and (*Z*)-2-butenes. Although the thermal reactions of **1** with haloalkanes occur via radical mechanisms, the insertion into O–H, Si–H and Si–Cl bonds proceeds concertedly via the three-membered cyclic transition states. The reaction of **1** with H_2SiCl_2 gives the Si–Cl insertion product exclusively, while the quantitative insertion to Si–H bond occurs when Me_2SiHCl is used as a substrate. The origin of the rather unusual Si–H/Si–Cl selectivity is elucidated using DFT calculations. Silylene **1** adds to C=C, C≡C, and C=O π bonds to afford the corresponding silacycles as stable compounds. The importance of the carbonyl silaylides during the reactions of silylenes with aldehydes and ketones is emphasized.

Keywords. Stable silylene; mechanisms; photoreaction; addition; insertion; DFT.
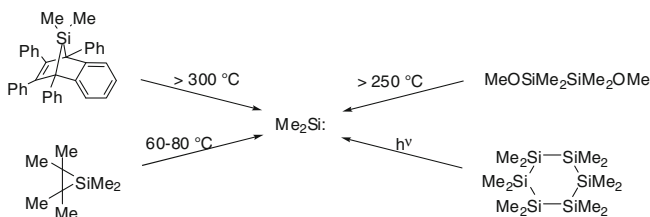
1. Introduction

Silylenes, silicon divalent compounds, are important reactive intermediates in organosilicon chemistry just like carbenes in organic chemistry. A number of organic and inorganic silylenes have been studied as transient species since more than 40 years. As a typical organosilylene, dimethylsilylene is generated by various methods including thermolysis of 7,7-dimethylsilanorbornadiene at 350°C,[1] 1,2-dimethoxytetramethyldisilane at 225°C,[2] and hexamethylsilirane at >60°C,[3] and photolysis of linear and cyclic permethylpolysilanes at lower temperatures,[4] as shown in scheme 1.

A number of other silylenes such as di-*tert*-butyl-silylene,[5] phenylmethylsilylene,[6] diphenylsilylene,[7] and bis[(2-dimethylaminomethyl)phenyl]silylene[8] are also available as transient silylenes using related generation methods as above. It is, therefore, natural that the reactions of the transient silylenes with various reagents have been investigated extensively.[9] Transient silylenes dimerize to disilenes, insert into various single bonds such as L–H (L = O, N, S, B, Si, Ge, halogens, etc.) and Si–X (X = Si, halogens), add to unsaturated bonds (C=C, C≡C, C=O, C=N, etc.) to form the corresponding silacycles and their derivatives, and complex to transition metals. Some of these reactions provide useful synthetic methods for the organosilicon compounds that

are difficult to be synthesized by other methods, and are important as *silylene trapping* reactions to prove the generation and existence of transient silylenes in different systems. Although much attention has been focused on the mechanistic aspects of the unique silylene reactions, the studies have often been limited because of the transient nature of the silylenes.

We have synthesized an isolable dialkylsilylene **1** in 1999,[10] after the synthesis of stable decamethylsilico-cene **2**[11] and cyclic diaminosilylenes **3**,[12] **4**,[13] **5a**,[14] and **5b**[15] (chart 1). Silicocene **2** is a rather exceptional silicon divalent compound with η^5-pentamethylpentadi-enyl ligands. Diaminosilylenes **3**–**5b** are stable divalent dicoordinate silylenes but stabilized electronically by the strong interaction between the vacant p_π-orbital at the divalent atom and filled p_π-type lone-pair orbitals of neighbouring heteroatoms. More recently, Driess *et al.* have succeeded to synthesize diaminosilylene **6**[16] as a novel stable silylene.[17,18] Dialkylsilylene **1** is less electronically perturbed than **3**–**6** and close to dialkyl- and diarylsilylenes in the electronic nature, while the steric bulkiness of **1** is much larger than the transient dialkyl- and diarylsilylenes.

Various unimolecular and bimolecular reactions of silylene **1** are discussed here, apart from the synthesis, structure, and spectroscopic properties of **1** that have been previously reviewed.[10b−e] The reactions and
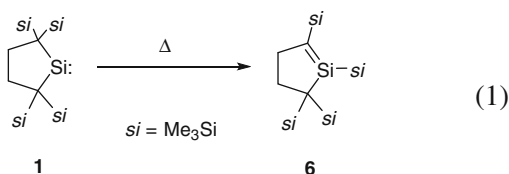
Scheme 1. Transient dimethylsilylene generated by different methods.

have shown that the silylene–silene relative energy is small but the barrier is high, while they are strongly dependent on the substituents.[9f,21] Typically, Nagase and Kudo[21b] have shown that the isomerization between **7a** and **8a** and that between **7c** and **8c** is almost thermoneutral, while ethylsilylene **7b** is 10.3 kcal mol^{-1} less stable than methylsilene **8b** at the MP3/6-31G* level (eq. 2). The barrier heights for the isomerization of **7a**, **7b**, and **7c** into **8a**, **8b**, and **8c** are calculated to be 43.0, 44.4, and 24.8 kcal mol^{-1}, indicating that the barrier for 1,2-silyl migration (**7c** → **8c**) is remarkably lower than those for 1,2-hydrogen and 1,2-methyl migration.

mechanisms of **1** will be compared directly with those of dialkyl- and diarylsilylenes accumulated over long periods of time.[9]

2. Intramolecular 1,2-silyl migration

Isolable dialkylsilylene **1** is storable at 0°C in the solid state but isomerizes slowly to the corresponding silaethene **6** via an apparent 1,2-silyl migration at room temperature in solution (eq. 1, hereafter, si = SiMe$_3$ unless otherwise noted).[10a,19] The first-order rate constants for the isomerization in hexane have been determined UV-vis spectroscopically at various temperatures; the rate constant, activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$) at 298 K are 6.24×10^6 s^{-1}, 18.49 ± 0.43 kcal mol^{-1} and -20.32 ± 1.35 cal mol^{-1} K^{-1}, respectively.

$$\text{7a, X = H} \quad \text{8a, X = H}$$

(2)

(1)

Relative stability between a silene and the corresponding silylene and the barrier separating the two species have intrigued both experimental and theoretical silicon chemists. Experimentally, very few studies have been proposed that silene-to-silylene isomerization occurs during the high-temperature thermolysis of silacyclobutanes and polysilanes.[20] Theoretical studies

The relatively large negative $\Delta S^{\ddagger}$ value for the isomerization of **1** to **6** suggests that the transition state of this isomerization would have a significantly restricted structure, and therefore, any multi-step mechanism involving bond-cleavage at the rate controlling step may be eliminated from possible mechanisms. The $\Delta H^{\ddagger}$ value is consistent with the theoretical barrier for the isomerization from **7c** to **8c** calculated by Nagase and Kudo ($E_a = 24.8$ kcal mol^{-1} at MP3/6-31G* level),[21b] suggesting that the present isomerization is a concerted *intramolecular* 1,2-silyl migration via the cyclic transition state similar to that located theoretically for the isomerization of **1c** to **2c**. Silene **6** is thermally very stable; no reaction occurred when **6** was heated in benzene at 90°C for 25 days. The irreversible thermal silylene-to-silene isomerization suggests that silylene **3** is more than 3 kcal mol^{-1} less stable than silene **4** in this particular case.

Germanium and tin analogues of silylene **1** are thermally stable,[22] showing no isomerization into the corresponding germene and stannene occurs even at 100°C. The results are in agreement with the general trend that group-14 divalent species become more stable relative to the corresponding doubly bonded compounds with
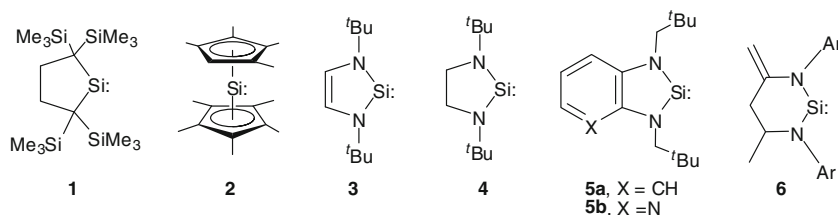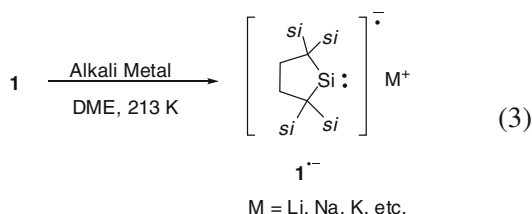

Chart 1. Isolable base-free silylenes.

increasing the atomic number among the heavier group-14 metal elements. A theoretical study on the isomerization of **1** to **6** (eq. 1, si = SiH$_3$) and its germanium and tin versions has shown that the activation energy and the relative stability of metallylene both increased in the order E = Si < Ge < Sn.[19]

3. One-electron reduction forming radical ion

Although a number of studies of the formation of silylene, germylene and stannylene radical anions have been reported, there are very few reports on the formation via the direct one electron reduction of the corresponding metallylenes; radical anions of stable germylene and stannylene have been produced by alkali metal reduction in solution and characterized by ESR spectroscopy.[23] West *et al*. have reported that reduction of stable diaminosilylene **3** with potassium graphite in THF gave the corresponding 1,2-dipotassiodisilane which would be formed via fast dimerization of the silylene radical anion.[24]

One-electron reduction of dialkylsilylene **1** using alkali metals generates the corresponding radical anion as a relatively persistent species at low temperatures in solution (eq. 3).[25] Using ESR spectroscopy, unique structural characteristics of the radical anion have been revealed. Related radical (anion) species have been investigated by Apeloig *et al*.[26] and Sekiguchi *et al*.[27]

$$ \textbf{1} \xrightarrow[\text{DME, 213 K}]{\text{Alkali Metal}} \left[\begin{array}{c} si \quad si \\ Si : \\ si \quad si \end{array} \right]^{\cdot -} M^+ \qquad (3) $$

1$^{\cdot -}$

M = Li, Na, K, etc.

The ESR parameters of **1**$^{\cdot -}$ with K$^+$ as a countercation in DME are the following: a(^{29}Si$^\alpha$)/mT = 2.99, a(^{29}Si$^\gamma$)/mT = 1.30 and 1.66, and g = 2.0077. The ESR parameters are independent of the countercations, indicating **1**$^{\cdot -}$ is free in DME. The a(^{29}Si$^\alpha$) value of **1**$^{\cdot -}$ is the smallest and its g factor is the largest among those of related trialkylsilyl and *tris*(trialkylsilyl)silyl radicals reported. According to the local symmetry of silylenes (R$_2$Si:, C_{2v}), the singly occupied MO of **1**$^{\cdot -}$ should be comprised of a pure 3p$_\pi$ orbital perpendicular to the R$_2$Si plane. Since the a(^{29}Si$^\alpha$) value involves no direct contribution from the s character of the SOMO, the hfs would originate mostly from the spin polarization of the C–Si$^\alpha\sigma$ bonds. The large g factor is ascribed to the contribution of the small excitation energy of n→SOMO(3p$_\pi$) in **1**$^{\cdot -}$. Formation of the persistent anion radical by the reduction of silylene **1** and its ESR

spectrum is a good indication of the existence of the low-lying p$_\pi$ LUMO of silylene **1**.

4. Photo-excited state and its addition reactions to C=C bonds

Because silylenes are usually in the singlet ground state and absorb Uv-vis lights, the silylenes can form the singlet excited states by photo-irradiation. However, little is known about the properties of the excited states, whereas several unimolecular reactions of the excited states of matrix-isolated silylenes at low-temperatures have been investigated.[28]

Irradiation of silylene **1** with filtered light (λ > 420 nm) at room temperature in benzene affords the corresponding silacycloheptatriene in the quantitative yield (eq. 4), whereas only the isomerization of **1** into **6** is observed in the dark.[29a]

$$ \textbf{1} \xrightarrow{h\nu \ (\lambda > 420 \text{ nm}), \text{ rt}} \qquad (4) $$

9
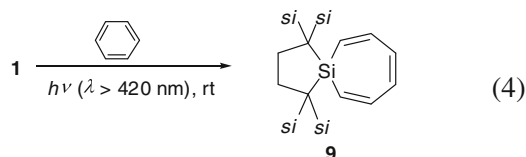
Singlet nature of the excited state responsible for the photoreaction of **1** is evidenced by fluorescence quenching in the presence of benzene.[29b] The fluorescence maximum $\lambda^{\text{fl}}_{\text{max}}$ of **1** in hexane is observed at 610 nm with the life time (τ_0) of 80.5 ns; the $\lambda^{\text{fl}}_{\text{max}}$ value is close to that reported for dimethylsilylene in a 3-methylpentane matrix $\left(\lambda^{\text{fl}}_{\text{max}} = 650 \text{ nm} \right)$.[30] Using the dependence of the life time on the concentration of benzene, the quenching rate constant k_q was determined to be 9.4 × 10^6 M^{-1} s^{-1}. The above photoreaction is suggested to occur through the collision between the singlet excited state of **1**^{1*} and benzene. Why the reacting excited state is not the lowest triplet state (^{3}B$_1$) but the lowest singlet state (^{1}B$_1$, **1**^{1*}) is rationalized by the El-Sayed rule.[31] Although the ^{3}B$_1$ state is lower lying than the ^{1}B$_1$ state, intersystem crossing from ^{1}B$_1$ to ^{3}B$_1$ requires either a 3p or an n electron spin inversion, and hence, the process is forbidden according to the El-Sayed rule; large ^{3}B$_1$−^{1}B^1 energy difference of ca. 30 kcal mol^{-1} will also contribute to the lifetime extension. Relatively long lifetime of **1**^{1*} allows the reaction of the excited state with benzene.

The detailed mechanism for the reaction of **1**^{1*} with benzene may be delineated by the analogy of well-known aromatic silyl radical substitution.[29a] Because **1**^{1*} is a singlet 1,1-biradical in nature, the addition to benzene gives the 1,3-biradical intermediate. Successive cyclization to the corresponding silanorcaradiene

followed by the C–C bond cleavage leads to the final silacycloheptatriene **9** (eq. 5).


(5)
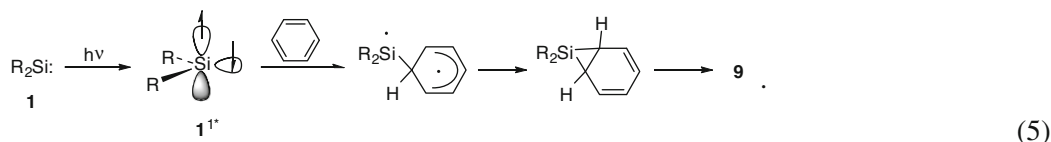
Although a transient silylene has been reported to react with benzene thermally by Tokitoh, Okazaki, *et al.*[32] silylene **1** at the ground state does not react with benzene. The reason is ascribed to the steric hindrance between silylene **1** and benzene. Because benzene serves usually as a nucleophile, it should favour to approach the LUMO of **1**. However, the pπ LUMO is sterically well protected by the helmet-like bidentate ligand. In contrast, the less hindered in-plane radical site of **1**[1*] may approach the benzene to accomplish aromatic radical addition, as shown in eq. 5.

The photochemical addition of **1** to various aromatic and aliphatic C=C bonds occurs smoothly if the double bond is not sterically hindered (eqs 6–8). Silylene **1** reacts with (*E*)-2-butene stereospecifically under irradiation to afford the corresponding silirane **13** in the quantitative yield, while the thermal reaction of **1** with the butene give a complex mixture; thermal addition reactions of **1** to alkenes are discussed more in detail in the later section.


(6)

(7)

(8)
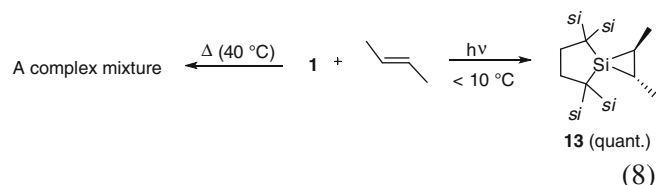
5. Insertion into σ bonds

Insertion into σ bonds is one of the fundamental and useful reactions of heavy group-14 divalent species including silylenes.[9] The insertion of silylenes into various σ bonds such as O–H, N–H, C–X (C-halogen, strained C–O, intramolecular C–H, etc.) and Si-X (X=H, O, N, halogen, and Si) bonds has been extensively studied so far both experimentally and theoretically. Isolable dialkylsilylene **1** insert probably concertedly into various σ bonds such as O–H and Si–H bonds in high yields (eq. 9).[10a]


(9)
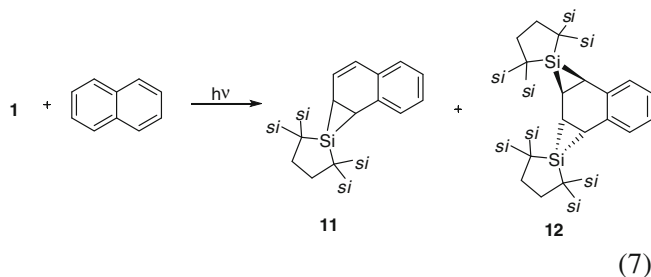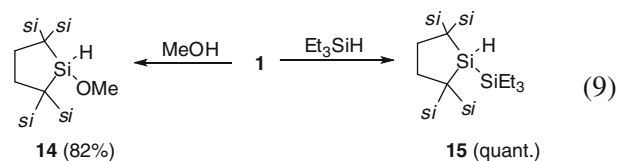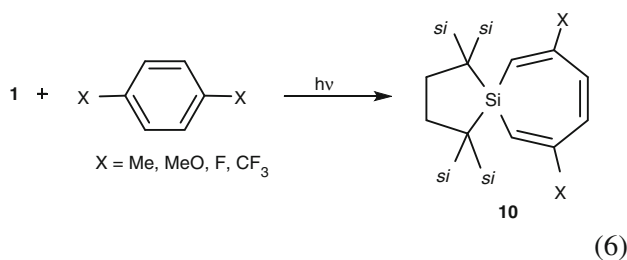
Insertion of **1** into C-halogen bonds is not straightforward. Although the insertion of **1** into the C-halogen bonds of MeI and *n*-BuCl gives simple insertion products **16a** and **16b** but that into cyclopropylmethyl chloride affords a rather unusual 1:2 adduct **17** in 70% yield together with dichlorosilane **18** in 15% yield (eq. 10).[33] The reaction profile suggests that the reactions of **1** with various alkyl halides proceed through a radical mechanism rather than the ionic or concerted mechanisms.[33,34]


(10)
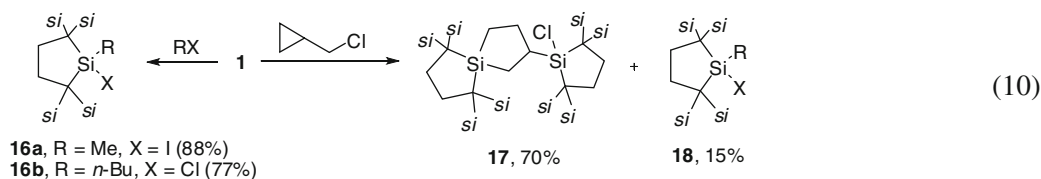
Dialkylsilylene **1** has been found to insert smoothly into a Si–Cl bond of tetrachlorosilane and other chlorosilanes (scheme 2).[35] In contrast to the insertion into C-halogen bonds, the Si–Cl insertion would undergo the concerted process.
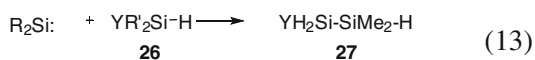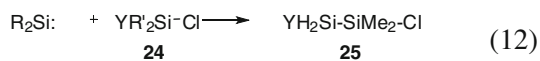
However, interesting differences are found in the reactivity between Si–H and Si–Cl insertion reactions.[35b] Silylene **1** inserts into the Si–H bond of triethylsilane, while **1** does not react with trimethylchlorosilane. The reaction of **1** with H_2SiCl_2 gives the Si–Cl insertion product **23** exclusively, while the insertion to Si–H bond occurs to give **22** when Me_2SiHCl is used as a substrate (eq. 11).
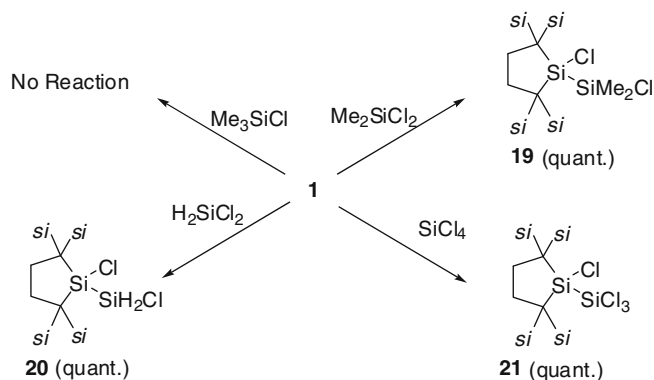
Scheme 2. Reactions of **1** with various chlorosilanes.

$$(11)$$
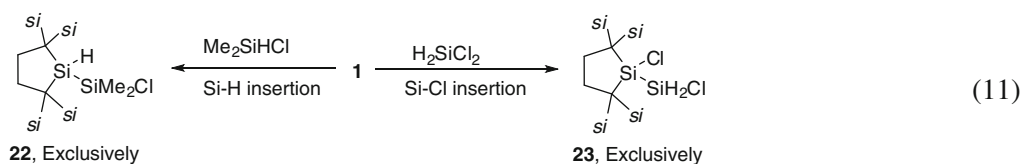
To understand rather unexpected selectivity of the insertion (Si–H/Si–Cl selectivity), insertion reactions of dimethylsilylene and silylene **1'** into a Si–H and a Si–Cl bond of various substituted hydro- and chlorosilanes have been studied computationally using DFT with the 6-31++G(d,p) basis set (eqs 12 and 13).[36,37]

$$R_2Si: \; + \; YR'_2Si\text{-}Cl \longrightarrow YH_2Si\text{-}SiMe_2\text{-}Cl \qquad (12)$$
$$\qquad\qquad\quad \textbf{24} \qquad\qquad\qquad \textbf{25}$$

$$R_2Si: \; + \; YR'_2Si\text{-}H \longrightarrow YH_2Si\text{-}SiMe_2\text{-}H \qquad (13)$$
$$\qquad\qquad\quad \textbf{26} \qquad\qquad\qquad \textbf{27}$$

$R_2Si: = \textbf{1'} [= \textbf{1} \; (si = SiH_3)]$ or Me_2Si. $R' = H, Me, {}^iPr, {}^tBu$, etc.

$Y = H, Me, NH_2, OH, F, SiH_3, PH_2, SH, Cl$

All the insertion reactions investigated are largely exothermic and proceed via the three-membered cyclic transition states with one substituent (Y) of a hydro- and chlorosilane in the ring plane and two other substituents (R') out of the plane, as shown schematically in figure 1.[36]
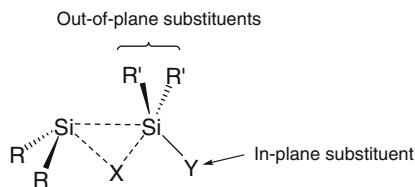
Figure 1. Schematic representation of the transition states for the insertion of a silylene into Si–X bonds (X = H, Cl).

Our theoretical calculations indicate that while the activation energy for the prototype insertion of a dialkylsilylene into a Si–H bond of SiH_4 is only 1.5 kcal mol^{-1} lower than that for the insertion into a Si–Cl bond of SiH_3Cl, the energy is strongly affected by the substituents on silane and silylene silicon atoms. Substituent effects on the activation free energy of the insertion of a dialkylsilylene into a Si–X bond (X = H, Cl) are separated into three roughly independent factors; (i) electronic in-plane and (ii) steric out-of-plane substituent effects of Si–X compounds and (iii) steric bulkiness of the dialkylsilylene. Difference in the Si–H/Si–Cl selectivity observed between the reactions of silylene **1** with H_2SiCl_2 and Me_2SiHCl is explained by strong directing effects of chlorine substituent, which lowers the $\Delta G^{\neq}$ value as an in-plane substituent but increases it as an out-of-plane substituent.[36c]

The insertion reaction of **1** to a Si–Cl bond is applied to the synthesis of various stable compounds with silicon–silicon unsaturated bonds such as a trisilaallene and related trimetallaallenes,[35a,38a] tetrasila-1,3-diene,[39] and aryldisilenes[40] (eqs 14–16).

$$(14)$$

$$(15)$$
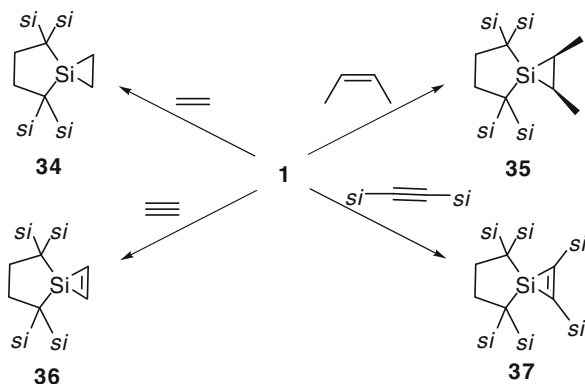

$$(16)$$

Ar = 1-Naphthyl,
9-phenanthryl,
9-Anthryl
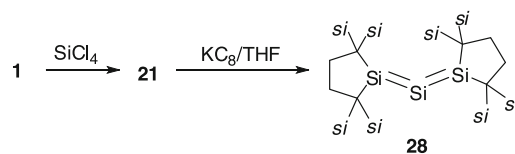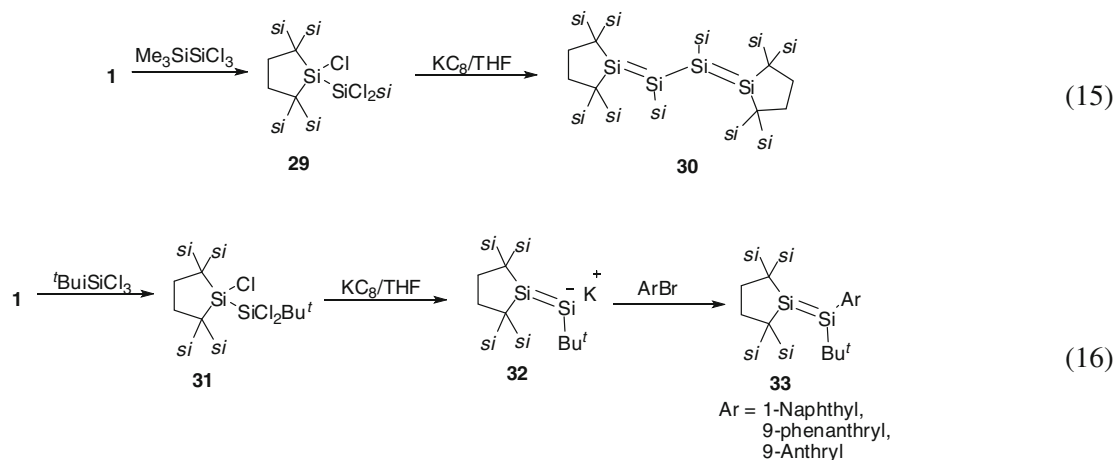
6. Addition to π bonds

The reactions of silylene **1** with ethylene, (*Z*)-2-butene, acetylene, bis(trimethylsilyl)acetylene, and 2,3-dimethylbutadiene at room temperature gave the corresponding silacycles in high yields (scheme 3).[41] Usually, the *C*-unsubstituted silacyclopropanes and silacyclopropenes are highly reactive in the air but compounds **34** and **36** are isolated as air-stable compounds because of the effective steric protection at silicon.[42] The reaction of **1** with (*E*)-2-butene gives a complex mixture indicating no formation of the corresponding silirane, in contrast to the photochemical reaction of **1** with the alkene (vide supra). These reactions are supposed to occur concertedly similar to the addition of singlet carbenes to unsaturated bonds. The reactivity difference between (*Z*)- and (*E*)-2-butenes to **1** is compatible with the relative addition rate of silylenes to (*Z*)-/(*E*)-2-butenes; the rates for the stereospecific [1 + 2] cycloaddition of dimesitylsilylene to (*Z*)-2-butene have been reported to be 25–28 times faster than that to (*E*)-2-butene.[43]

Although the reactions of silylenes with 1,3-butadienes are well-known to afford the corresponding vinylsiliranes and silacyclopent-3-enes, the selectivity and its origin have not been well understood even now.[9d, 44] The reaction of **1** with 2,3-dimethylbutadiene affords the corresponding [1 + 4] cycloadduct **38** in 90% yield without contamination of the [1 + 2] cycloadduct **39** (scheme 4).[10a, 41] Theoretical mechanistic studies on the selective 1,2-/1,4-addition reactions of dialkylsilylenes with butadienes are in progress.

The reactions of transient silylenes with aldehydes and ketones have been investigated extensively as one of the fundamental reactions of silylenes.[9] The reactions gave diverse types of final products including 1:1 and 1:2 adducts depending on the structures of silylenes and carbonyl compounds. We have investigated the reactions of isolable dialkylsilylene **1** with different types of ketones.[45] All the reactions proceeded smoothly at room temperatures to afford single 1:1 adducts in high yields without formation of any secondary or side-reaction products.

The reaction of **1** with adamantanone gives the corresponding silaoxirane **40**, while that with acetone, an enolizable ketone, gives the corresponding silyl enol ether **41** (eq. 17).


Scheme 3. Reactions of silylene **1** with alkenes and alkynes.
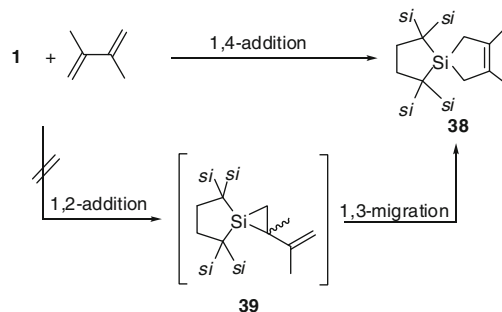
Scheme 4. Two possible pathways of the reaction of **1** with 2,3-dimethylbutadiene giving a 1,4-adduct.

(17)
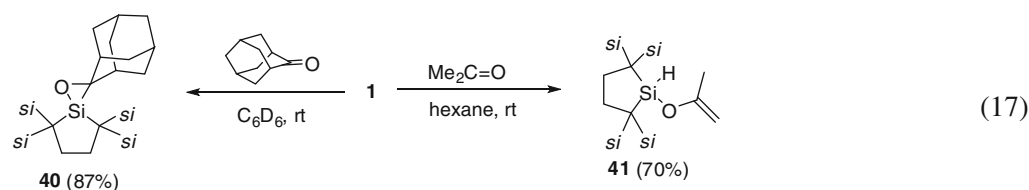
Benzophenone reacts with **1** to afford 2-oxasilacyclopentene **42** as yellow crystals, which gradually aromatize to **43** at room temperature (eq. 18).

(18)
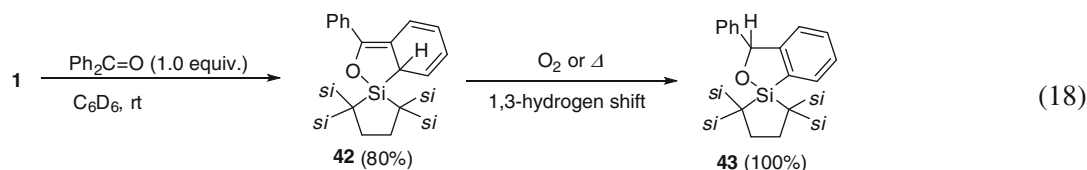
Rather unusual products **44a** and **44b** are obtained during the reactions of **1** with di-*tert*-butyl- and diphenylcyclopropenones, respectively, as single diastereomers (eq. 19).

(19)

44a, R = ^{t}Bu (77%)
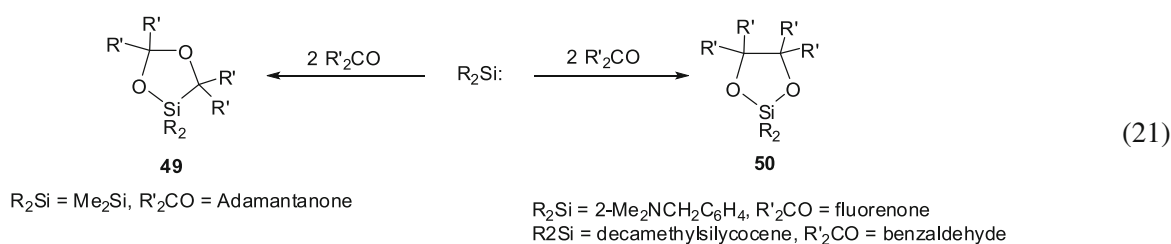**44b**, R = Ph (81%)
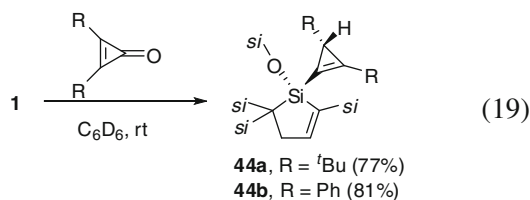
The diverse reaction modes of silylene **1** and other transient silylenes with carbonyl compounds may be explained by taking into account the initial formation of the corresponding carbonyl silaylides, as widely accepted. The carbonyl silaylides cyclize to the corresponding silaoxiranes and react with another carbonyl molecule to afford the 1:2 adduct. However, the electronic nature of carbonyl silaylides as 1,3-dipoles should be dependent on the substituents on both silicon and carbonyl carbon atoms, as shown by the two representative resonance forms in eq. 20.
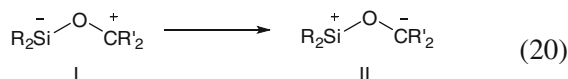
Actually, theoretical calculations at the B3LYP/6-31+G(d) level for $Me_2Si-O-CR_2$-type silaylides have shown that the charge distribution and geometry of the 1,3-dipoles at the optimized structure are remarkably modified by the substituents on carbon or the nature of the carbonyl compounds.[45] The Mulliken charge on Me_2Si moiety is negative for carbonyl silaylide **45** but increases in the order **45** < **46** < **47** < **48**, while the group charge of R'_2C decreases in the same order (chart 2). Sum of bond angles at the Si atom ($\Sigma@Si$) increases in the same order, indicating the pyramidal character at the Si atom decreases in the order **45** > **46** > **47** > **48**. Evidently, with increasing electron accepting ability of substituents on carbonyl carbon of the carbonyl silaylides, both the positive charge on SiR_2 and $\Sigma@Si$ increase.

The reaction of dimethylsilylene with adamantanone gives 1:2 adduct **49** among other products,[46] while the reaction of bis(2-dimethylaminomethylphenyl)silylene with fluorenone[47] and that of decamethylsilicocene with benzaldehyde[48] give the corresponding 1:2 adducts **50** with different regioselectivity (eq. 21), which will be ascribed to the difference in nature among intermediate silaylides.
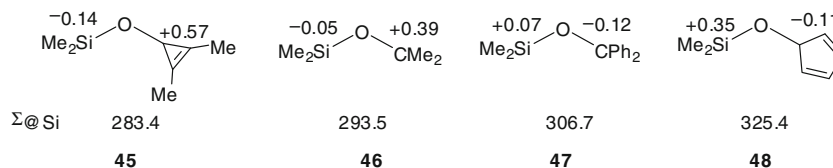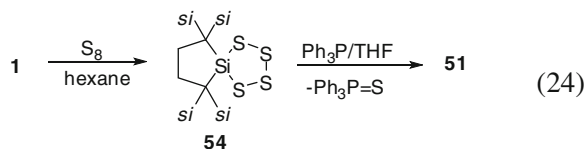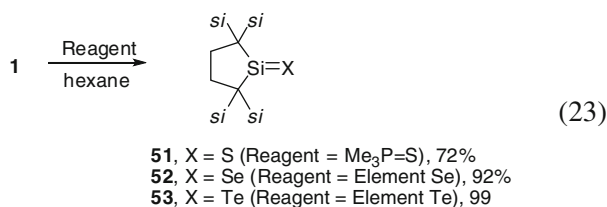

(20)

(21)

49

$R_2Si = Me_2Si$, R'_2CO = Adamantanone

50

$R_2Si = 2-Me_2NCH_2C_6H_4$, R'_2CO = fluorenone
$R2Si$ = decamethylsilycocene, R'_2CO = benzaldehyde

Chart 2. Substituent dependence of Mulliken charge distributions of carbonyl silaylides. The left and right numbers on a molecule show the group charge of Me$_2$Si and alkyl moieties, respectively.

The products of the reactions of silylene **1** with cyclopropenones (eq. 19) will be obtained through the rearrangement of the corresponding carbonyl silaylide intermediates as shown in eq. 22.


$$(22)$$
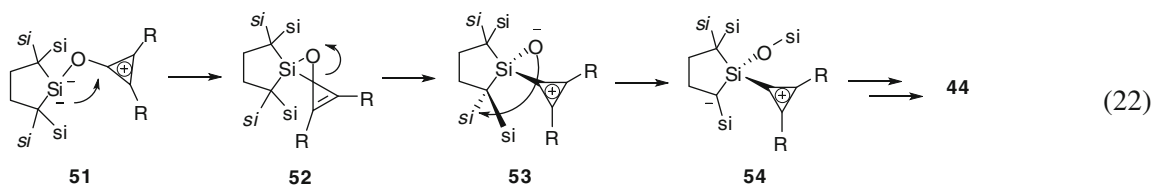
7. Miscellany

Heavy metallanechalcogenones are known to be derived by the reactions of the corresponding metallylenes with chalcogens and their equivalents.[49] Silylene **1** reacts with phosphine sulphide and elemental selene and tellurium to give the corresponding silicon–chalcogen double bond compounds **51–53** (eq. 23).[50] When **1** is treated with elemental sulphur S$_8$, tetrathiasilolane **54** is obtained as the major product, which is transformed to silanethione **51** quantitatively by treating with triphenylphosphine (eq. 24).

$$(23)$$

51, X = S (Reagent = Me$_3$P=S), 72%
52, X = Se (Reagent = Element Se), 92%
53, X = Te (Reagent = Element Te), 99

$$(24)$$

Silylene **1** reacts with isocyanides with a bulky substituent at the nitrogen atom to afford isolable silaketeneimines **55** and **56** in high yields (eq. 25). Silaketeneimines **55** and **56** are stable in the solid state below 0°C but dissociate to silylene **1** and the corresponding isocyanides in solution even at −30°C.

$$(25)$$

55, R = 2,6-diisopropylphenyl, 89%
**56**, R = 1-Adamantyl, 85%
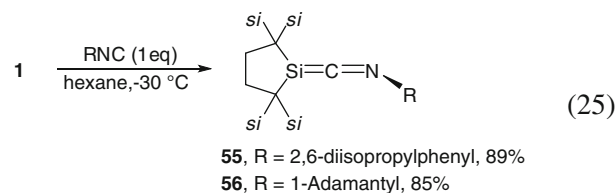
Tokitoh, Okazaki *et al*. have first synthesized silaketeneimines with bulky aryl-substituents at silicon and have concluded that they are characterized as silylene–isocyanide complexes rather than silaketenimines on the basis of spectroscopic data, theoretical calculations, and their reactions.[51] The X-ray structural analysis has shown that **55** and **56** are characterized to be allenic rather than zwitterionic or silylene–isocyanide complex. The bonding characteristics of silaketenimines are concluded to be affected strongly by the substituents on silicon and nitrogen atoms.[52]

Since the pioneering works by Zybill *et al.*[53a] and Tilley *et al.*,[53b] various base-stabilized and base-free silylene complexes have been synthesized and their versatile reactivity has been explored.[54] Products of the reaction of **1** with (Cy$_3$P)$_2$Pd depend strongly on the ratio of the two substrates. The reaction of the 1:1 molar ratio of silylene **1** to (Cy$_3$P)$_2$Pd gives the corresponding monosilylenepalladium complex **57** in a high yield as an air-sensitive purple oil, whereas the isolation was unsuccessful due to the contamination of free

tricyclohexylphosphine.[55a] When the 2:1 ratio of **1** to $(Cy_3P)_2Pd$ is used, the corresponding bis(silylene)Pd **58** is obtained in a high yield (eq. 26).[55a,b] The reaction

of the 1:2 mixture of **1** to $(Cy_3P)_2Pd$ affords a dinuclear palladium complex with a bridging dialkylsilylene ligand **59**.[55b]

$$(26)$$
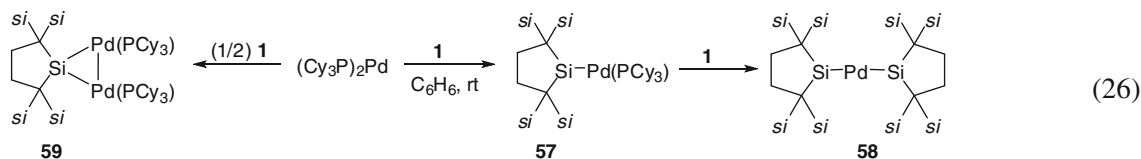
The reaction of silylene **1** with *bis*(1,5-cyclooctadiene)nickel $[Ni(cod)_2]$ in toluene gives (monosilylene)nickel complex **60** almost quantitatively (eq. 27).[55c] A similar (monosilylene)nickel complex is obtained by the reaction of diaminosilylene **6** with $Ni(cod)_2$,[56] while diaminosilylenes **3** and **5a** have been reported to react with $Ni(cod)_2$ to afford nickel complexes with three and four silylene ligands.[57]

$$(27)$$
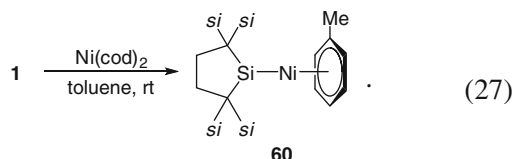
8. Conclusion

Studies of the reactions of isolable dialkylsilylene **1** have revealed that the reaction modes are not limited to σ bond insertion and π bond addition that are usually found for transient organic silylenes such as dimethylsilylene and diphenylsilylene, but are more diversified including the bimolecular photoreactions, one-electron reduction, and intramolecular isomerization. Silylene **1** and other stable silylenes are useful as precursors for the synthesis of stable silicon unsaturated compounds and other unique silicon compounds. As a distinctive electronic system, the stable silylenes may fulfil a central function in optoelectronic devices.

Acknowledgements

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