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Award Accounts

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A Helmeted Dialkylsilylene

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Structural characteristics, spectroscopic properties, and unique reactions of a helmeted dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl, that was synthesized as the first isolable dialkylsilylene and its application to the synthesis of novel silicon unsaturated compounds are surveyed. The silylene was found to be the least electronically perturbed among known stable silylenes by ^{29}Si NMR and UV–vis spectroscopies. The silylene reacts not only with well-known trapping reagents for transient silylenes, such as alcohols, triethylsilane, and 2,3-dimethylbutadiene, but also with less reactive haloalkanes and halosilanes to give the corresponding adducts. One-electron reduction of the silylene using alkali metals affords the corresponding radical anion as a relatively persistent species at low temperatures in solution. Irradiation of the silylene using visible light generates a singlet excited state with a lifetime of 80.5 ns, which reacts with various aromatic compounds and alkenes to give the corresponding silepins and siliranes in a highly regio- and stereoselective manner. The silylene is utilized for the synthesis of unique silicon unsaturated compounds, such as Si=X doubly bonded compounds (X = S, Se, Te, C=NR, etc.), a trisilaallene, a 1,3-disilagermaallene, and silylene transition-metal complexes.

1. Introduction

Silylenes, silicon analogues of carbenes, are usually singlet in the ground state ($^1A_1$) and have two low-lying excited states, $^1B_1$ and $^3B_1$, with singlet and triplet 1,1-diradical natures, respectively (Fig. 1). Because the simple electronic configurations and unique properties of silylenes and other heavier group-14 divalent species are strongly affected by substituents, much attention has been focused on the chemical behavior of these species both theoretically and experimentally.[1]

Whereas these divalent species usually appear as key reactive intermediates in numerous thermal and photochemical reactions of organosilicon compounds, we synthesized the first isolable dialkylsilylene **1** in 1999 that is sterically well-protected from dimerization by a helmet-like bidentate ligand with four bulky trimethylsilyl groups (Chart 1).[2] In this account, we would like to discuss the progress of the chemistry of silylene **1**.[3] Since stable dialkylgermylene **2**[4] and dialkylstannylene **3**[5] with the same helmet ligand had been synthesized prior to silylene **1**, a systematic and straightforward discussion of the element dependence of the intrinsic properties of the group-14 element divalent compounds has been made possible by the synthesis of **1**.[6]

Historically, the first convincing evidence for the generation of dimethylsilylene as a representative of dialkylsilylenes was obtained by the high-temperature thermolysis of the corresponding 7-silanorbornadiene derivative in 1964 (Eq. 1).[7] More recently, thermolysis of 1,2-dimethoxytetramethyldisilane at 250 °C[8] and hexamethylsilacyclopropane at 60–80 °C[9] have been widely used among various methods for the thermal generation of dimethylsilylene (Eqs. 2 and 3). The generation of dimethylsilylene has been evidenced by using various trapping reactions with alcohols, 1,3-butadienes, hydrosilanes, and so on.[1i,10] Photolysis of linear and cyclic permethylpolysilanes

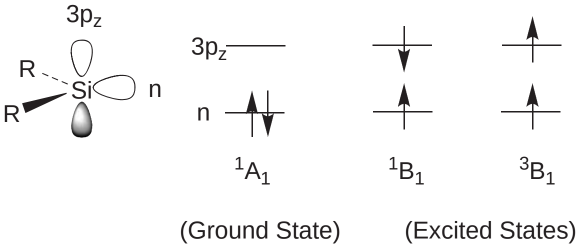
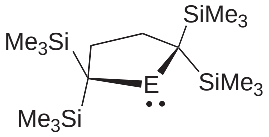


Fig. 1. Important electronic configurations of a silylene.



1, E = Si
2, E = Ge
3, E = Sn

Chart 1.

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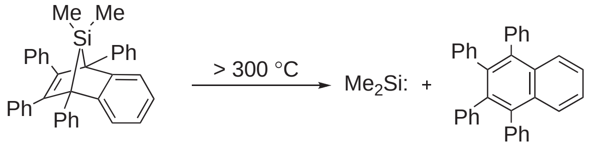
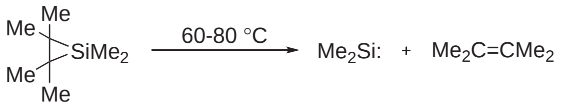
(Eq. 4)[11] was found to be an excellent method for the generation of dimethylsilylene, and the spectroscopic detection of dimethylsilylene isolated in a low-temperature matrix was first achieved using the photolysis in 1970.[12]



(1)

$$\mathrm{MeOSiMe_2SiMe_2OMe} \xrightarrow{> 250\ ^\circ\mathrm{C}} \mathrm{Me_2Si{:}} + \mathrm{Me_2Si(OMe)_2} \quad (2)$$



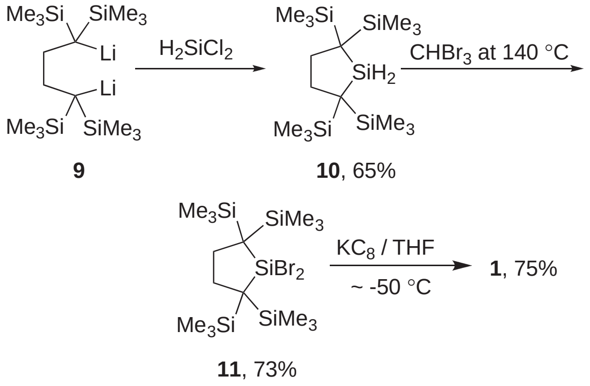
(3)

$$cyclo\text{-}[\mathrm{Me_2Si}]_6 \xrightarrow{h\nu} \mathrm{Me_2Si{:}} + [\mathrm{Me_2Si}]_n\ (n = 4, 5) \quad (4)$$

For a long time, stable silylenes were unknown with the exception of decamethylsilicocene **4** having pentahapto-cyclopentadienyl ligands (Chart 2).[13] The first stable dicoordinate silylenes were synthesized in a different research stream. Stable dicoordinate divalent species of tin, germanium, and lead with bulky aryloxy- and amino-substituents were synthesized in late 1970's[14] and isolable singlet carbenes having related hetero atom substituents have been known since 1988.[15] The successful synthesis of a stable *N*-heterocyclic carbene by Arduengo et al. in 1991 was followed by the synthesis of the first stable cyclic diaminosilylenes **5**[16] and **6**[17] by West et al. in 1994. Characteristic structure and reactions of these stable diaminosilylenes **5** and **6** and related silylenes **7**[18] and **8**[19] developed by Lappert et al. have been investigated extensively (Chart 2). These cyclic diaminosilylenes as well as related *N*-heterocyclic carbenes are however stabilized electronically by the strong interaction between the vacant pπ-orbital at the divalent atom and filled π-type lone-pair orbitals of neighboring heteroatoms, and hence, their electronic nature is different from the parent divalent species. Dialkylsilylene **1** is the least electronically perturbed among known stable silylenes.

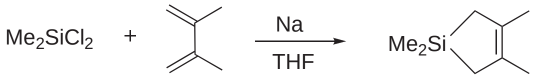
2. Synthesis

Dialkylsilylene **1** is synthesized using the following sequence of reactions (Eq. 5). The reaction of 1,4-dilithiobutane **9**[20] with dichlorosilane gives the corresponding dihydrosilane **10** in 65% yield, which is transformed to dibromosilane **11** in 73% yield by the reaction with bromoform. Finally, the reduction of **11** with potassium graphite in THF at −50 °C affords silylene **1** in 75% yield as air- and moisture-sensitive orange crystals.[2] Because 1,4-dilithiobutane **9** is prepared quantitatively by the reduction of 1,1-bis(trimethylsilyl)ethylene with lithium,[20] the overall yield of **1** from the starting ethylene is more than 30%. Silylene **1** is relatively stable in the solid state with a decomposition point of 91 °C but decomposes slowly with the half-life of 31 h at 25 °C in a hexane solution; the decomposition mode will be discussed in a later section.

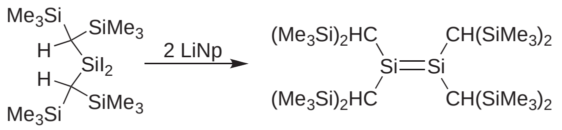


(5)

Although the generation of dimethylsilylene was proposed during the reduction of dimethyldichlorosilane with sodium in the presence of 2,3-dimethylbutadiene,[21] the reaction has been thought to proceed via the initial reduction of 2,3-dimethylbutadiene (Eq. 6).[10] Our success in the synthesis of silylene **1** indicates that the reduction of a dihalosilane with alkali metal is a potential route to the formation of the corresponding silylene. The major reason why silylene **1** is isolable is ascribed to the effective steric protection by a helmet-like bidentate ligand to prevent the dimerization; the reduction of a structurally similar but less hindered dihalosilane, $[(\mathrm{Me_3Si})_2\mathrm{CH}]_2\mathrm{SiI_2}$, with lithium naphthalenide has been reported to afford a dimer of the corresponding silylene (Eq. 7).[22]



(6)



(7)

3. Structure and Spectroscopic Properties

The molecular structure of silylene **1** was determined by single crystal X-ray diffraction.[2] The shortest distance between the divalent silicon atoms in the crystal is 7.210(1) Å, indicating that **1** is monomeric in the solid state. The averaged C–Si1 bond length of 1.908(6) Å in **1**, which is longer than normal Si–C single bond lengths (ca. 1.87 Å), and the relatively small C–Si–C angle of 93.88(7)° are suggestive of the larger p-character of the silicon hybrid orbitals used in the C–Si1 single bonds. As shown in the space-filling model for dialkylsilylene **1** (Fig. 2), the divalent silicon center of **1** is well protected by four bulky trimethylsilyl groups from dimerization but still has

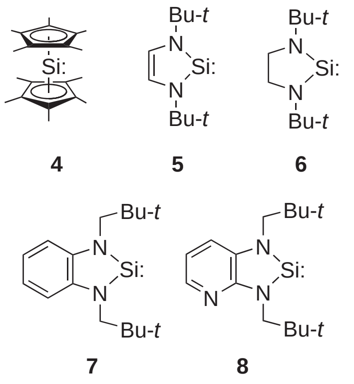


Chart 2.

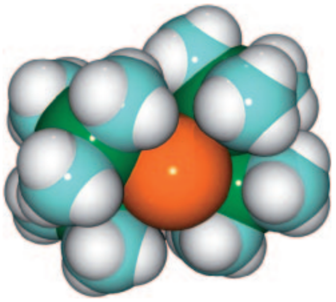


Fig. 2. Space-filling model for silylene **1**.

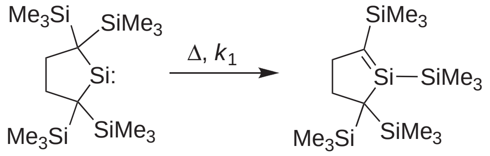
an enough space to react with small molecules.

The most remarkable structural characteristics of **1** were obtained by UV–vis and ^{29}Si NMR spectroscopies. A UV–vis spectrum of **1** in hexane shows band maxima at 260 nm (ε 1700) and 440 nm (ε 500). The weak and broad band at 440 nm is assigned to the forbidden n(Si) → 3pπ(Si) transition, and the relatively intense band at 260 nm is due to the σ(C–Si) → 3pπ(Si) transition. While the n(Si) → 3pπ(Si) transition of silylene is known to be strongly affected by the substituents,[23,24] the maximum at 440 nm is close to that for dimethylsilylene (λ_{max} 453 nm)[12] and 1-silacyclopentane-1,1-diyl (λ_{max} 436 nm)[24] observed in 3-methylpentane matrix at 77 K (Table 1). In contrast, the n(Si) → 3pπ(Si) bands of cyclic diaminosilylenes have been found at much shorter wavelengths (292–344 nm),[17–19] which is indicative of substantial orbital interaction between nitrogen lone-pair orbitals and the silicon vacant 3pπ orbital.

Interestingly, the ^{29}Si resonance for the divalent silicon in **1** was found at +567.4 ppm in benzene-d_6, which is the lowest field ^{29}Si resonance reported to date.[25] The low field ^{29}Si resonance is characteristic of divalent dicoordinate silylene as shown by gauge-independent atomic orbitals (GIAO) calculations (Table 1); the ^{29}Si resonance for 2,2,5,5-tetrakis(trihydrosilyl)silacyclopentane-1,1-diyl as a model of **1** was calculated to be 755 ppm. On the other hand, the ^{29}Si resonances for stable cyclic diaminosilylenes appear at +78 to +117 ppm,[17–19] which are much higher than the calculated values for the parent H_2Si: and dialkylsilylenes. Although electron-donation to the formally vacant Si 3pπ-orbital from the neighboring C–Si σ bonding orbitals (σ–π conjugation) may be significant in **1**, the extent is far smaller than the electronic perturbation by amino substituents in **5–8**, as indicated by the low-energy n(Si) → 3pπ(Si) transition and the very low-field ^{29}Si resonance of the divalent silicon. Since a linear relationship between the band maxima and the ^{29}Si resonances was found by Müller,[29] both n(Si) → 3pπ(Si) transition energies and ^{29}Si NMR resonances of the silylene silicon nuclei are good indices for the extent of the electronic perturbation of the silylenes by the substituents.

4. Reactions

4.1 Thermal Isomerization. The most intriguing reactivity of silylene **1** is the facile 1,2-migration of the neighboring trimethylsilyl group to give the corresponding silaethene derivative **12**;[2] however, the corresponding germylene **2** and stannylene **3**, which show no such isomerization even at 100 °C. Silylene **1** isomerizes gradually to silaethene **12** at room temperature in hexane, while **1** is rather stable in the solid state. Although facile isomerization of silylmethylsilylene to silylsilaethene is shown theoretically to occur very easily,[30] the present results give the first experimental evidence for the isomerization.[31]



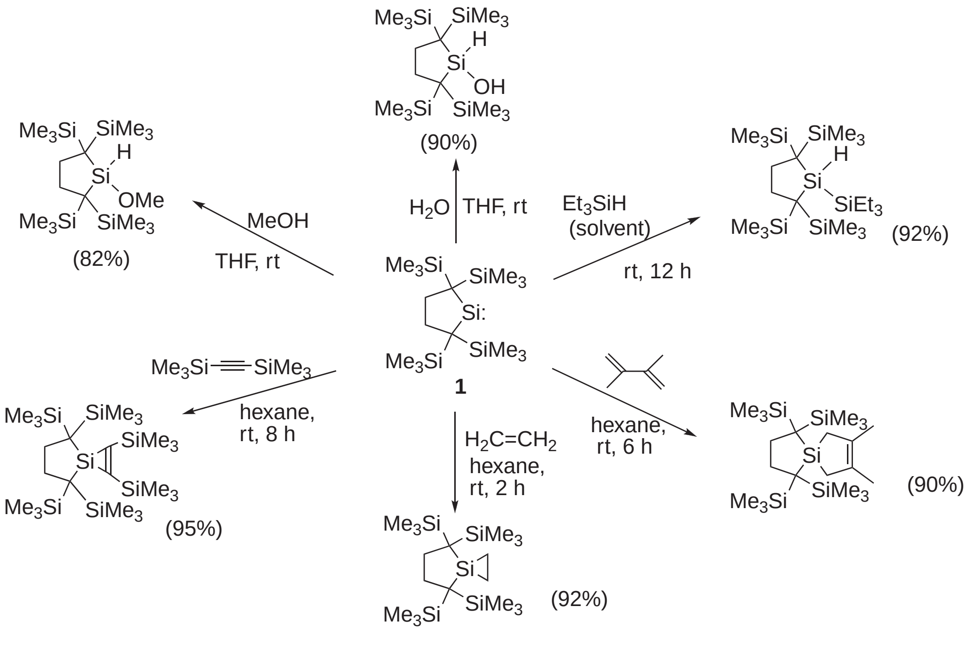
1 **12** (8)

4.2 Bimolecular Reactions. Silylene **1** reacts with water, methanol, bis(trimethylsilyl)acetylene, 2,3-dimethyl-1,3-butadiene, and other well-known trapping reagents for transient

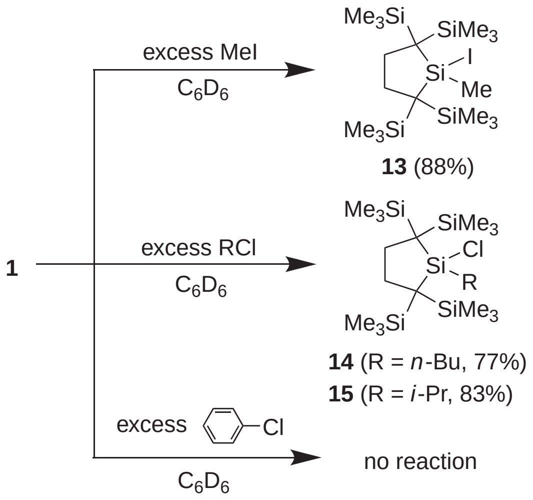
Table 1. UV–Vis and ^{29}Si NMR Spectral Data of **1** and Related Silylenes

Silylene	UV–vis		^{29}Si NMR[a)]	Ref.
	λ_{max}/nm (ε)	Conditions	(ppm)	
1	260 (1700), 440 (500)	Hexane, rt	567.4 (601.8)[b)]	1
H_2Si:	—	—	(817)	26
Me_2Si:	453	3-MP, 77 K	—	6, 12
	436	3-MP, 77 K	(754.8)	23b
t-Bu_2Si:	480	3-MP, 77 K	—	27a
Ph_2Si:	495	3-MP, 77 K	—	24a
Mes_2Si:	577	3-MP, 77 K	—	27b
$(i\text{-}Pr_2N)_2Si$:	335	3-MP, 77 K	—	28
4	—	—	−397	13
5	—	—	78	16
6	268, 292	Hexane, 298 K	119 (114.7)	17a
7	344 (sh)	Hexane, rt	96.9	18
8	302 (3300)	Hexane	95.1	19

a) A theoretical value calculated at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level is shown in parentheses. b) Calculated value for a model compound, 2,2,5,5-tetrakis(trihydrosilyl)-silacyclopentane-1,1-diyl.



Scheme 1.



13 (88%)

14 (R = *n*-Bu, 77%)
15 (R = *i*-Pr, 83%)

Scheme 2.

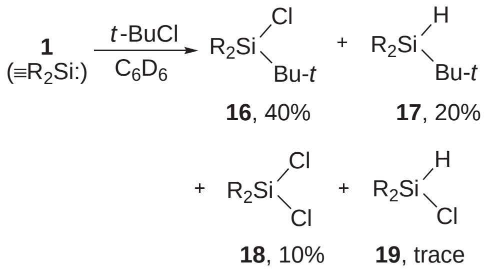
silylenes to give the corresponding adducts as shown in Scheme 1.

Whereas highly reactive reagents are required for trapping transient silylenes, stable silylenes can react in general with less reactive reagents. Typically, a marginally stable diarylsilylene generated by Suzuki, Tokitoh, and Okazaki[32] was found to react with benzene, although benzene has never been used for a trapping reagent of transient silylenes. Using stable silylene **1**, reaction modes and mechanisms of dialkylsilylenes with a wide variety of reagents have been elucidated.

4.2.1 Reactions with Haloalkanes: Only a few reactions of silylenes with haloalkanes have been reported,[33–36] in spite of the possible importance in the direct synthesis of alkylhalosilanes by the reactions of silicon with haloalkanes.[37] The reactions of the transient silylenes with haloalkanes have been explained by invoking zwitterionic intermediates (R_2Si^{-}–$X^{+}R'$) formed at the initial stage.[33] Whereas several reactions of isolable silylenes, decamethylsilicocene, and cyclic diaminosilylenes with haloalkanes have been studied, the mechanisms have not been discussed in detail.[35,36]

Silylene **1** reacts with primary and secondary monohaloalkanes to give the corresponding insertion products into carbon–halogen bonds, while **1** does not react with chlorobenzene (Scheme 2).[38]

The reaction of **1** with *t*-butyl chloride gives a mixture of products **16**–**19** together with isobutene (Eq. 9), indicating that the reaction is not a simple concerted insertion of **1** into a C–Cl bond, while the detailed mechanism remains still open (vide infra).[39]



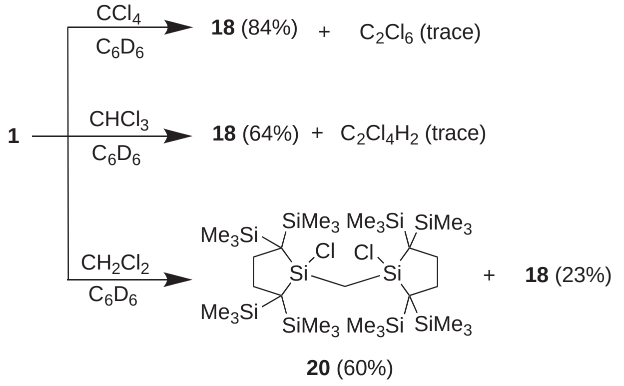
16, 40%   **17**, 20%
18, 10%   **19**, trace
(9)

As shown in Scheme 3, reactions of dialkylsilylene **1** with excess carbon tetrachloride and chloroform in benzene occur smoothly to give the corresponding dichlorosilane **18** in 84 and 64% yields, respectively. Small amounts of Cl_3CCCl_3 and HCl_2CCCl_2H are detected by mass spectrometry during the reactions of **1** with CCl_4 and $CHCl_3$, respectively. Rather unexpectedly, the reaction of **1** with excess dichloromethane in benzene gives double silylene insertion product **20** in 60% yield together with dichlorosilane **18** (23% yield). No single silylene insertion product is observed in the reaction mixture, even though the concentration of **1** is much lower than that of dichloromethane. A similar double insertion has been observed in the reaction of bis[bis(trimethylsilyl)methyl]stannylene with dichloromethane.[40]

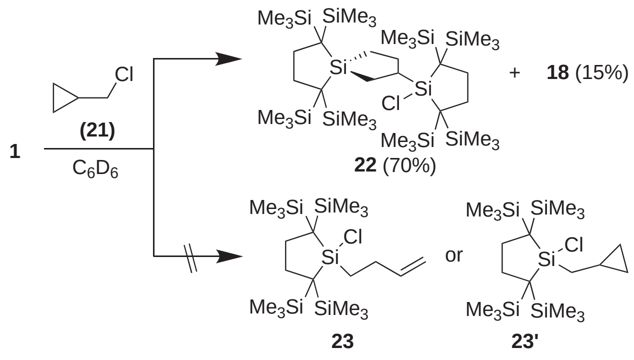
The reaction of **1** with excess (chloromethyl)cyclopropane (**21**) gives a 2:1 adduct (**22**) in 70% yield together with **18** (15% yield); no 1:1 adducts, such as **23** and **23′**, have been detected (Scheme 4).

The diverse reactions of silylene **1** with various haloalkanes suggest the complicated nature of the reaction mechanisms. The initial event in all the reactions may be the formation of a Lewis acid–base complex of the haloalkane with **1** as proposed previously.[41] The fate of the complex may depend on the haloalkanes that were used and the reaction conditions. The complexation of a silylene with a haloalkane weakens the carbon–chlorine bond to facilitate (a) homolytic cleavage giving a pair of the corresponding carbon radical and chlorinated silyl radical, (b) heterolytic cleavage giving a silyl anion–alkyl cation pair, or (c) concerted C–Cl bond insertion (Scheme 5). Because carbon tetrachloride and chloroform should give less stable carbocations by the heterolysis (pathway b), the homolysis giving a pair of chlorosilyl radical and the corresponding alkyl radical (path a) is favored, and chlorine abstraction of the chlorosilyl radical from the corresponding haloalkanes affords dichlorosilane **18**. In the reactions of primary and secondary monohaloalkanes with silylene **1**, either heterolysis or C–Cl bond insertion may give formal insertion products. It is difficult to understand why compound **17** forms during the reaction of **1** with *t*-butyl chloride (Eq. 9); however, one possible route to **17** would be the reaction of *t*-butyl radical formed via homolysis with silylene **1** giving *t*-BuR$_2$Si• followed by the abstraction of a hydrogen from *t*-butyl radical.

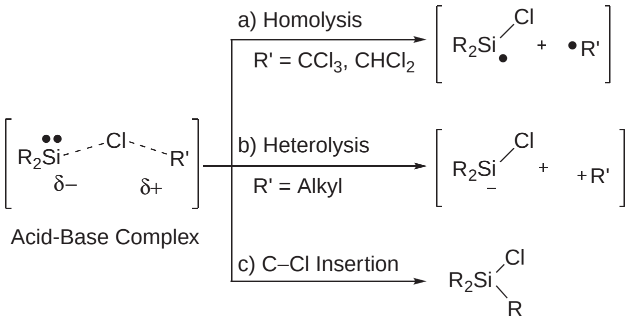
The major reaction pathways of **1** with dichloromethane and (chloromethyl)cyclopropane **21** may not be explained by a simple dissociation of C–Cl bonds; in these reactions, a chloroalkane molecule reacts with two silylene molecules even in the presence of a large excess amount of the chloroalkane. As shown in Scheme 6, in the reaction of **1** with dichloromethane, the methylene carbon in the initial silylene–dichloromethane complex is attacked by another silylene to form a chlorosilyl anion and a (chloromethyl)silyl cation stabilized by intramolecular complexation followed by the nucleophilic attack of the silyl anion on the chloromethyl carbon to afford **20**. Similarly, in the reaction of **1** with **21**, the reaction of a similar acid–base complex with another molecule of **1** affords the chlorosilyl anion and the corresponding 3-butenylsilyl cation with intramolecular π complexation, which reacts with the chlorosilyl anion to afford the final product **22**, as shown in Scheme 6. The reaction mode of **1** with **21** is quite different from that of the photochemically generated transient silylene Ph(Me$_3$Si)Si:, observed by Ishikawa, Kumada, et al.;[33c] in the latter reaction, the silylene simply inserts to the C–Cl bond of **21** to give the corresponding (cyclopropylmethyl)chlorosilane without formation of any ring-opening products. The difference between the two reactions may be rationalized by the difference in the silylene concentration; the concentration of **1** was ca. 0.2 M during the reaction with **21**, while the steady-state concentration of Ph(Me$_3$Si)Si: was not known but should be far smaller than 0.2 M. In the reaction of Ph(Me$_3$Si)Si: with **21**, intra-complex nucleophilic attack of the silylene on the chlorinated carbon in the initial complex



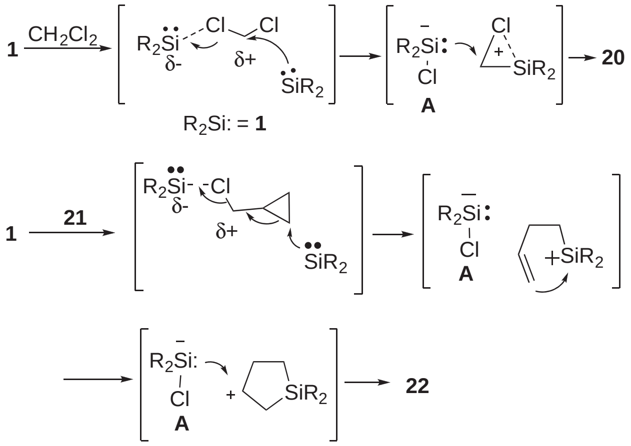
Scheme 3.



Scheme 4.



Scheme 5.



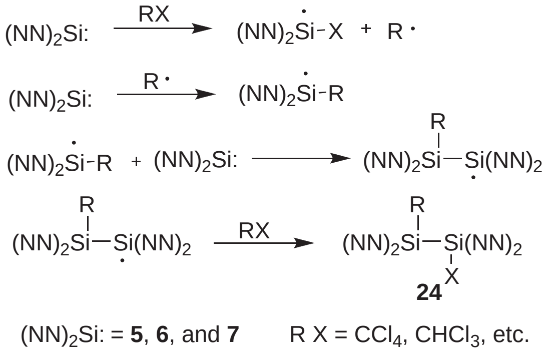
Scheme 6.

would occur exclusively to afford the simple insertion product.

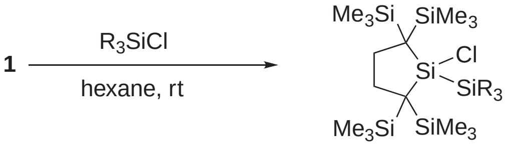
Recently, the reactions of stable diaminosilylenes **5**, **6**, and **7** with haloalkanes have been studied extensively.[42,43] The reaction mode of these diaminosilylenes is somewhat different from that of **1**. Most remarkably, the reactions of these diaminosilylenes with a haloalkane give the corresponding 2:1 adducts **24** with a Si–Si bond (Scheme 7); typically, the reaction of **5** with chloroform gives **24** in >98% yield.[43b] Although the reaction mechanism is still a matter of discussion both theoretically[44] and experimentally, a radical chain mechanism[36b,43b] that was proposed recently may be most probable (Scheme 7). A single electron transfer from the silylenes to the haloalkane proposed for the formation of a halosilyl radical[43b] appears compatible with the electron-rich nature of the diaminosilylenes.

4.2.2 Reactions with Chlorosilanes: Among previous studies, the insertion reactions of silylenes into Si–Cl bonds are postulated as a key step in the redistribution reactions of chlorodisilanes.[45] Belzner et al. have recently reported insertions of transient silylenes, which are generated by thermolysis of the corresponding cyclotrisilanes, into Si–Cl bonds,[46] and Si–Cl bond insertion reactions of stable diarylgermylene and diarylstannylene compounds with tetrachlorosilane and trichloro(methyl)silane have been reported by Lappert et al.[47] More recently, Gehrhus et al. have reported the reactions of diaminosilylene **7** with various halosilanes.[48]

Stable silylene **1** reacts smoothly with various chlorosilanes giving the corresponding Si–Cl bond insertion products. The reactions of **1** with tetrachlorosilane and dichlorodimethylsilane in hexane at room temperature afford the corresponding chlorinated disilanes **25** and **26** in 72 and 65% yields, respectively (Eq. 10). The reaction of **1** with excess dichlorosilane gives the corresponding 1:1 adduct **27** in quantitative yield as determined by NMR, which further reacts with another molecule of **1** to give the 2:1 adduct **28** in 56% yield (Eq. 11).

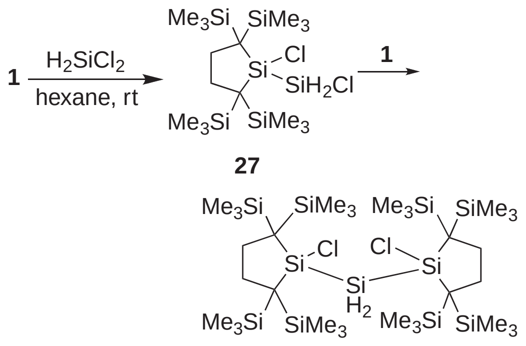


Scheme 7.



(10)

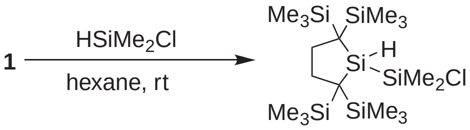
25, $R_3Si = Cl_3Si$ (72%);
26, $R_3Si = ClMe_2Si$ (65%);



(11)

28, 56%

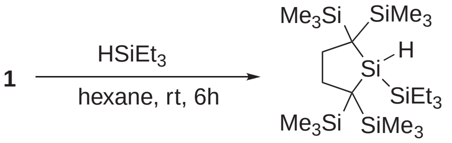
The reaction of **1** with dichlorosilane is interesting because the results indicate that the Si–Cl bond insertion occurs exclusively, while reaction of **1** with dimethylchlorosilane affords only the Si–H insertion product **29** (Eq. 12).



(12)

29, 79%

No reaction occurs between **1** and chlorotrimethylsilane, while **1** reacts with triethylsilane to give the corresponding Si–H insertion product **30** in 92% yield (Eq. 13), which indicates that the Si–Cl insertion is highly sensitive and that Si–H insertion is insensitive to steric hindrance from the substituents on silicon atom. As suggested by the reactions of **1** with chloroalkanes,[38] in the Si–Cl insertion reactions, the nucleophilic attack of silylene **1** on the chlorosilane silicon center may be important, while the initial electrophilic interaction between **1** and a hydride in a hydrosilane is the controlling factor of the Si–H insertion reactions. More detailed studies are required for the elucidation of the mechanistic differences between the two insertion reactions.

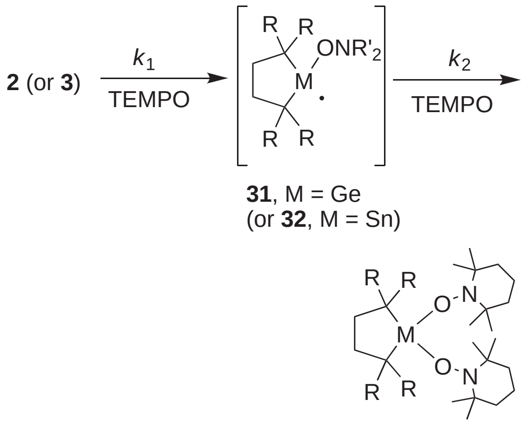


(13)

30, 92%

4.2.3 Reactions with Radicals: In spite of the fundamental importance, the reactions between doublet radicals and heavier group-14 divalent species with a singlet electronic configuration had never been investigated until our recent studies,[49] although the reaction of triplet diphenylcarbene with a persistent nitroxide radical, such as 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO), was found by Scaiano and co-workers[50,51] to be very fast giving benzophenone and 2,2,6,6-tetramethylpiperidine. The second-order rate constant was determined to be $2.7 \times 10^8\ M^{-1}\ s^{-1}$ in acetonitrile at room temperature.

As expected, the reactions of germylene **2** and stannylene **3** with TEMPO proceed via the intermediary formation of radicals **31** and **32** to give the corresponding 1:2 adducts **33** and **34**, respectively (Eq. 14).

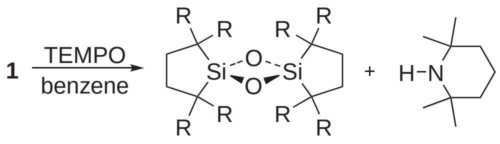


31, M = Ge
(or **32**, M = Sn)

33, M = Ge
(or **34**, M = Sn)

(14)

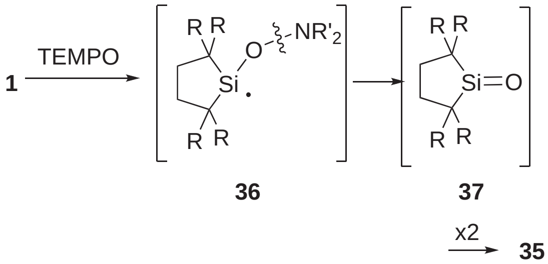
Interestingly, 1,3-disiladioxetane derivative **35** was obtained in 66% yield together with 2,2,6,6-tetramethylpiperidine (71% yield) during the reaction of silylene **1** with 1 equiv of TEMPO in benzene (Eq. 15).[49a,49b] Even when a large excess amount of TEMPO was used, a 1:2 adduct, a silicon analog of **33** (or **34**), was never produced.



35

(15)

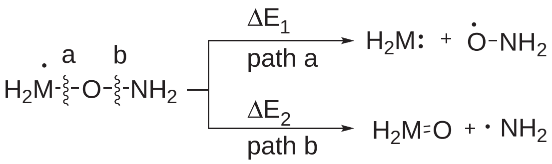
Disiladioxetane **35** could be formed via a cleavage of the N–O bond of radical intermediate **36** giving silanone **37** followed by the dimerization (Eq. 16).



36 **37**

35 (16)

Apparent difference of **1** from **2** and **3** in their reactivity toward TEMPO can be ascribed to faster N–O cleavage in **36** than the radical coupling between **36** and TEMPO. DFT calculations of the following model reactions (Scheme 8) at the B3LYP/6-311+G(2d,p) level showed that ΔE_1 of path a decreases in the order Si > Ge > Sn, while that of path b decreases in the inverse order; Sn > Ge > Si (Table 2). A major factor determining the order of ΔE_1 is the relative stability of H_2M:, which is in the order Sn > Ge > Si. The relative stability of the M=O bond decreases in the order Si > Ge > Sn, and it is reflected in the order of ΔE_2. Theoretical calculations showed clearly that ΔE_1 is larger than ΔE_2 for M = Si and Ge, while ΔE_1 is smaller than ΔE_2 for M = Sn. The results predict that N–O bond fission (path b) is favored for M = Si and Ge and M–O bond fission (path a) is favored for M = Sn, being in good accord with our experimental results.



Scheme 8.

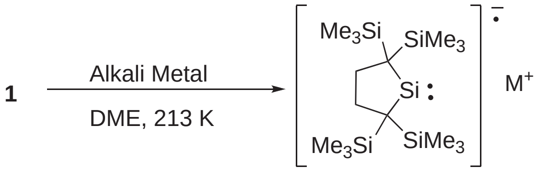
Table 2. Theoretical Energies for M–O and N–O Bond Fissions in the Reactions in Scheme 8[a)]

M	ΔE_1/kcal mol^{-1}	ΔE_2/kcal mol^{-1}
Si	42.1 (49.6)	11.4 (−2.0)
Ge	28.6 (28.0)	20.0 (13.8)
Sn	23.0	31.2

a) Calculations were performed at the B3LYP/LANL2DZ level and at the ROB3LYP/LANL2DZ levels for closed-shell and open-shell molecules, respectively. In parentheses are shown the results obtained by the calculations at the B3LYP/6-311+G(2d,p) and ROB3LYP/6-311+G(2d,p) levels for closed-shell and open-shell molecules, respectively.

4.3 One-Electron Reduction. Since silylene and related singlet group-14 divalent compounds have low-lying vacant pπ orbitals, the corresponding radical anions are a unique class of reactive intermediates that could be generated by one-electron reduction. Parent silylene radical anion $SiH_2^{\bullet-}$ produced in a low-pressure discharge source upon admission of SiH_4 has been studied by laser photoelectron spectroscopy.[52] We reported the first generation and an ESR study of silylene anion radical $\mathbf{1}^{\bullet-}$ in 2003.[54] Prior to our study, an ESR study of related radical anions of stable germylene and stannylene was reported.[55] West et al. reported that the reduction of a stable diaminosilylene with potassium graphite in THF gave the corresponding 1,2-dilithiodisilane, which would be formed via fast dimerization of the silylene radical anion.[53] A closely related lithiosilyl radical was observed by ESR by Apeloig et al.[56]

One-electron reduction of dialkylsilylene **1** using alkali metals generated the corresponding radical anion as a relatively persistent species at low temperatures in solution (Eq. 17).[54] Unique structural characteristics of the radical anion have been observed by using ESR spectroscopy (Fig. 3).



$\mathbf{1}^{\bullet-}$

M = Li, Na, K, etc.

(17)

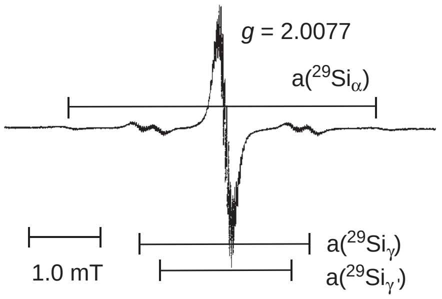
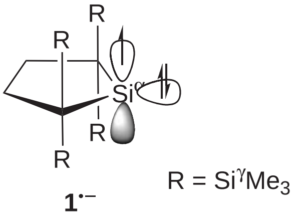


Fig. 3. An ESR spectrum of $\mathbf{1}^{\bullet-}/K^+$ in DME solution at 213 K.

The ESR parameters of silylene radical anion $\mathbf{1}^{\bullet-}$ with K^+ as a counter cation 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 mainly independent of the counter cations, indicating $\mathbf{1}^{\bullet-}$ is free in DME. The $a(^{29}Si^{\alpha})$ value of $\mathbf{1}^{\bullet-}$ is the smallest and its g factor is the largest among those of related trialkylsilyl and tris(trialkylsilyl)silyl radicals. According to the local symmetry of silylenes (R_2Si:, C_{2v}), the singly occupied MO of $\mathbf{1}^{\bullet-}$ should be $1b_1$, which is comprised of a pure 3p orbital perpendicular to the R_2Si 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^{α} σ bonds. The large g factor is ascribed to the contribution of the small excitation energy of $n \rightarrow SOMO(3p\pi)$ in $\mathbf{1}^{\bullet-}$ (Fig. 4).

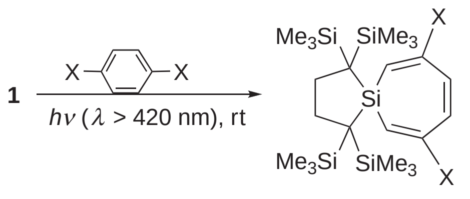
4.4 Excited-State Reactions. As described in the Introduction, silylenes are usually singlet in the ground state ($^1A_1$) and have two low-lying excited states, $^1B_1$ and $^3B_1$, with singlet and triplet 1,1-diradical natures, respectively (Fig. 1). However, little is known about the properties of their excited states, although several unimolecular reactions of the excited states of silylenes have been investigated in low-temperature matrices.[27a,57]

Under irradiation with filtered light ($\lambda > 420$ nm), silylene **1** reacts with benzene derivatives to give the corresponding silacycloheptatrienes in quantitative yield (Eq. 18).[58] The photochemical reactions occur regiospecifically at the unsubstituted double bonds in the substituted benzenes. Irradiation of a 1:1.5 mixture of **1** and naphthalene in hexane for 2 h at room temperature gave a nearly 1:1 mixture of mono(silylene) **39** and bis(silylene) adducts **40** as shown in Eq. 19. Mono(silylene) adduct **39** is thermally unstable at room temperature and undergoes the reverse dissociation to naphthalene and **1** or reacts photochemically with **1** giving bis(silylene)adduct **40**.



1$^{\bullet-}$

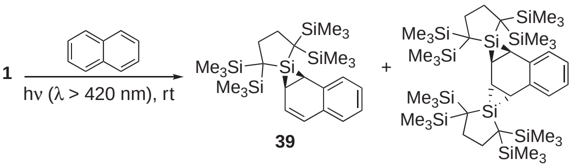
Fig. 4. Electronic configuration of $\mathbf{1}^{\bullet-}$.



X = H, Me, MeO, F, CF3

38

(18)

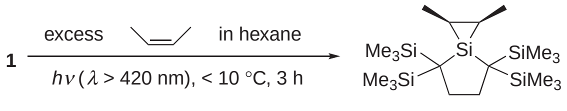


39

40

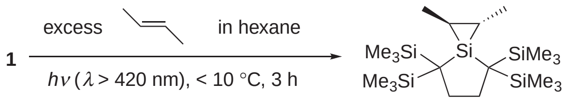
(19)

Photochemical additions of **1** to alkenes occur more cleanly than the related thermal addition reactions. Photoreactions of **1** in (*E*)- and (*Z*)-2-butenes with light with $\lambda > 420$ nm at <10 °C afford stereospecifically the corresponding (*E*)- and (*Z*)-2,3-dimethylsilacyclopropanes, (*E*)-**41** and (*Z*)-**41**, respectively, in quantitative yields (Eqs. 20 and 21).[59] Irradiation of a mixture of **1** and excess bicyclopropylidene in hexane at <10 °C gives the corresponding silacyclopropane **42** quantitatively (Eq. 22).[59] The excited state of **1** appears to be responsible for these reactions, because no reaction occurs in the dark at <10 °C. The thermal reaction of **1** with (*Z*)-2-butene at 30 °C for 6 h gives (*Z*)-**41** quantitatively; however, a similar reaction of **1** with (*E*)-2-butene is very slow even at 40 °C to afford a complex mixture after 2 days via the isomerization of **1** to the corresponding silaethene **12** (Eq. 8).



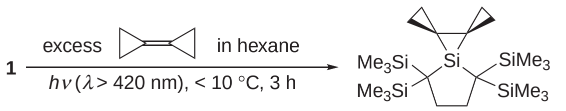
(*Z*)-**41** (quant.)

(20)



(*E*)-**41** (quant.)

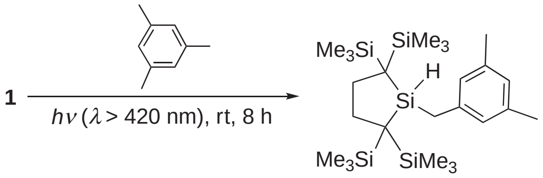
(21)



42 (quant.)

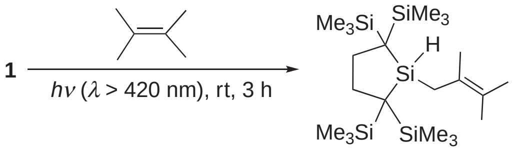
(22)

Interestingly, similar irradiations of silylene **1** in mesitylene and tetramethylethylene do not give the corresponding silepin or silirane due to the severe steric hindrance at C–C double bonds but produce **43** and **44**, respectively, in high yields through the insertion into benzylic and allylic C–H bonds (Eqs. 23 and 24).[58]



43, ca. 60%

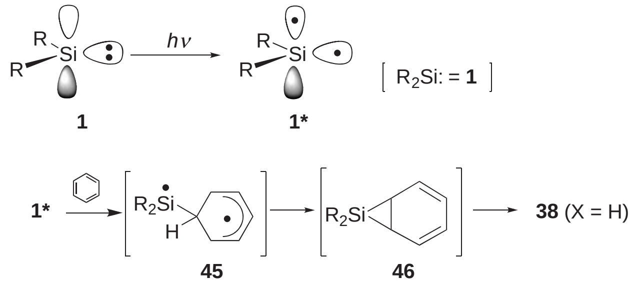
(23)



44, quant.

(24)

All these features of the photoreactions of **1** with aromatics and alkenes are compatible with the 1,1-biradical nature of the excited silylene. Since homolytic aromatic addition of silyl radicals is a well-known process,[60] the excited state of **1** (**1***) most likely adds to benzene to give the 1,3-biradical intermediate **45**. Successive cyclization to the corresponding silanorcaradiene **46** followed by the ring-opening leads to the final



Scheme 9.

silepin **38** (Scheme 9).

Whereas a diarylsilylene, Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl), has been reported to add thermally to benzene and naphthalene by Suzuki, Tokitoh, and Okazaki,[32] silylene **1** does not react with the aromatic compounds, even at 80 °C in the dark, but isomerizes to the corresponding silaethene **12** (Eq. 8). Discussions of the reactivity difference between Tbt(Mes)Si: and **1** at the ground states are interesting. Because a ground-state silylene has a high-lying lone-pair orbital and a low-lying vacant p-orbital, the silylene is amphiphilic and serves as both a nucleophile and an electrophile.[38] In the thermal reaction of a silylene with benzene as a π base, the interaction between the vacant p-orbital of the silylene and a benzene π HOMO (electrophilic approach) is more important than the interaction between the lone-pair orbital of the silylene and a benzene π LUMO (nucleophilic approach). Favorable electrophilic approach is probably achieved in the reaction of Tbt(Mes)Si: with benzene; however, it is prohibited in the reaction of **1** because its vacant p-orbital is sterically well protected by the helmet-like bidentate ligand.[32] In contrast, during the photoreaction of **1** with benzene, the less hindered in-plane orbital of the two singly occupied orbitals in **1*** may approach the benzene to accomplish homolytic aromatic addition, as shown in Scheme 9.

Singlet nature of the excited state responsible for the photoreactions is evidenced by various experiments. Broad absorption and fluorescence band maxima of **1** due to transitions between $^1B_1$ and $^1A_1$ states are observed at 440 nm (ε 500) and 610 nm, respectively, both in hexane and in benzene at room temperature (Fig. 5).[59] The spectral features are similar to those for dimethylsilylene, of which the absorption and fluorescence maxima are observed at 450 and 650 nm, respectively, at 77 K in a 3-methylpentane glass matrix.[27a] As the intersection point of the mirror image absorption and fluorescence spectra, the 0–0 transition energy of **1**, i.e. the energy gap between $^1A_1$ and $^1B_1$, is estimated to be 55 kcal mol^{-1}, which is in excellent agreement with the calculated value for dimethylsilylene at the CISD+Q/DZ(d)//SCF/DZ(d)level (54.2 kcal mol^{-1}).[61] On the basis of the fluorescence spectra and the theoretical energy gap between $^1A_1$ and $^3B_1$ for dimethylsilylene (25.1 kcal mol^{-1}), the state diagram for **1** is drawn as shown in Fig. 6; the energy gap between the $^1B_1$ and $^3B_1$ states (ΔE_{ST}) is estimated to be roughly 30 kcal mol^{-1}.

Time-resolved fluorescence spectra of **1** (excited at 440 nm and observed at 610 nm) in hexane show that the fluorescence decay obeys a first-order rate law with a lifetime (τ_0) of 80.5 ns. The fluorescence lifetime (τ) in a benzene–hexane mixture depends on the concentration of benzene according to Eq. 25, indicating that benzene effectively quenches the fluorescence. From the slope of the plot of τ_0/τ vs [benzene] and the τ_0 value, the quenching rate constant k_q is determined as 9.4×10^6 M^{-1} s^{-1}. The k_q value would be acceptable as the rate constant for the addition of the highly reactive $^1B_1$ state of **1** having a singlet 1,1-biradical nature to benzene, because the rate constant is only twenty times larger than that for the addition of triethylsilyl radical to benzene (4.6×10^5 M^{-1} s^{-1}).[62]

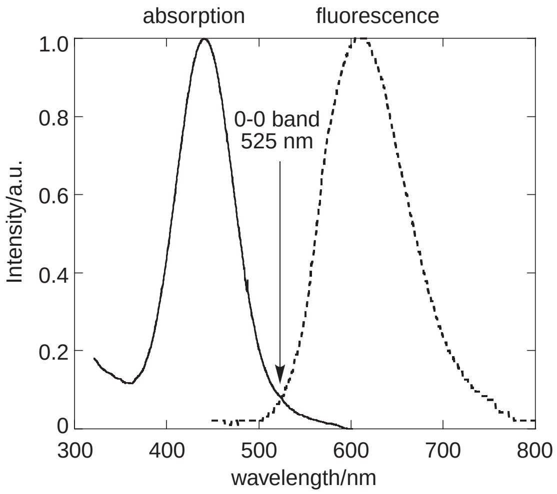


Fig. 5. UV–vis and fluorescence spectra of **1** in hexane at rt.

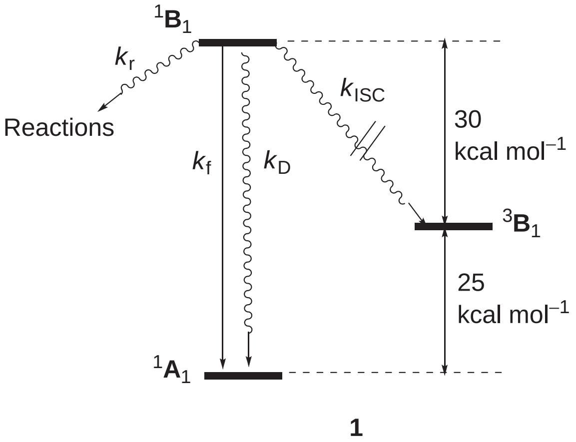
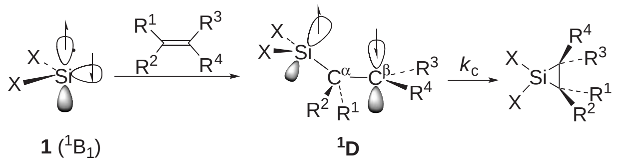


Fig. 6. Schematic state energy diagram for silylene **1**.

$$\tau_0/\tau = 1 + k_q\tau_0[\text{benzene}]. \tag{25}$$

The photoreactions of **1** with alkenes should also be stepwise, but the ring closure rates of the intermediate 1-silatrimethylene-1,3-diyl diradicals (**D**) are very fast with rates of roughly 10^9 s^{-1} according to the stereospecific addition modes of silylene **1** to (*E*)- and (*Z*)-2-butanes, and no cyclopropane-ring opening occurs during the photoaddition of **1** with bicyclopropylidene. The rapid cyclization of the intermediate diradicals **D** is only compatible with the singlet nature of **D** (Scheme 10).

These results imply that though the $^3B_1$ state is more stable than $^1B_1$, intersystem crossing from $^1B_1$ to $^3B_1$ is too slow to



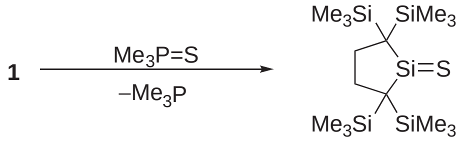
Scheme 10.

compete with other processes, such as fluorescence, radiationless decay, and reactions. Neither phosphorescence nor any ESR signals due to the $^3B_1$ state are observed during the irradiation of **1** in a 3-methylpentane glass matrix at 77 K. Formation of $^3B_1$ from $^1B_1$ cannot be rationalized in terms of the electronic configurations of $^1B_1$ and $^3B_1$ states and ΔE_{ST} in **1**. Because the $^1B_1 \rightarrow {}^3B_1$ transition must involve either a 3p or an n electron spin inversion (Scheme 1), the transition should be forbidden according to the El-Sayed rule.[63] In addition, the large ΔE_{ST} value should reduce the rate for the intersystem crossing from $^1B_1$ to $^3B_1$ (Fig. 6).

5. Application to the Synthesis of Novel Unsaturated Silicon Compounds

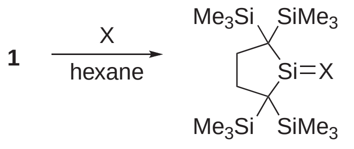
5.1 Silicon–Chalcogen Doubly Bonded Compounds. Although heavier group-14 element-group-16 element doubly bonded compounds, metallanechalcogenones ($R_2E{=}X$: E = Si, Ge, Sn, and Pb; X = S, Se, and Te), constitute an important class of compounds as heavier congeners of ubiquitous ketones, the synthesis and chemical properties of stable metallanechalcogenones still remain to be elucidated. A number of stable $R_2E{=}X$ type compounds have been reported;[64] all these metallanechalcogenones bear aryl substituents. Hence, their electronic properties of E=X bonds are strongly affected by the π substituents.

The synthesis of a series of dialkylsilanechalcogenones **47**–**49** has been achieved using **1** (Eqs. 26 and 27).[65]



(26)

47, 72%



(27)

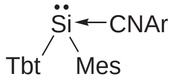
48: X = Se, 92%
49: X = Te, 99%

X-ray analysis reveals that in the solid state, the unsaturated silicon atom in **47**–**49** adopts a planar geometry, and the extent of the shortening of Si=X double bonds from the corresponding Si–X single bonds decreases in the order **47** < **48** < **49**. In the absorption spectra, $\pi \rightarrow \pi^*$ transition bands were distinctly observed in addition to $n \rightarrow \pi^*$ transition bands. Both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are red-shifted in the order **47** < **48** < **49**, which would be due to raising n and π orbitals and lowering π^* orbitals with increasing atomic number of chalcogen atoms. The red-shift depending the chalcogen atoms can be reproduced by using TD-DFT calculations of model compounds.

5.2 Silaketenimines. As a unique class of stable multiply bonded compounds of heavy group-14 elements, silicon, germanium, tin, and lead analogues of ketenimines have attracted much attention.[66] Their bonding characteristics are often described as intermediate between two resonance structures, allenic and zwitterionic structures (Scheme 11) and may be significantly modified by substituents on the terminal elements. In addition, a silylene–isocyanide complex with weak coordination of isocyanide carbon to E may exist. The complex should have a much larger E–C distance than a typical E–C single bond and, hence, should be differentiated from the zwitterionic structure using an arrow description as shown in Scheme 11.

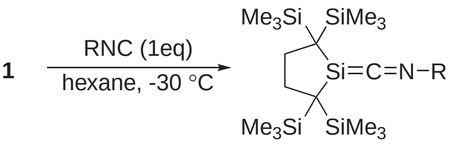
Tokitoh, Okazaki et al. have synthesized formal silaketenimines **50a**–**50c** with bulky aryl-substituents.[67] However, they concluded that **50a**–**50c** were better characterized as silylene–isocyanide complexes rather than silaketenimines on the basis of spectroscopic data, theoretical calculations, and their reactions (Chart 3).

Synthesis of stable silaketenimines with strong allenic character was achieved using stable dialkylsilylene **1**.[68] Silaketenimines **51a** and **51b** are synthesized using the reactions of isolable silylene **1** with the corresponding isocyanides (Eq. 28). Both **51a** and **51b** are stable in the solid state below 0 °C but dissociate to silylene **1** and the corresponding isocyanides in solution even at low temperatures.



50a, Ar = 2,4,6-trisopropylphenyl;
50b, Ar = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
50c, Ar = 2,4,6-tri-*t*-butylphenyl

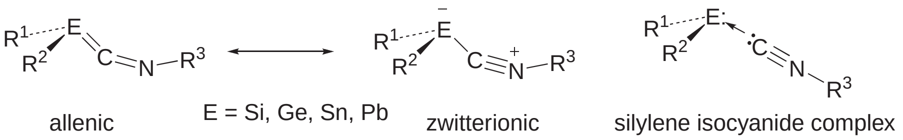
Chart 3.



(28)

51a: R = 2,6-diisopropylphenyl, 89%
51b: R = 1-adamantyl, 85%

Molecular structure of **51a** determined by X-ray analysis is



Scheme 11.

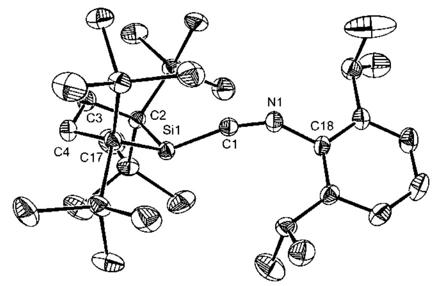


Fig. 7. Molecular structure of silaketenimine **51a**.

shown in Fig. 7. The Si1–C1 bond lengths of **51a** (1.794(3) Å) and **51b** (1.782(2) Å) are remarkably shorter than a typical Si–C single bond length (1.860 Å), while slightly longer than Si=C double bond lengths of typical silaethenes (1.693–1.764 Å). Their C1–N1 distances are much longer than the corresponding N≡C distances of aryl isocyanides. The C–N–C bond angles are considerably narrower than 180°, indicating that the nitrogen atom is sp^2-hybridized rather than sp-hybridized. All of the structural parameters indicate that **51a** and **51b** are allenic rather than zwitterionic.

Interestingly, the bonding characteristics of **51a** and **51b** are quite different from those of silaketenimines **50a–50c** reported by Tokitoh et al.;[67] **50a–50c** were concluded to be silylene–isocyanide complexes rather than silaketenimines. Theoretical calculations have revealed that the bonding characteristics of silaketenimines are remarkably sensitive to the substituents. (*N*-aryl)diarylsilaketenimines are zwitterionic but (*N*-alkyl)dialkylsilaketenimines are allenic, and (*N*-aryl)dialkyl derivatives are allenic and zwitterionic depending on the rotational conformation of *N*-aryl ring. Similar electronic substituent effects on the structure of ketenimines have been discussed by Wentrup et al.[69]

In hexane, **51a** and **51b** show two absorption bands; λ_{max}/nm (ε) values are 645 (127) and 374 (5.08×10^3) for **51a** and 465 (86) and 346 (4.26×10^3) for **51b**. The longer and shorter wavelength bands are assignable to $\pi(\text{Si=C}) \rightarrow \pi^*(\text{C=N})$ and $\pi(\text{Si=C}) \rightarrow \pi^*(\text{Si=C})$ transitions, respectively, on the basis of TD-DFT calculations for model compounds. The red-shift of the $\pi(\text{Si=C}) \rightarrow \pi^*(\text{C=N})$ band of **51a** from that of **51b** is ascribed to lowering $\pi^*(\text{C=N})$ orbital level due to significant $\pi^*(\text{C=N})$–$\pi^*(\text{aryl})$ orbital interaction in **51a**.

5.3 Trisilaallene and Related Compounds. Although the sp-hybridized carbon atoms are commonly found in acetylenes, nitriles, allenes, carbon dioxide, etc., heavy group-14 element analogues of these compounds are very limited. Stable silicon,[70a,70b] germanium,[70c,70d] tin,[70e] and lead[70f] analogues of acetylene derivatives have been obtained only very recently. Stable trisilaallene **52** was synthesized as the first silicon compound with a formal sp-silicon atom starting from stable silylene **1** in 2003.[71]

The reaction of **1** with silicon tetrachloride giving Si–Cl bond insertion product **25** (Eq. 10) followed by the reduction with KC_8 affords trisilaallene **52** in overall 42% yield (Eq. 29). Trisilaallene **52** is sensitive to air but thermally rather stable with a melting point of 198–200°. The structure of **52** was determined by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and X-ray crystallography.

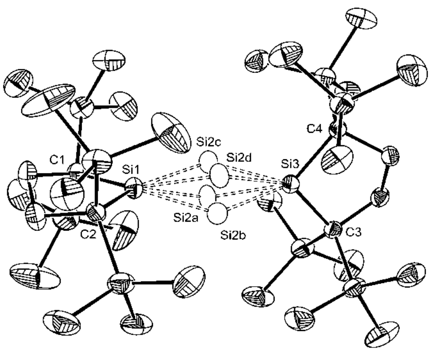
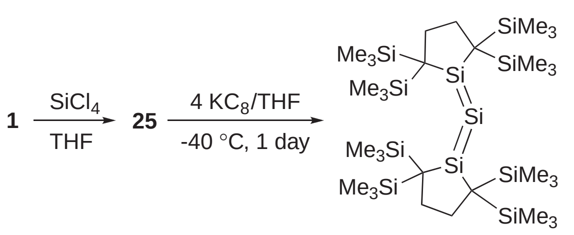


Fig. 8. Molecular structure of trisilaallene **52** showing dynamic disorder of Si2 atom.

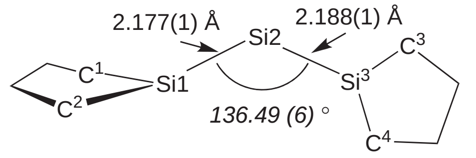


(29)

52

X-ray single crystal analysis shows a quite unusual structural feature of trisilaallene **52** (Fig. 8). In contrast to carbon allenes, the trisilaallene skeleton is not linear but bent. The central silicon atom (Si^2) in the crystal is found at four positions labelled Si^{2a}–Si^{2d} in Fig. 8 at higher temperatures than −50 °C, indicating that four structurally similar isomers **A–D** exist. The populations for **A** through **D** are independent of crystals but significantly temperature-dependent. The energy differences between isomers **A–D** are estimated to be within 1.1 kcal mol^{-1}, suggesting a dynamic disorder mediated by a rotation of the Si^2 atom around the Si^1–Si^3 axis.

The details of the molecular parameters of isomer **A** of trisilaallene **52** at −150 °C are as follows (Fig. 9). (1) The Si^1–Si^2–Si^3 skeleton is significantly bent with a bond angle of 136.49(6)°, indicating that the bonding at Si^2 atom cannot be described by using simple sp-hybridization anymore. (2) The two Si–Si bond lengths in **52** (2.177(1) and 2.188(1) Å) are in the range of those for typical stable disilenes. (3) The two five-membered rings are almost perpendicular to each other; the dihedral angle between the C^1–Si^1–C^2 and C^3–Si^3–C^4 planes is 92.5°. (4) The geometry around the two terminal silicon atoms is not planar but a little pyramidalized; the sum of



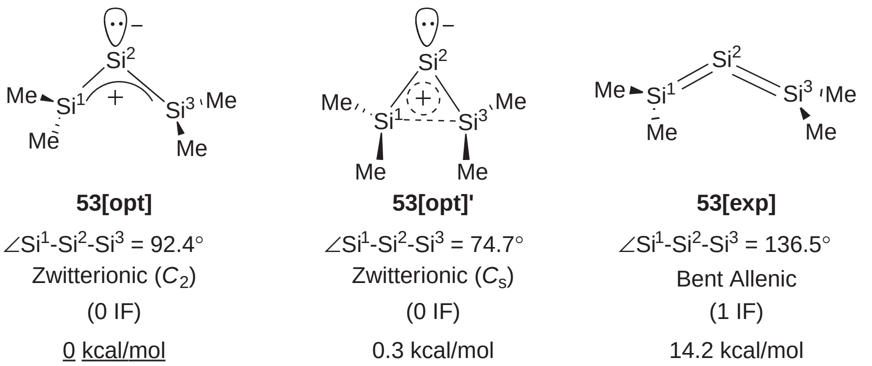
Dihedral angles

Si^3-Si^2-Si^1-C^2 = 65.6 (1) °

Si^1-Si^2-Si^3-C^4 = 60.1 (2) °

C^1-Si1-C^2 plane/C^3-Si^3-C^4 plane = 92.5 °

Fig. 9. Structural parameters of isomer **A** of trisilaallene **52** at −150 °C.



53[opt]
$\angle Si^1$-Si^2-Si^3 = 92.4°
Zwitterionic (C_2)
(0 IF)
0 kcal/mol

53[opt]'
$\angle Si^1$-Si^2-Si^3 = 74.7°
Zwitterionic (C_s)
(0 IF)
0.3 kcal/mol

53[exp]
$\angle Si^1$-Si^2-Si^3 = 136.5°
Bent Allenic
(1 IF)
14.2 kcal/mol

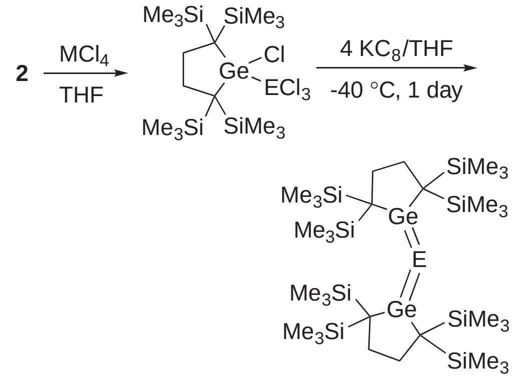
Fig. 10. Theoretical structures and relative energies of tetramethyltrisilaallene (**53**). IF = number of imaginary frequencies.

the bond angles around Si1 and Si3 is 354.1 and 354.9°, respectively. (5) The dihedral angles Si^3–Si^2–Si^1–C^2 and Si^1–Si^2–Si^3–C^4 are 65.6(1) and 60.1(2)°, respectively, indicating a *trans*-bent arrangement around Si^1–Si^2 and Si^3–Si^2 bonds. All of these structural features indicate that trisilaallene **52** is bent-allenic with two cumulated *trans*-bent Si=Si double bonds.

The DFT calculations for a model trisilaallene Me_2Si=Si=$SiMe_2$ (**53**) at the B3LYP/6-31+G(d,p) level have shown that the optimized structure (**53[opt]**) is characterized to be neither linear nor bent allenic but zwitterionic (Fig. 10); the Si^1–Si^2–Si^3 skeleton is remarkably bent with a bond angle of 92.4° and two C–Si–C planes are slightly twisted from each other. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) for **53[opt]** are a symmetric and an antisymmetric π orbitals delocalized to the trisilaallyl π system, respectively. Molecular orbital calculations were performed for **53[exp]**, where the coordinates of four carbon and three silicon atoms in **53** were fixed to those observed for **52**. Twisted pπ-type orbitals at the terminal silicon atoms in **53[exp]** interact with both pπ-type and in-plane orbitals at the central silicon atom, indicating a bent-allenic electronic structure for **53[exp]**. Because **53[exp]** is only 14.2 kcal mol^{-1} higher in energy than **53[opt]** (Fig. 10), the distortion from a zwitterionic to a bent-allenic structure is feasible due to steric effects. In other words, the bulky terminal substituents in **52** not only serve as steric protecting groups for Si=Si bonds but also adjust the electronic structure. Actually, theoretical calculations for molecule **52** reveal that its optimized structure is very close to that observed by X-ray crystallography with the bond angle of 136.2°.

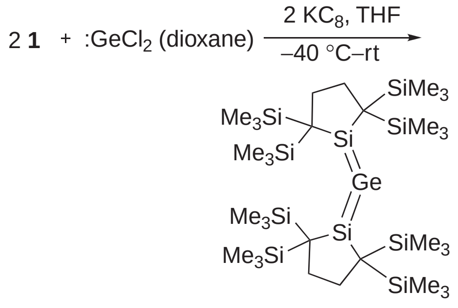
The unusual bonding nature of **52** in the solid state is also applicable to that in solution. The fluxional nature of **52** in solution is evidenced by the highly symmetric ^{1}H, ^{13}C, and ^{29}Si NMR spectra; 72 ^{1}H, 24 ^{13}C, and 8 ^{29}Si nuclei in 8 trimethylsilyl groups and 8 ^{1}H and 4 ^{13}C in two methylene groups are all equivalent. The ^{29}Si NMR resonances of **52** found at 157 and 197 ppm in benzene-d_6 are assigned to Si^2 and Si^1 (Si^3) nuclei, respectively. They are in good accord with the theoretical values calculated at the GIAO/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level for **53[exp]**; the theoretical ^{29}Si resonances for Si^2 and Si^1(Si^3) nuclei for **53[exp]** are 144 and 221(212) ppm, respectively, while they are 39 and 355 ppm for **53[opt]**. The ^{1}H NMR spectra for **52** are essentially independent of temperatures in toluene-d_8 between rt and −80 °C, indicating low-energy barriers for the interchange among **A**–**D** isomers. UV–vis absorption maxima are found at 390 nm (ε 21300) and 584 nm (ε 700) in hexane. The red shift of the longest absorption band compared with that for tetramethyldisilene (λ_{max} 350 nm)[72] as well as the two-splitting band feature for **52** are consistent with significant conjugation between the two Si=Si double bonds as suggested by the molecular orbital calculations; the extent of the conjugation is even larger than that found for a spiropentasiladiene.[73]

To elucidate the origin and properties of the unusual bonding and structure observed in trisilaallene **52**, we have synthesized several silicon and germanium congeners of trimetallaallenes **54**–**56**.[74] A similar method used for the synthesis of **52**[71] can be applied to the synthesis of trigermaallene **54** and digerma-2-silaallene **55** (Eq. 30).[74a] 2-Germadisilaallene **56** is synthesized by the reduction of a 2:1 mixture of isolable dialkylsilylene **1** and $GeCl_2$–dioxane complex with KC_8. (Eq. 31).[74b] All these trimetallaallenes are oxygen and moisture-sensitive but thermally very stable in the solid state.



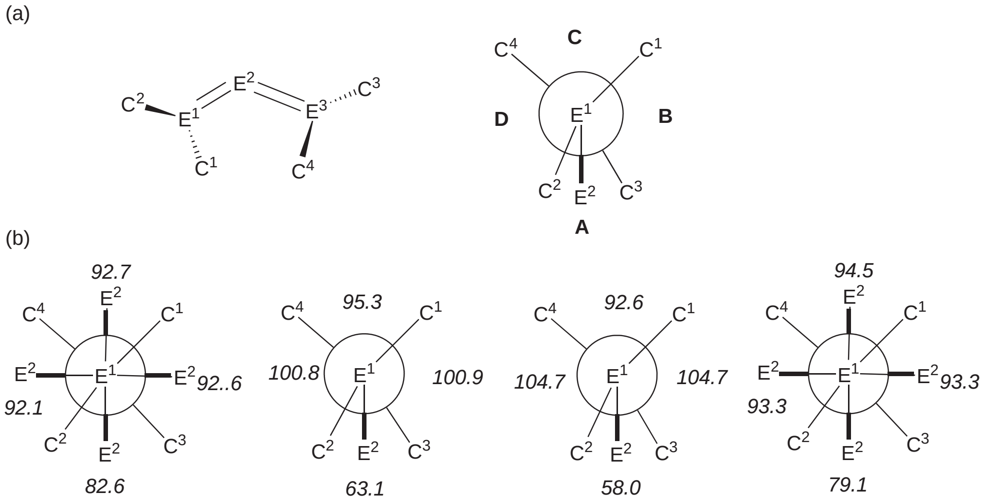
54, E = Ge, 26%
55, E = Si, 24%

(30)



56, 60%

(31)



52 (D) **54** (N) **55** (N) **56** (D)

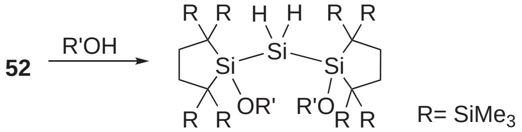
Fig. 11. (a) Labeling scheme of atoms and quadrants A–D of trimetallaallenes **52**, **54–56**. (b) Dihedral angles of quadrants of the trimetallallenes. (D) and (N) designate "dynamic disorder" and "no disorder," respectively.

Similarly to trisilaallene **52**, the E–E′–E skeletons in **54–56** are not linear but significantly bent. The E–E′–E bond angles of **54** and **55** (122.61(6) and 125.71(7)°, respectively) are significantly smaller than those of **52** and **56** (136.49(6) and 132.39(2)°, respectively). Terminal germanium atoms in **54** and **55** adopt strongly pyramidalized geometry compared to the terminal silicon atoms in **52** and **56**; the sums of the bond angles at Ge1 and Ge3 atoms in **54** and **55** are around $348.9 \pm 0.4^\circ$, while the sums at Si1 and Si3 atoms in **52** and **56** are $354.2 \pm 0.7^\circ$. The results are consistent with the known tendency that pyramidalization at germanium atoms in digermenes are larger than that at silicon atoms in the corresponding disilenes.[75] Interestingly, $E^1\cdots E^3$ distances for **52**, **54–56** are almost constant: 4.054, 4.080, 4.039, and 4.093 Å for **52**, **54**, **55**, and **56**, respectively. The intramolecular shortest van der Waals contact in these trimetallaallenes is found between a methyl group in a trimethylsilyl group on C^1 and that on C^3, and the shortest $C\cdots C$ distance found in **52**, **54–56** is similar (ca. 3.8 Å).

Remarkable dynamic disorder of trisilaallene **52** in the solid state discussed in a previous section is not found for trigermaallene **54** or digerma-2-silaallene **55** but observed for 2-germadisilaallene **56**. In other words, 1,3-digermametallaallenes do not show dynamic disorder but 1,3-disilametallaallenes do. The apparent difference in the dynamic behavior between 1,3-digermametallaallenes and 1,3-disilametallaallenes can be understood by the different environmental feature of the quadrants between them. The dihedral angles defining the quadrants A–D are shown in Fig. 11. Since the environment of the four quadrants of **52** and **56** is similar to the dihedral angles of $90 \pm 11^\circ$, the energy differences between the four rotational isomers should be very small. On the other hand, the dihedral angle for quadrant A in **54** and **55** is very small compared with those of the other three quadrants. It is suggested that for **54** and **55**, a rotational isomer having E^2 in quadrant A is ca. 3 kcal mol^{-1} lower in energy than other isomers that have E^2 in quadrants B–D. Apparently, the larger difference in the environment among the four quadrants of **54** and **55** than those of **52** and **56** is ascribed to the larger pyramidalization at terminal germanium atoms in **54** and **55**.

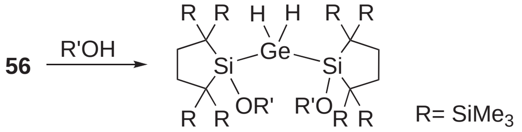
Similarly to **52**, **54–56** show highly symmetric ^{1}H, ^{13}C, and ^{29}Si NMR spectral patterns in solution, suggesting that they are fluxional in solution with the facile rotation of central allenic atom around the axis through E^1 and E^3. UV–vis spectral patterns of **54–56** in hexane at room temperature are similar to that of **52**, indicating significant conjugation in the $E^1{=}E^2$ and $E^2{=}E^3$ double bonds. The longest absorption band maxima red-shifts in the order **52** < **56** < **55** < **54**, and the absorptivity increase in the same order. $\lambda_{\max}$/nm (ε) is 584 (700), 630 (5300), 612 (3100), and 599 nm (1130) for **52**, **54**, **55**, and **56**, respectively.

Distinctive reactions of trisilaallene **52** and 2-germadisilaallene **56** with various reagents including water, alcohols, acetone, and haloalkanes are observed.[76] Trimetallaallenes **52** and **56** react with various hydroxylic compounds at room temperature to give the corresponding adducts **57a–57c**, **58a**, and **58b** in high yields and in a regiospecific manner (Eqs. 32 and 33).



(32)

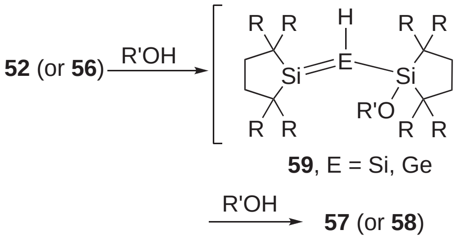
57a, R' = H; **57b**, R' = Me; **57c**, R' = Et.



(33)

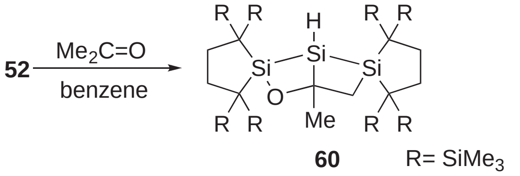
58a, R' = H; **58b**, R' = Me

These reactions should proceed stepwise and involve hydridodimetallenes **59** as important intermediates as shown in Eq. 34, while **59** is not detected during the reactions. The observed regiospecificity can be explained by invoking the unique electronic structure of **52** (and **56**) as well as the charge distribution of dimetallene intermediates **59**.



(34)

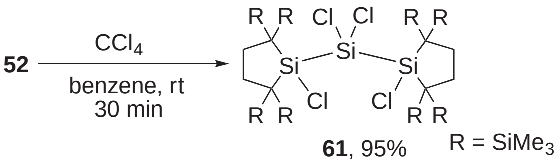
The reaction of trisilaallene **52** with acetone in benzene affords highly strained bicyclic compound **60** in high yield (Eq. 35). The unusual structure was confirmed by X-ray crystallography.



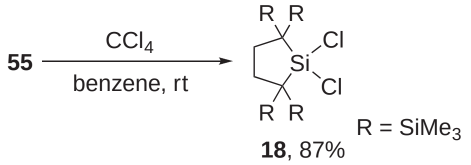
(35)

Because the above reaction is rather faster than the reactions of **52** with ethanol and isopropyl alcohol, the possibility that the substrate responsible for the initial addition is the corresponding enol formed via the keto–enol equilibrium of acetone may be excluded. A plausible mechanism would be the en-type addition of acetone to **1** to form **11** followed by the formal intramolecular $[2+2]$ addition between the residual Si=Si bond and C=C bond, while the formal $[2+2]$ addition may not be a concerted addition but a stepwise radical mechanism.[77]

The reaction of trisilaallene **52** with carbon tetrachloride at room temperature affords the corresponding tetrachlorotrisilane **61** almost quantitatively (Eq. 36).[76] The reaction shown in Eq. 36 is consistent with the biradical nature of disilenes and explained by stepwise chlorine abstraction from carbon tetrachloride. In contrast, the reaction of 2-germadisilaallene **55** with carbon tetrachloride gave dichlorosilane **18**, indicating the Si–Ge bond cleavage during the reaction (Eq. 37).

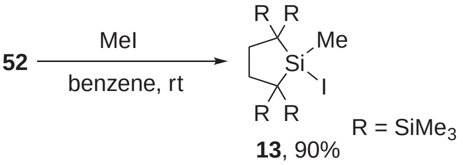


(36)



(37)

Silicon–silicon bond cleavage occurs during the reaction of **52** with methyl iodide to give iodosilane **13** (Eq. 38).[38]



(38)

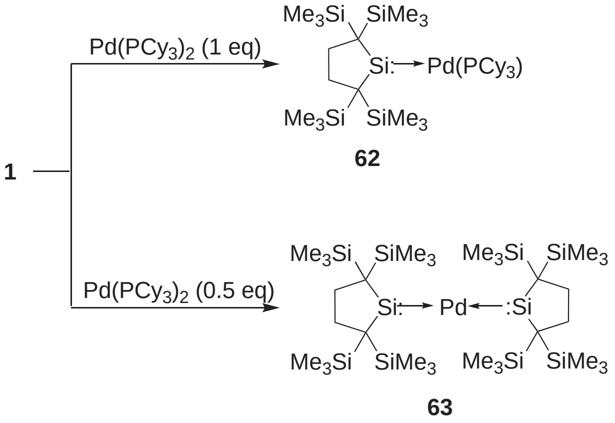
5.4 Silylene Transition Metal Complexes. Much attention has been focused recently on silylene transition-metal complexes as congeners of carbene transition-metal complexes, which have been utilized as useful catalysts for various important organic syntheses.[78] Although a number of base-stabilized silylene complexes have been isolated since 1987, very few base-free silylene complexes have been known until now.[79]

Using stable silylene **1**, (dialkylsilylene)(tricyclohexylphosphine)palladium **62** and bis(dialkylsilylene)palladium **63** were synthesized (Scheme 12).[80]

While the reaction of silylene **1** with 1 equiv of bis(tricyclohexylphosphine)palladium in benzene at room temperature gave mono(silylene)palladium complex **62** as an oil, a similar reaction of **1** with 0.5 equiv of bis(tricyclohexylphosphine)palladium gave bis(silylene)palladium complex **63** as air- and moisture-sensitive dark red crystals (mp 124 °C decomp.) in 40% yield. The ^{29}Si resonance of the unsaturated silicon nuclei of **63** appeared at 448 ppm is a little higher field than that for free silylene **1** (569 ppm) but reasonable as the resonance for a base-free silylene metal complex. X-ray analysis for **63** reveals that two dialkylsilylene ligands coordinate almost linearly to the central palladium with the Si–Pd–Si angle of 179.3°. The two silacyclopentane rings are almost perpendicular to each other with a C1–Si1–Si2–C3 dihedral angle of 94.7°. The geometry around the central palladium is similar to that of related bis(diaminocarbene)palladium complexes.[81] As expected for the less perturbed nature of dialkylsilylene **1**, theoretical calculations for a model bis(dialkylsilylene)complex and related complexes show that the extent of π back donation of bis(dialkylsilylene)palladium is significantly stronger than that of bis(diaminocarbene)- and bis(diaminosilylene)palladium complexes.

6. Conclusion

A comprehensive study, though still under way, of the structure, spectroscopic properties, and reactions of isolable dialkylsilylene **1** has disclosed the intrinsic properties of dialkylsilylenes that have never been revealed by studies on transient dimethylsilylene and other dialkylsilylenes. X-ray structural analysis and ^{29}Si NMR, UV–vis, and fluorescence spectroscopic studies of **1** allow estimating the electronic properties of ground and excited states of dialkylsilylenes. Though highly sterically protected, silylene **1** allows studies of the reactions



Scheme 12.

not only with well-known trapping reagents of a reactive dialkylsilylene, such as alcohols, triethylsilane, alkenes, acetylenes, and 2,3-dimethylbutadiene, but also with less reactive haloalkanes and halosilanes. Investigation of the generation and properties of the radical anion of **1** is usually difficult for the reactive dialkylsilylene but rather easy for silylene **1**. As a stable compound embodying unique electronic properties of reactive dialkylsilylenes, silylene **1** has been utilized as a synthetic reagent for various silicon unsaturated compounds, such as Si=X doubly bonded compounds (X = S, Se, Te, C=NR, etc.), a trisilaallene, a 1,3-disilagermaallene, and silylene transition-metal complexes. Although silylene **1** is still the sole known isolable dialkylsilylene, modification of ligands may lead to new entries for stable dialkylsilylenes that are designed for functional materials. Studies of these stable dialkylsilylenes are promising to create a new important field of silicon chemistry.

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