

Reactions of trisilaallene and 2-germadisilaallene with various reagents

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Abstract

A number of the distinctive reactions of trisilaallene **1** and 2-germadisilaallene **4** with various reagents including water, alcohols, acetone, and haloalkanes were studied. The addition reactions of **1** to water and alcohols occur in a regiospecific manner to afford 1,3-dioxytrisilanes in high yields. The additions are explained by a stepwise mechanism involving the initial nucleophilic attack of a hydroxy oxygen to a terminal allenic silicon to give an intermediate unsymmetric disilene. The regiospecificity is rationalized by the shape of the frontier molecular orbitals and the NPA charge distribution of trisilaallene **1** and the intermediate disilene.

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1. Introduction

Since the isolation of tetramesityldisilene as the first stable disilene in 1981 [1], a number of reactions of stable disilenes with various reagents such as hydroxylic compounds (water, alcohols, and phenols), haloalkanes, and carbon–carbon multiply bonded compounds (alkenes, alkynes, and 1,3-dienes) have been reported [2]. Whereas the mechanisms of these reactions have not been fully investigated yet, the reaction modes and reactivity of disilenes appear to be remarkably different from those of alkenes.

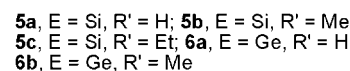
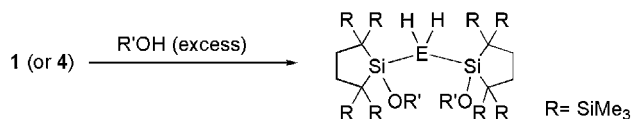
We have recently synthesized a set of heavier group-14 element congeners of allene, stable trimetallaallenes **1** [3a], **2** [3b], **3** [3b], and **4** [3c], and revealed their quite unique bonding nature. In contrast to rigid linear skeletons of carbon allenes, the skeletons of all these trimetallaallenes are significantly bent with the bond angle of 122.6–136.5° and fluxional both in the solid states and in solution. Trimetallaallenes **1–4** are sensitive to air but rather stable thermally with the melting point around 200 °C. We discuss herein the reactions of trisilaallene **1**

and 2-germadisilaallene **4** with various reagents including water, alcohols, acetone, and haloalkanes (see Chart 1).

2. Results and discussion

2.1. Reactions of trimetallaallenes **1** and **4** with hydroxylic compounds

Trisilaallene **1** reacts with water at room temperature to give 1,3-dihydroxytrisilane **5a** as a sole product in 74% yield [3a]. Similarly, the reactions of **1** with methanol and ethanol proceed with slower rates to afford 1,3-dialkoxytrisilanes **5b** and **5c** in high yields (Eq. (1)). No adducts were obtained in the reactions of **1** with bulkier alcohols like isopropyl alcohol and *t*-butyl alcohol. Reactions of **4** with water and methanol occur in a similar manner to give the corresponding adducts **6a** and **6b** in high yields. These results are summarized in Table 1.



(1)

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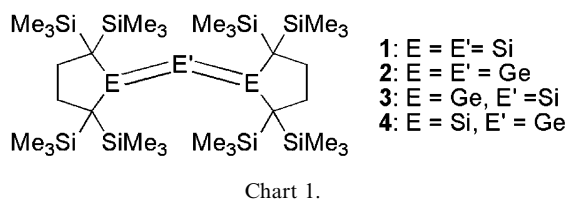


Table 1
Reactions of **1** and **4** with various hydroxylic compounds

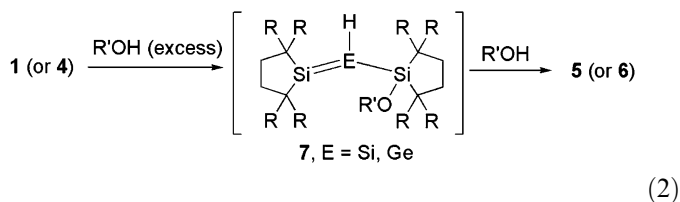
Trim- etallaallene	R'OH	Temperature (°C)	Reaction time	Product	Yield (%) ^a
1	H ₂ O	r.t.	< 5 min	5a	74
1	MeOH	r.t.	6 h	5b	94
1	EtOH	r.t.	12 h	5c	92
1	<i>i</i> -PrOH	80	5d	–	No reaction
1	<i>t</i> -BuOH	80	5d	–	No reaction
4	H ₂ O	r.t.	10 min	6a	86
4	MeOH	r.t.	6 h	6b	95

^a Isolated yield.

The structures of **5a–5c** and **6b** were unequivocally determined by an X-ray structural analysis. Molecular structures of **5a**, **5b**, **5c**, and **6b** are shown in Figs. 1–4 and selected structural parameters are summarized in Table 2. The Si–Si–Si bond angle [117.94(4)°] for water adduct **5a** is significantly smaller than those for **5b** and **5c** as shown in Table 2. The exceptionally acute Si–Si–Si bond angle for **5a** may be ascribed to the intramolecular hydrogen bonding between two hydroxy groups in addition to the smaller steric effect of hydroxy groups.

These reactions should proceed stepwise and involve hydridodimetalenes **7** as important intermediates as shown

in Eq. (2), while **7** are not detected during the reactions. The observed regioselectivity can be explained by the unique electronic structure of **1** (and **4**) as well as the charge distribution of disilene intermediates **7**



Theoretical calculations for a model trisilaallene, tetramethyltrisilaallene **8**, at the B3LYP/6-31+G(d, p) level have revealed that the unique electronic structure of trisilaallene **1** is responsible for the regioselectivity. As discussed in previous papers [3a–5], the optimized skeletal structure of **8** is quite different from that of experimentally observed for **1**. The Si¹–Si²–Si³ bond angle and the C¹–Si¹–Si²–Si³ dihedral angle in the optimized structure of trisilaallene **8** (**8**_{opt}) are 92.4° and 9.2°, respectively, while those for **1** are 136.5° and 28.7°, respectively (Fig. 5). Molecular orbital considerations of **8**_{opt} and **8**_{exp}, in the latter of which the coordinates of four carbon and three silicon atoms are fixed to those observed for **1**, have revealed that **8**_{opt} and **8**_{exp} are characterized to be zwitterionic and bent allenic, respectively. In **8**_{opt}, the HOMO and LUMO are both π-type but HOMO – 1 is in-plane n-type orbitals. On the other hand, in **8**_{exp}, the HOMO and HOMO – 1 are twisted bonding π orbitals and the LUMO and LUMO + 1 are the corresponding anti-bonding π (π*) orbitals. As shown in Fig. 6a, orbital coefficients of the HOMO – 1 and HOMO of **8**_{exp} are concentrated on Si² atom, while those of the LUMO and LUMO + 1 are distributed largely on terminal Si¹ and Si³ atoms.

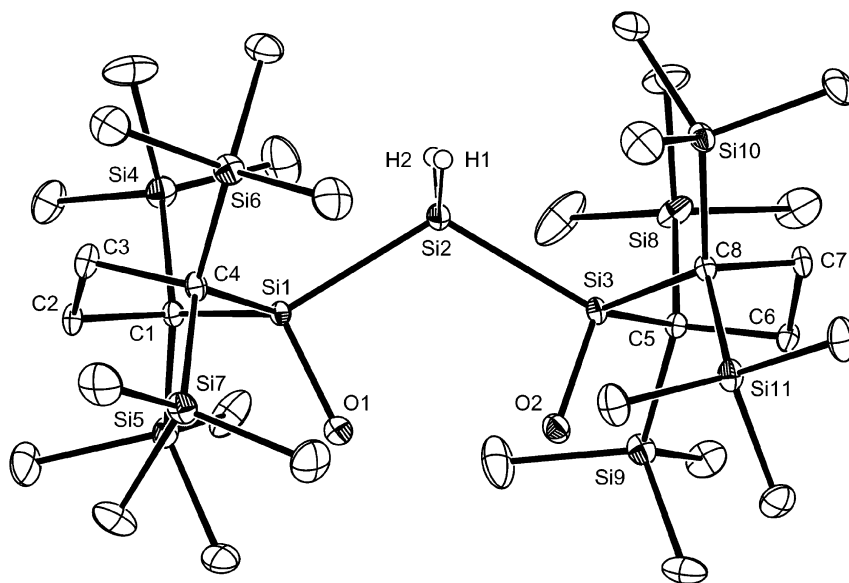


Fig. 1. Molecular structure of water adduct of **1**, **5a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for those on Si2 atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2 2.3818(11), Si2–Si3 2.3689(11), Si1–O1 1.686(2), Si3–O2 1.673(2), Si1–Si2–Si3 117.94(4).

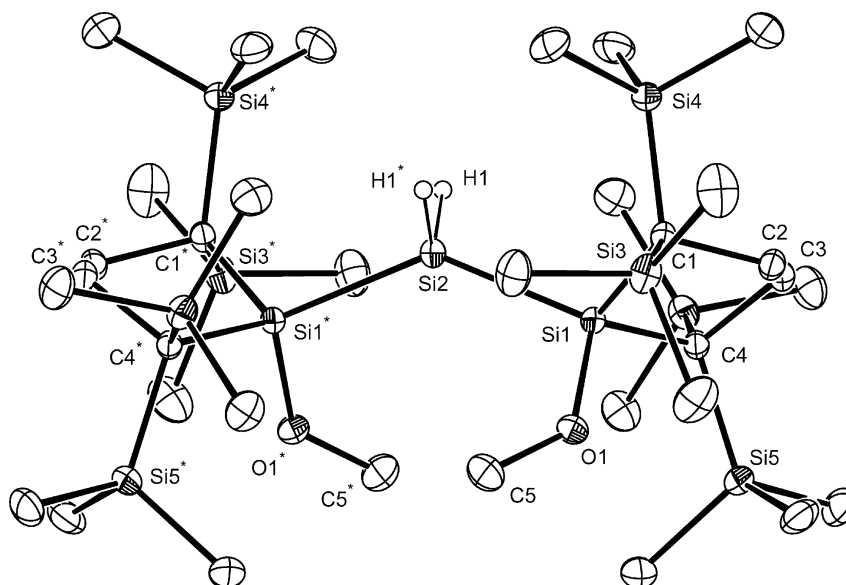


Fig. 2. Molecular structure of methanol adduct of **1**, **5b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for those on Si2 atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2 2.4042(8), Si1–O1 1.6568(1), Si1–Si2–Si1* 135.41(6).

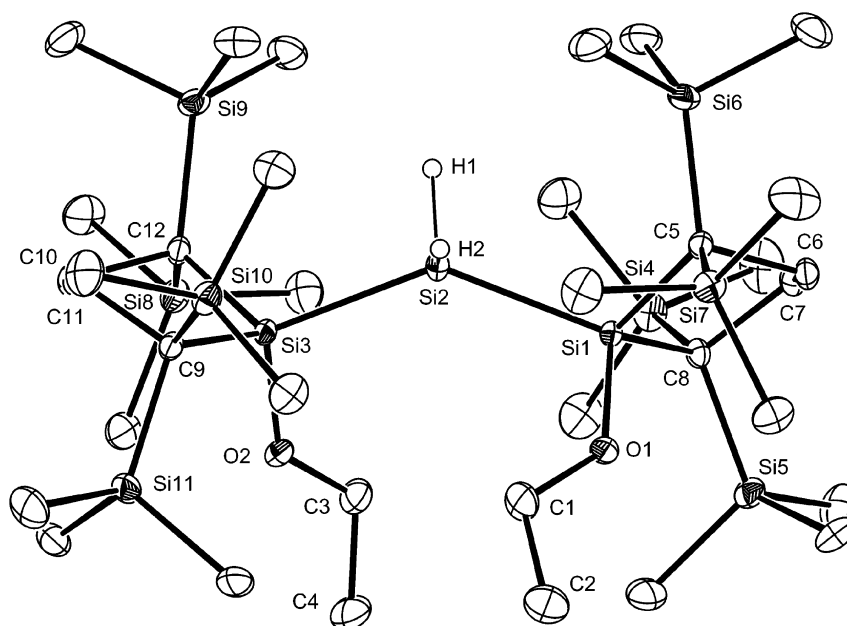


Fig. 3. Molecular structure of ethanol adduct of **1**, **5c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for those on Si2 atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2 2.4004(9), Si2–Si3 2.4051(9), Si1–O1 1.6582(16), Si3–O2 1.6583(17), Si1–Si2–Si3 136.43(4).

In accord with the above orbital description, positive and negative charges of $\mathbf{8}_{\text{exp}}$ distribute to the terminal Si¹ and Si³ atoms and a central Si² atoms, respectively, i.e., polar character of zwitterionic allene $\mathbf{8}_{\text{opt}}$ still remains in bent allene $\mathbf{8}_{\text{exp}}$ (Fig. 6b). Therefore, the nucleophilic attack of a hydroxy oxygen of an alcohol (or water) at terminal silicon atoms while the electrophilic attack of the hydroxylic hydrogen should occur at the central silicon atom. Most of the reported mechanistic studies of the addition of water (or an alcohol) to disilenes have shown that the addition reactions occur via the initial nucleophilic attack of a hydroxylic oxygen to a disilene

[6]. Our theoretical study of the mechanism has suggested that two bimolecular addition pathways are feasible [7]: one proceeds in a *syn*-addition manner via the initial electrophilic interaction of water hydrogen with disilene HOMO followed by the rate-determining nucleophilic attack of oxygen, while the other proceeds in an *anti*-addition manner via the initial nucleophilic interaction of water oxygen with disilene LUMO followed by the rate-determining electrophilic attack of the water hydrogen. Both the two pathways predict the regioselective formation of **7** in the first-step addition of a hydroxylic compound to **1**.

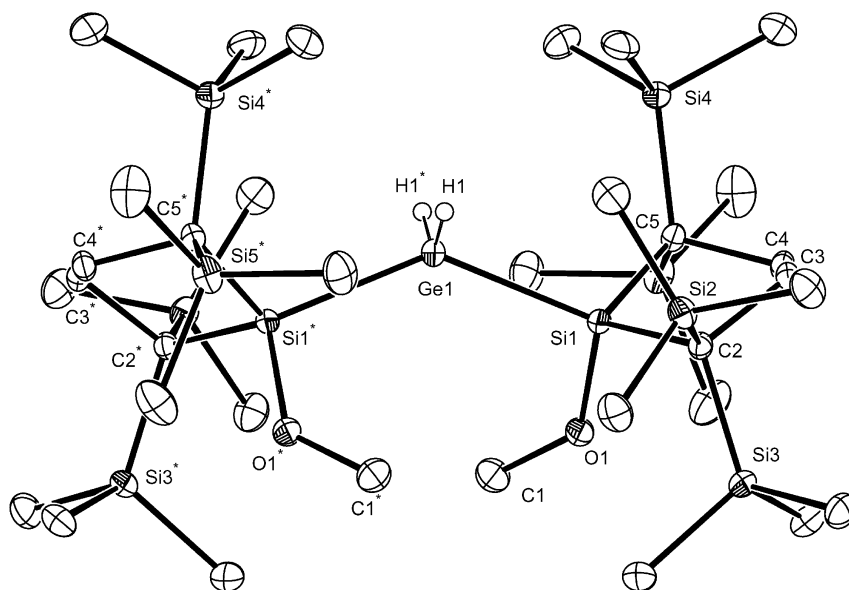


Fig. 4. Molecular structure of methanol adduct of **4**, **6b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for those on Ge1 atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–Si1 2.4369(10), Si1–O1 1.652(2), Si1–Ge1–Si1* 135.76(5).

Table 2
Selected structural parameters of **5a–5c**, **6b**, and **10**

Compound	$d(\text{Si–E})$ (Å) ^a	$d(\text{Si–O})$ (Å)	Si1–Si2–Si3 (°)
5a	2.3818(11)	1.686(2)	117.93(4)
	2.3689(11)	1.673(2)	
5b	2.4042(8)	1.6568(1)	135.41(5)
	2.4004(9)	1.6582(16)	136.43(4)
5c	2.4051(9)	1.6583(17)	
	2.4369(10)	1.652(2)	135.76(5)
10	2.365(2),	1.684(3)	129.15(7)
	2.349(2)		

^a E = Si or Ge.

To understand the regioselectivity of the second water addition to **7**, natural population analysis (NPA) charge distribution of 1,1-dimethyl-2-silyldisilene **9** as a

model for **7** was calculated at the B3LYP/6-31+G(d,p) level (Fig. 6b). Unsymmetrically substituted disilene **9** was found to have a strongly polar Si=Si bond, in which hydrido-substituted unsaturated silicon is negative and the dialkyl-substituted unsaturated silicon is positive. The calculated charge distribution as well as the frontier MO shape supports the regioselective nucleophilic attack of water oxygen to **7** occurring at the terminal silicon atom to form 1,3-dihydroxytrisilane **5a**.

The reaction of trisilaallene **1** with acetone in benzene affords highly strained bicyclic compound **10** in high yield (Eq. (3)). The unusual structure was confirmed by the X-ray crystallography (Fig. 7).

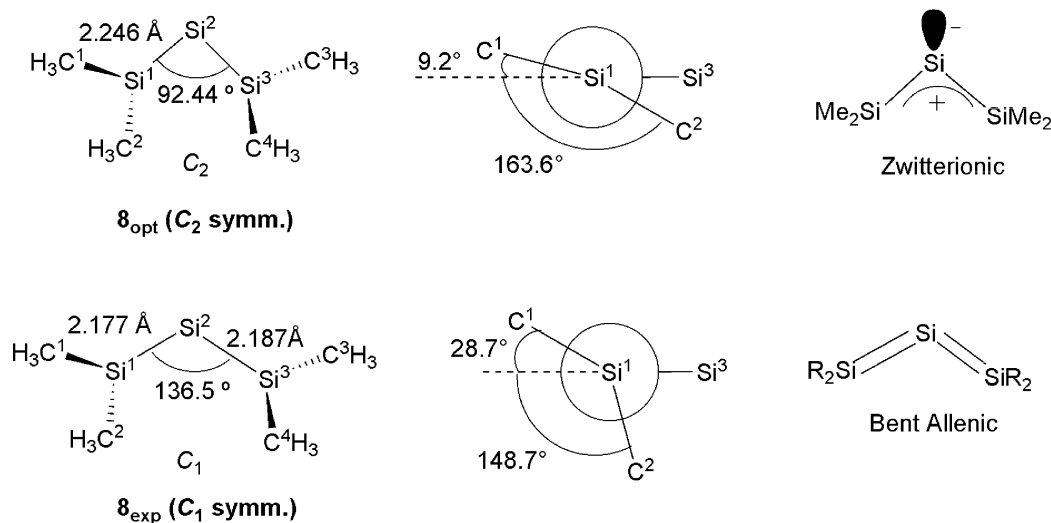


Fig. 5. Experimental (δ_{exp}) and optimized (δ_{opt}) geometries of tetramethyltrisilaallene.

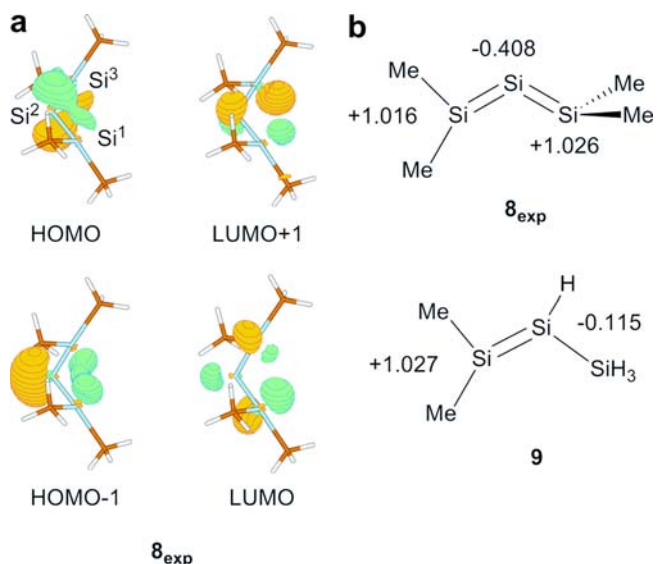
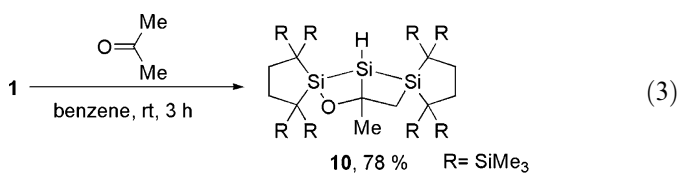
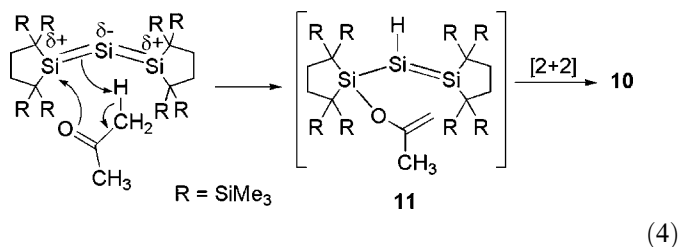


Fig. 6. (a) Frontier orbitals of $\mathbf{8}_{\text{exp}}$ and (b) NPA charge distribution of $\mathbf{8}_{\text{exp}}$ and $\mathbf{9}$ calculated at the B3LYP/6-31+G(d,p) level.



Because the above reaction is rather faster than the reactions of $\mathbf{1}$ 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 $\mathbf{1}$ to form $\mathbf{11}$ followed by the *formal* intramolecular [2 + 2] addition between the residual Si=Si bond and C=C bond (Eq. (4)), while the formal [2 + 2] addition may not be a concerted addition but a stepwise radical mechanism [8].



2.2. Reactions of trisilaallene $\mathbf{1}$ with haloalkanes

West et al. [9] and our group [10] have reported recently that disilenes react with various haloalkanes giving several types of products. On the basis of several mechanistic studies [10b,11], these reactions are rationalized by the initial formation of a pair of the corresponding halodisilanyl radical and alkyl radical followed by recombination or disproportionation in the cage or abstraction of the second halogen by the halodisilanyl radical out of the cage (Eq. (5)). Typically, tetrakis(*tert*-butyldimethylsilyl)disilene $\mathbf{12}$ reacts with various halomethanes to afford the corresponding 1,2-dichlorodisilanes $\mathbf{13}$ and/or the corresponding 1-alkyl-2-chlorodisilanes $\mathbf{14}$ (Scheme 1).

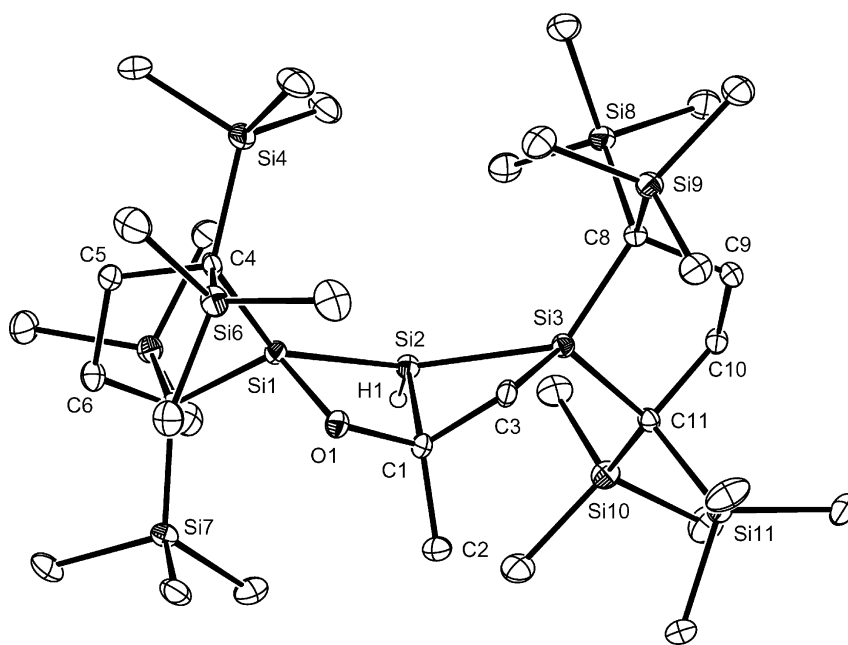
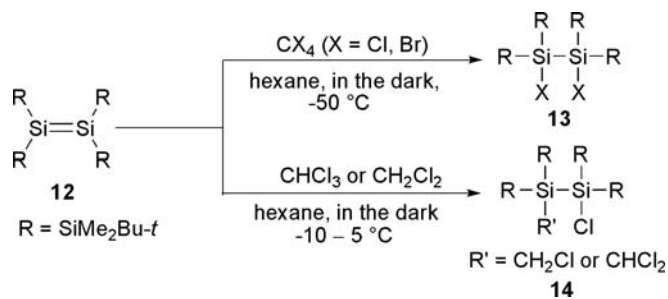
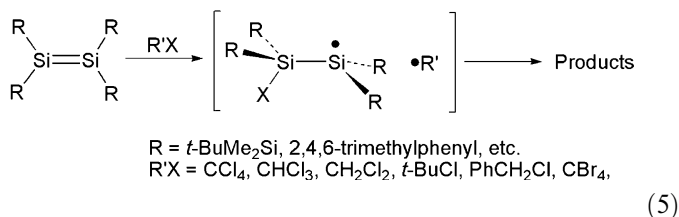


Fig. 7. Molecular structure of acetone-adduct $\mathbf{10}$. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms except for that on Si2 atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2 2.365(2), Si2–Si3 2.349(2), Si1–O1 1.684(3), Si2–C1 1.963(5), Si3–C3 1.922(5), O1–C1 1.475(5), C1–C3 1.562(5), C1–C2 1.515(6), Si1–Si2–Si3 129.15(7), Si2–Si1–O1 81.0(1), Si1–O1–C1 106.4(3), Si2–C1–O1 101.5(3), Si3–Si2–C1 77.5(1), Si2–C1–C3 95.5(3), Si3–C3–C1 101.9(3), O1–C1–C2 108.5(3), C3–C1–C2 110.8(4), Si2–C1–C2 128.2(3).

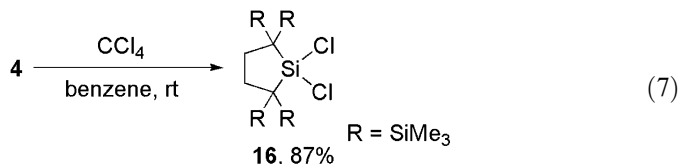
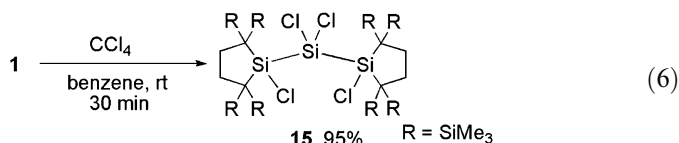


Scheme 1.

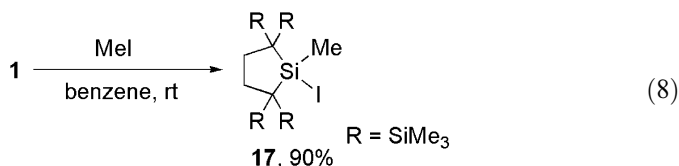


R = *t*-BuMe₂Si, 2,4,6-trimethylphenyl, etc.
R'X = CCl₄, CHCl₃, CH₂Cl₂, *t*-BuCl, PhCH₂Cl, CBr₄,

The reaction of trisilaallene **1** with carbon tetrachloride at room temperature affords the corresponding tetrachlorotrisilane **15** almost quantitatively (Eq. (6)). Structure of tetrachlorotrisilane **15** was confirmed by various NMR spectroscopies, although **15** has low solubility to various solvents, and gave no good single crystals suitable for the X-ray analysis. The reaction shown in Eq. (6) is consistent with a biradical nature of disilenes and explained by the stepwise chlorine abstraction from carbon tetrachloride. In contrast, the reaction of 2-germadisilaallene **4** with carbon tetrachloride gave dichlorosilane **16**, indicating the Si–Ge bond cleavage during the reaction (Eq. (7)).



Silicon–silicon bond cleavage of **1** was observed during the reaction of **1** with methyl iodide to give iodo(methyl)silane **17** (Eq. (8)) [12].



Trisilaallene **1** does not react with tetramethylethylene, 2-methyl-2-butene, phenylacetylene, or 2,3-dimethylbutadiene.

3. Experimental

3.1. General methods

All operations were performed in flame-dried glassware under the atmosphere of dry argon. ¹H (400 MHz), ¹³C (100 MHz), and ²⁹Si (79 MHz) NMR spectra were measured on a Bruker AVANCE400 spectrometer. ¹H and ¹³C NMR chemical shifts were referenced to residual ¹H and ¹³C resonances of the solvents; benzene-*d*₆ (¹H δ 7.15 and ¹³C δ 128.0). ²⁹Si NMR chemical shifts were given in ppm relative to externally referenced tetramethylsilane (δ 0). EI mass spectra were recorded on a JEOL JMS-600 D mass spectrometers. Trisilaallene **1** and 2-germadisilaallene **4** were prepared by the procedure according to the literature [3a,3c].

3.2. Reaction of trisilaallene **1** with methanol

A mixture of dry methanol (5 ml) and benzene (10 ml) was added to trisilaallene **1** (75 mg, 0.010 mmol) and the mixture was stirred at room temperature for 6 h. After removal of solvent in vacuo, recrystallization from hexane at –30 °C gave 1,3-dimethoxytrisilane **5b** (79 mg, 0.094 mmol) in 94% yield. **5b**: colorless crystals, m.p. 190–200 °C; ¹H NMR (C₆D₆, 400 MHz, δ) 0.27 (s, 36H), 0.36 (s, 36H), 1.90–2.00 (m, 8H), 3.55 (s, 6H), 3.73 (s, 2H); ¹³C NMR (C₆D₆, 100 MHz, δ) 3.8, 4.7, 19.0, 34.1, 55.4; ²⁹Si (C₆D₆, 79 MHz, δ) –107.5, 1.2, 3.9, 45.6; MS (EI, 70 eV) *m/z* (%) 823 (M⁺ – Me, 5), 403 (100), 372 (78); Anal. Calc. for C₃₄H₈₈O₂Si₁₁: C, 48.73; H, 10.58. Found: C, 48.60; H, 10.62%.

3.3. Reaction of trisilaallene **1** with ethanol

1,3-Diethoxytrisilane **5c** (80 mg, 0.092 mmol, 92% yield) was obtained in a similar manner from **1** (75 mg, 0.10 mmol) and ethanol (5 ml) in benzene (10 ml). **5c**: colorless crystals; m.p. 200–205 °C. ¹H NMR (C₆D₆, 400 MHz, δ) 0.31 (s, 36H), 0.38 (s, 36H), 1.31 (t, *J* = 7.2 Hz, 6H), 1.90–2.10 (m, 8H), 3.76 (s, 2H), 3.95 (q, *J* = 7.2 Hz, 4H); ¹³C NMR (C₆D₆, 100 MHz, δ) 4.1, 4.9, 17.7, 19.1, 34.2, 63.2; ²⁹Si NMR (C₆D₆, 79 MHz, δ) –105.9, 1.5, 3.5, 41.2; MS (EI, 70 eV) *m/z* (%) 851 (M⁺ – Me, 10), 417 (100), 373 (37). Anal. Calc. for C₃₆H₉₂O₂Si₁₁: C, 49.93; H, 10.71. Found: C, 49.87; H, 10.79%.

3.4. Reaction of germadisilaallene **4** with water

1,3-Dihydroxy-2-germatrisilane **6a** (45 mg, 0.053 mmol, 86% yield) was obtained in a similar manner from **4** (50 mg, 0.06 mmol) and water (5 ml) in benzene (10 ml). **6a**: colorless crystals; m.p. 190–200 °C; ¹H NMR (400 MHz, C₆D₆, δ) 0.32 (s, 36H, SiMe₃), 0.37 (s, 36H, SiMe₃), 1.90–2.10 (m, 8H, CH₂), 3.08 (s, 2H, SiOH), 3.85

(s, 2H, GeH₂); ¹³C NMR (100 MHz, C₆D₆, δ) 4.7 (Si(CH₃)₃), 4.9 (Si(CH₃)₃), 18.6 (C(SiMe₃)₂), 34.0 (CH₂); ²⁹Si NMR (79 MHz, C₆D₆, δ) 1.9 (SiMe₃), 3.8 (SiMe₃), 42.9 (SiOH); MS (EI, 70 eV) *m/z* (%) 839 (M⁺ – Me, 10), 390 (100), 373 (75). Anal. Calc. for C₃₂H₈₄GeO₂Si₁₀: C, 44.98; H, 9.91. Found: C, 45.21; H, 10.07%.

3.5. Reaction of germadisilaallene **4** with methanol

1,3-Dimethoxy-2-germatrisilane **6b** (51 mg, 0.058 mmol, 95% yield) was obtained in a similar manner from **4** (50 mg, 0.06 mmol) and methanol (5 ml) in benzene (10 ml). **6b**: colorless crystals; m.p. 195–205 °C; ¹H NMR (400 MHz, C₆D₆, δ) 0.27 (s, 36H, SiMe₃), 0.37 (s, 36H, SiMe₃), 1.90–2.10 (m, 8H, CH₂), 3.55 (s, 6H, SiOMe), 3.62 (s, 2H, GeH₂); ¹³C NMR (100 MHz, C₆D₆, δ) 4.2 (Si(CH₃)₃), 5.1 (Si(CH₃)₃), 19.2 (C(SiMe₃)₂), 34.2 (CH₂), 55.5 (OCH₃); ²⁹Si NMR (79 MHz, C₆D₆, δ) 1.4 (SiMe₃), 3.6 (SiMe₃), 47.1 (SiOMe); MS (EI, 70 eV) *m/z* (%) 867 (M⁺ – Me, 12), 404 (100), 373 (63). Anal. Calc. for C₃₄H₈₈GeO₂Si₁₀: C, 46.27; H, 10.05. Found: C, 46.15; H, 9.75%.

3.6. Reaction of trisilaallene **1** with acetone

Acetone-adduct **10** (83.9 mg, 0.100 mmol, 78%) was obtained by the reaction of **1** (100 mg, 0.13 mmol) with acetone (20 mg, 0.34 mmol) in benzene (10 ml) at r.t. for 3 h. **10**: colorless crystals; m.p. 60 °C (decomp.); ¹H NMR (C₆D₆, 400 MHz, δ) 0.19 (s, 9H, SiMe₃), 0.26 (s, 9H, SiMe₃), 0.28 (s, 9H, SiMe₃), 0.32 (overlapping s, 18H, SiMe₃), 0.36 (s, 9H, SiMe₃), 0.42 (s, 9H, SiMe₃), 0.45 (s, 9H, SiMe₃), 1.75 (s, 2H, CH₂), 1.87 (s, 3H, CH₃), 1.80–2.30 (m, 8H, CH₂), 4.42 (s, 1H, SiH); ¹³C NMR (C₆D₆, 100 MHz, δ) 3.5, 3.6, 3.8, 4.1, 4.1, 4.3, 4.8, 5.3, 14.3, 14.6, 16.2, 18.5, 29.2, 34.1, 34.8, 35.5, 36.8, 47.9, 80.0; ²⁹Si NMR (C₆D₆, 79 MHz, δ) –66.8, 2.0, 2.1, 3.0, 3.6, 3.7, 4.3 (overlapping), 7.6, 23.0, 47.9; MS (EI, 70 eV) *m/z* (%) 832 (M⁺, 8), 817 (5), 373 (100). Anal. Calc. for C₃₅H₈₆O₂Si₁₁: C, 50.53; H, 10.42. Found: C, 50.47; H, 10.37%.

3.7. Reaction of trisilaallene **1** with carbon tetrachloride

A mixture of carbon tetrachloride (1 ml) and benzene (7 ml) was added to trisilaallene **1** (45 mg, 0.058 mmol) in a Schlenk flask equipped with a magnetic stirrer bar. After the mixture was stirred at room temperature for 30 min in the dark, removal of the volatiles in vacuo gave tetrachlorotrisilane **15** (50.6 mg, 0.055 mmol) in 95% yield. **15**: colorless crystals; m.p. 248 °C; ¹H NMR (400 MHz, C₆D₆, δ) 0.41 (s, 36H, SiMe₃), 0.43 (s, 36H, SiMe₃), 1.90–2.10 (m, 8H, CH₂); ¹³C NMR (100 MHz, C₆D₆, δ) 5.1 (Si(CH₃)₃), 5.5 (Si(CH₃)₃), 19.0 (C(SiMe₃)₂), 34.7 (CH₂); ²⁹Si NMR (79 MHz, C₆D₆, δ) –0.8 (SiCl₂), 4.0 (SiMe₃), 6.8 (SiMe₃), 42.1 (SiCl); Anal. Calc. for C₃₂H₈₀Cl₄Si₁₁: C, 41.97; H, 8.81. Found C, 42.10; H, 8.91%.

3.8. Reaction of germadisilaallene **4** with carbon tetrachloride

A mixture of carbon tetrachloride (5 ml) and benzene (10 ml) was added to germadisilaallene **4** (50 mg, 0.061 mmol) in a Schlenk flask equipped with a magnetic stirrer bar. After the mixture was stirred at room temperature for 30 min in the dark, removal of the volatiles in vacuo gave dichlorosilane **16** (47.2 mg, 0.106 mmol) in 87% yield [12].

3.9. Reaction of trisilaallene **1** with methyl iodide

In a sealed NMR tube, trisilaallene **1** (48 mg, 0.062 mmol) and iodomethane (25 mg, 0.176 mmol) were placed. Into the tube, benzene-*d*₆ was added and the NMR tube was sealed. After the mixture was kept at room temperature overnight, removal of the volatiles in vacuo gave iodo(methyl)silane **17** (57 mg, 0.112 mmol) in 90% yield [12].

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 600067, 600068, 600069, 600070, and 600071 for compounds **5a**, **5b**, **5c**, **6b**, and **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.063.

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