

Review

Bonding and structure of disilenes and related unsaturated group-14 element compounds

By Mitsuo KIRA^{*1,†}

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Abstract: Structure and properties of silicon-silicon doubly bonded compounds (disilenes) are shown to be remarkably different from those of alkenes. X-Ray structural analysis of a series of acyclic tetrakis(trialkylsilyl)disilenes has shown that the geometry of these disilenes is quite flexible, and planar, twist or *trans*-bent depending on the bulkiness and shape of the trialkylsilyl substituents. Thermal and photochemical interconversion between a cyclotetrasilene and the corresponding bicyclo[1.1.0]tetrasilane occurs via either 1,2-silyl migration or a concerted electrocyclic reaction depending on the ring substituents without intermediacy of the corresponding tetrasila-1,3-diene. Theoretical and spectroscopic studies of a stable spiropentasiladiene have revealed a unique feature of the spiroconjugation in this system. Starting with a stable dialkylsilylene, a number of elaborated disilenes including trisilaallene and its germanium congeners are synthesized. Unlike carbon allenes, the trisilaallene has remarkably bent and fluxional geometry, suggesting the importance of the π - σ^* orbital mixing. 14-Electron three-coordinate disilene-palladium complexes are found to have much stronger π -complex character than related 16-electron tetracoordinate complexes.

Keywords: silicon, germanium, double bond, synthesis, structure, theoretical calculations

Introduction

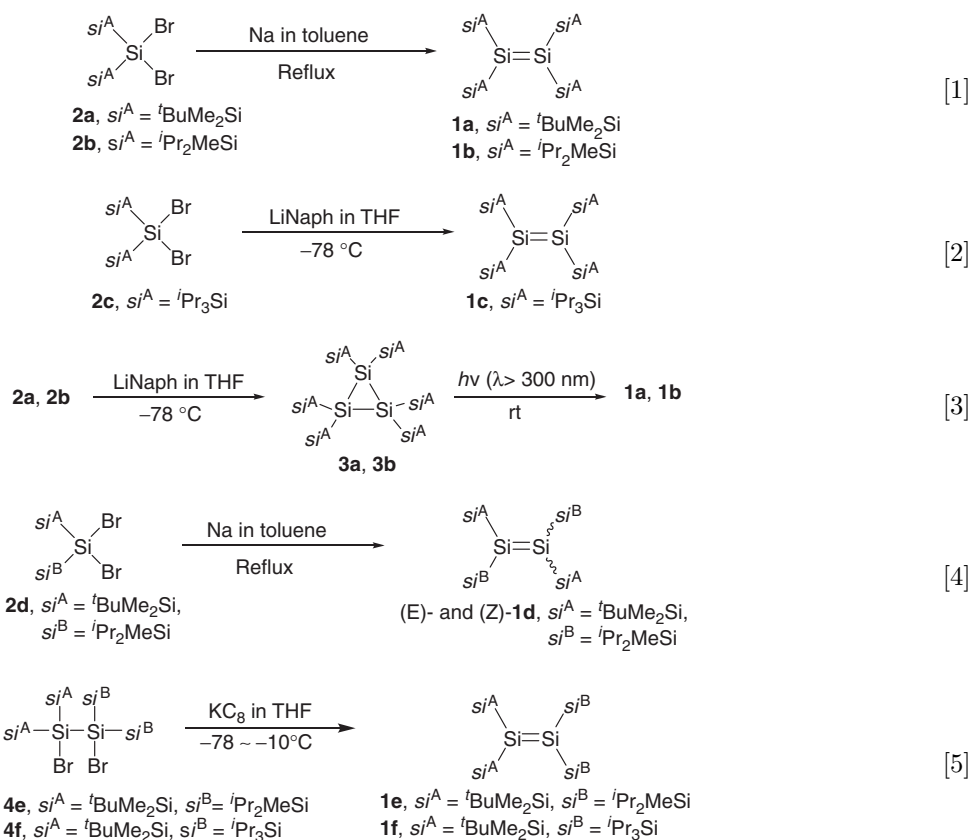
So-called “double-bond rule” states that unlike carbon, the elements with a valence principal quantum number of three or greater do not effectively participate in π bonding.¹⁾ In accord with this rule, multiply bonded compounds of silicon had been believed to be non-existent or highly unstable until the first synthesis of stable disilene ($\text{Mes}_2\text{Si}=\text{SiMe}_2$; Mes = 2,4,5-trimethylphenyl)²⁾ and silaethene [$\text{Ad}(\text{Me}_3\text{SiO})\text{C}=\text{Si}(\text{SiMe}_3)_2$, Ad = 1-adamantyl]³⁾ were achieved by West *et al.* and Brook *et al.*, respectively, in 1981. Since then, much attention has been focused on various aspects of the chemistry of silicon unsaturated compounds including their bonding and structure, spectroscopic properties, reactivity, and application to the synthesis of novel

types of organosilicon compounds; a number of reviews have been published for their experimental⁴⁾ and theoretical aspects.⁵⁾ Now studies in this research field look heading for two directions, in addition to further synthetic development of new types of unsaturated silicon compounds; (1) application of their unique electronic properties towards the material science and (2) restructuring of a general theory of bonding and structure of heavy main group elements including silicon. The former is just its beginning but the latter looks biding its time. Actually, thanks to interplay between theory and experiment, remarkable distinctions of bonding and structure between silicon unsaturated compounds and their carbon congeners have been accumulated.

We have created a number of thermally stable silicon unsaturated compounds with Si=Si, Si=C, and Si=X (X = S, Se, Te, etc.) bonds and elucidated their unique properties since 1994.⁶⁾ In this account, the results are discussed with a focus on the differences in bonding and structure between carbon and silicon unsaturated compounds and their origin.

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1. Stable acyclic tetrakis(trialkylsilyl)disilenes

1.1. Synthesis. A series of acyclic tetrakis(trialkylsilyl)disilenes **1a–1c** are synthesized typically using reductive coupling of the corresponding bis(trialkylsilyl)dibromosilanes **2a–2c** (eqs [1]–[3]).^{7),8a)} The products of the reduction of **2a–2c** are dependent on the reaction conditions and steric bulkiness of the substituents. For example, the reduction of **2a** and **2b** with sodium in toluene affords disilenes **1a** and **1b** but the reduction of **2a** and **2b** with lithium naphthalenide (LiNaph) in THF at $-78\text{ }^\circ\text{C}$ gives the corresponding cyclotrisilanes **3a** and **3b**, which are further converted to **1a** and **1b** by the photolysis using a high-pressure Hg lamp (eq [3]).^{8a)} Disilene **1c** with bulkier silyl substituents is obtained directly by the reduction of **2c** using LiNaph/THF at the low temperature (eq [2]), while **1c** is not formed by reducing **2c** with Na in toluene.^{8a)} (*E*)- and (*Z*)-tetrakis(trialkylsilyl)disilenes, (*E*)-**1d** and (*Z*)-**1d**, are synthesized using a similar reductive coupling of dibromosilane **2d** with two different silyl substituents (eq [4]). The reduction

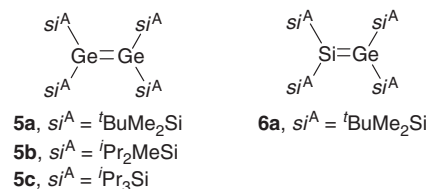


Chart 1.

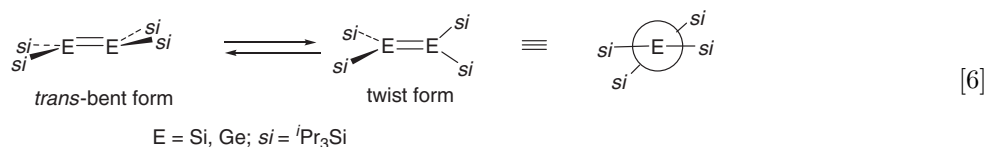
affords a ca. 2:1 mixture of (*E*)- and (*Z*)-**1d** in solution but pure (*E*)-**1d** is obtained as single crystals by recrystallization of the mixture from hexane.^{8b)} $\text{A}_2\text{Si}=\text{SiB}_2$ type disilenes **1e** and **1f** are synthesized by the reduction of the corresponding tetrasilyl-1,2-dibromodisilanes **4e** and **4f**, respectively (eq [5]).^{8c)} Digermenes **5a–5c**^{8d),8e)} and germsilene **6a**^{8e)} are synthesized using similar reduction methods (Chart 1).

All these dimetallenes are thermally stable and can be handled in a glove box at ambient temperatures but are highly air- and moisture-sensitive in solution and in the solid state.

Table 1. UV-vis absorption maxima and absorptivity (in parentheses)^{a)} and ²⁹Si NMR chemical shifts for unsaturated silicon nuclei of tetrasilyldimetalenes

Compound	λ_{\max}/nm ($\epsilon/10^3$)	$\delta(^{29}\text{Si})/\text{ppm}$	Ref.
1a	290 (2.5), 360 (1.9), 420 (2.8)	142.1	8a
1b	293 (2.1), 357 (1.4), 412 (7.6)	144.5	8a
1c	296 (5.4), 370 (2.4), 425 (1.9), 480 (2.2)	154.5	8a
1d	— ^{b)}	141.9	8b
1e	293 (2.6), 359 (2.0), 413 (5.0)	132.4, 156.6	8c
1f	— ^{b)}	142.0, 152.7	8c
8	290 (8.2), 375 (2.0), 612 (1.3)	155.5	10
5a	266 (5.3), 295 (2.6), 362 (3.1), 421 (7.0)	—	8d, 8e
5b	361 (2.9), 413 (16.1)	—	8d
5c	277 (3.5), 367 (2.2), 432 (2.1), 472 (2.0)	—	8d
6a	359 (2.0), 413 (5.0)	144.0	8e

a) In hexane or 3-methylpentane. b) Not measured.



1.2. Spectroscopic properties. Tetrasilyldisilenes **1a–1c** are yellow to light orange in the solid state, and expectedly, the UV-vis spectra of disilenes **1a–1c** measured in KBr pellets are similar to each other with the band maxima at around 420 nm.^{8a)} In Table 1 are summarized the UV-vis absorption spectra of acyclic tetrasilyldimetalenes **1a–1f** and related dimetalenes at room temperature in a hydrocarbon solvent. Interesting spectral features of tetrasilyldimetalenes are found in the table: (1) Whereas these tetrasilyldisilenes have no aromatic substituents, the longest absorption maxima are found at a wavelength longer than 400 nm. Sterically less hindered dimetalenes **1b**, **1e**, **5a**, **5b**, and **6a** show the longest wavelength band maxima at around 420 nm with relatively large absorptivity ($\epsilon > 5000$); the λ_{\max} is even similar to that for $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (**7**).⁹⁾ The band assignable to the $\pi \rightarrow \pi^*$ transition of normal or less distorted dimetalenes appears at much longer wavelengths than those of alkenes, which are usually transparent in the wavelength region longer than 300 nm. It is suggested that the energy splitting between π and π^* MOs in these dimetalenes is similar irrespective of the central elements that are silicon or germanium, while the splitting is much smaller than that in alkenes. (2) Absorption spectral behavior of disilene **1c** and

digermene **5c** with relatively bulky silyl substituents is rather unusual. In solution, **1c** and **5c** show the longest wavelength band at much longer wavelength of 480 and 472 nm with relatively smaller absorptivity than those for dimetalenes categorized as (1). The spectra of **1c** and **5c** with bulky tri(isopropyl)silyl substituents are remarkably temperature dependent with increasing absorptivity of the 420 nm bands at lower temperatures. The behavior may be explained by the temperature-dependent equilibrium between *trans*-bent and twist forms in solution as shown in eq [6], where the twist form is supposed to have a smaller π - π^* splitting energy than that for the *trans*-bent form. The explanation is consistent with the UV-vis spectral characteristics of a disilene with bulkier di(*t*-butyl)methylsilyl substituents **8** [$(^t\text{Bu}_2\text{MeSi})_2\text{Si}=\text{Si}(\text{SiMe}^t\text{Bu}_2)_2$] reported by Sekiguchi *et al.*¹⁰⁾ that has remarkably twisted geometry around the Si=Si bond (twist angle, 55°); the longest wavelength band of **8** shows the maximum at 620 nm with the absorptivity of 1300. (3) Disilene **1a** and digermene **5a** with intermediate bulkiness of silyl substituents show the longest wavelength band at around 420 nm but with smaller absorptivity and broad bandwidth than those of dimetalenes categorized as (1). The bands sharpened remarkably at lower temperatures. The less remarkable temperature

Table 2. Structural parameters for tetrasilyldimetalenes and related dimetalenes

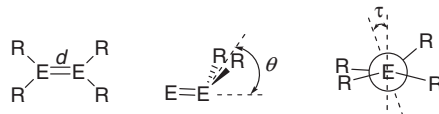


Chart 2.

Compound	Si=Si distance $d/\text{\AA}$	Bent angle ^a θ/deg	Twist angle ^b τ/deg	Ref.
<i>Disilenes</i>				
1a	2.202(1)	0.1	8.9	8a
1b	2.228(2)	5.4	0.0	8a
1c	2.251(1)	10.2	0.0	8a
1d	2.196(3)	0.65	0.0	8b
1e^c	2.198(1), 2.1942(8)	0.0, 0.0	8.97, 11.73	8c
1f	2.2011(9)	0.0	27.95	8c
Mes ₂ Si=SiMes ₂ (7)	2.143	12, 14	3	13
7 /C ₇ H ₈	2.160	18	12	9
7 /THF	2.146	0	13	13
(^t Bu ₂ MeSi) ₂ Si=Si(SiMeBu ^t) ₂ (8)	2.2598(18)	~0	54.5	10
<i>Digermenes</i>				
5a	2.2703	0.3	7.47	8e
5b^c	2.268(1), 2.266(1)	5.9, 7.1	0.0, 0.0	8d
5c	2.298(1)	16.4	0.0	8d
Mes ₂ Ge=GeMes ₂ (9)	2.2856(8)	33.4	2.9	14
Tip ₂ Ge=GeTip ₂ (10)	2.213(1)	12.3	13.7	15
<i>Germasilenes</i>				
6a	2.2208(8)	0.6	7.51	8e
Mes ₂ Ge=Si(SiBu ^t) ₂ (11)	2.2769(8)	0	24.67	16

a) Bent angle (θ) in deg is defined as the angle between E-E bond and R-E-R plane. b) Twist angle (τ) in deg is defined as the angle between two R-E-R planes. c) Two crystallographically independent molecules show slightly different structural parameters.

dependence of the spectra of **1a** and **5a** than that of **1c** and **5c** may not be compatible with the equilibrium shown in eq [6] but suggest significant fluctuation around their *trans*-bent geometry.

²⁹Si NMR chemical shifts for the unsaturated silicon nuclei of acyclic tetrasilyldisilenes are shown in Table 1. The chemical shifts are in the range of 136–157 ppm, which are much lower field shifted than those for typical alkyl- and aryl-substituted disilenes; δ 63.7 for **7**⁹⁾ and δ 90.3 for (*E*)-^tBu(Mes)Si=Si(Mes)^tBu (**9**).⁹⁾ The origin of remarkable lower field shift of ²⁹Si resonances for tetrasilyldisilenes has been studied by the analysis of their chemical shift tensors in the solid state.¹¹⁾ Extremely large deshielding along one principal axis for disilenes **1b** and **1c** is related to their low $\sigma \rightarrow \pi^*$ transition energies; the values δ_{11} , δ_{22} , and δ_{33} are found to be 414, 114, and

–100 for **1b**; 412, 149, and –69 for **1c**, while 181, 31, and –22 for **7**.¹¹⁾

1.3. Molecular structures determined by X-ray crystallography. Structural parameters of dimetalenes **1a–1f**, **5a–5c**, and **6a** determined by X-ray crystallography are listed in Table 2, together with those of related dimetalenes reported by other groups; E=E bond distances (d) in \AA , bent angles (θ) in deg defined as the angle between E-E bond and R-E-R plane, and twist angle (τ) in deg, the angle between two R-E-R planes for R₂E=ER₂. The geometry around E=E double bond of all the dimetalenes is diversified depending on the trialkylsilyl substituents. Disilenes **1b** and **1c** and digermenes **5b** and **5d** are bent without twisting with the bend angles in the order **1b** < **5b** < **1c** < **5c**. Disilenes **1a**, **1e**, **1f**, and **7**, digermene **5a**, and

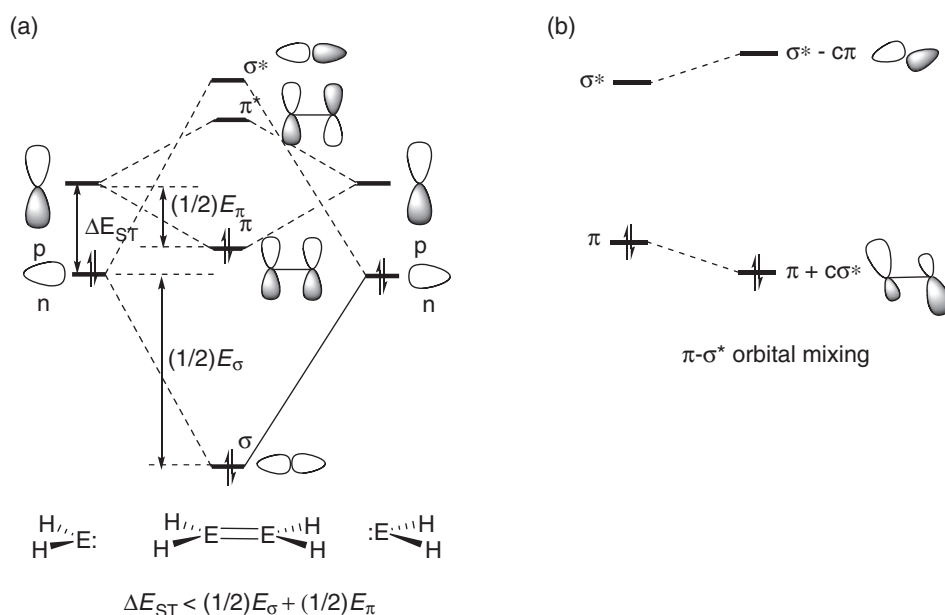


Fig. 1. (a) Schematic MO representation of the formation of dimetallenes by dimerization of the corresponding metallylene. (b) Stabilization of the bonding π MO level by its secondary interaction with a higher-lying σ^* MO orbital.

germasilene **6a** are twisted without bending with the twist angles in the order **5a~6a** < **1a** < **1e** \ll **1f** \ll **7**. Disilene (*E*)-**1d** has highest planarity among dimetallenes shown in the table probably because the two different substituents in (*E*)-**1d** can be arranged so as to minimize the steric strain between the substituents at the planar geometry. Dimetallenes having isopropyl-substituted silyl groups favor *trans*-bent geometry in the solid state, while dimetallenes with *t*-butyl-substituted silyl groups tend to twist. Because electronic effects of all trialkylsilyl groups studied here are similar to each other, the distortion modes seem to be determined mainly by the effects of the size and shape of the substituents. Theoretical studies have revealed that the geometry around an E=E bond of simple dimetallenes like H₂E=EH₂ and Me₂E=EMe₂ is *trans*-bent,⁵⁾ while (H₃Si)₂E=E(SiH₃)₂¹²⁾ features planar geometry. The geometrical preference of tetrakis(trialkylsilyl)dimetallenes found experimentally suggest that the geometry is very flexible and the major factor determining the preference is the steric effects. In the next section, electronic models for the distortion around E=E bond and important factors controlling the geometrical preference are discussed more in detail.

1.4. Theoretical models for distortion modes around double bond. Theoretical studies have shown that optimized geometry of heavy group-14

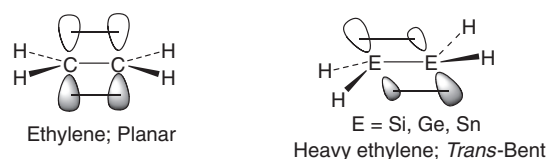


Chart 3.

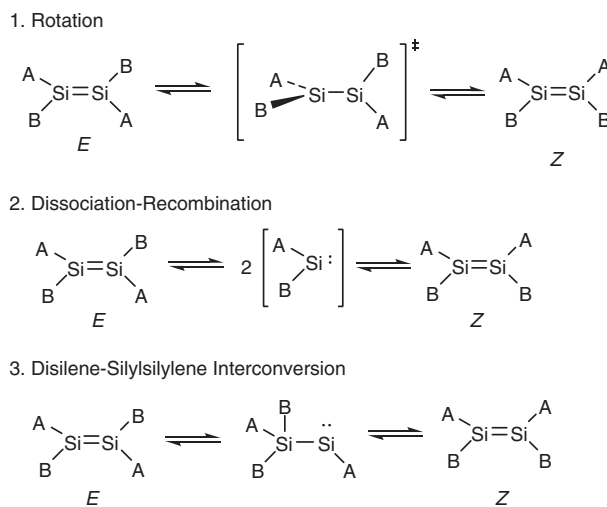
ethylenes (dimetallenes; H₂M=MH₂, M = Si, Ge, and Sn) is *trans*-bent in contrast to planar ethylene (E = C) (Chart 3).⁵⁾

Bonding nature of the E=E double bonds is outlined using the CGMT (Carter-Goddard-Malrieu-Trinquier) model¹⁷⁾ as follows: When two EH₂ groups having an in-plane *n* orbital and an out-of-plane *p*_π orbital approach to each other to form a planar E=E double bond, an overlap between the two *n* orbitals form σ and σ^* orbitals and an overlap between the two *p*_π orbitals forms π and π^* orbitals, where the orbital energy levels of *p*_π, *n*, σ , σ^* , π and π^* are given by $\varepsilon_{p\pi}$, ε_n , ε_σ , ε_{σ^*} , ε_π and ε_{π^*} , respectively (Fig. 1a). The *n* orbital is usually lower in energy than *p*_π orbital with $\Delta\varepsilon_{pn}$, which is often replaced by ΔE_{ST} (singlet-triplet energy difference, $E_T - E_S$) in the CGMT model.^{17c)} The σ - σ^* and π - π^* splitting energies are reasonably assumed to be the σ and π bond energies E_σ and E_π , respectively; $E_\sigma = \varepsilon_{\sigma^*} - \varepsilon_\sigma$,

and $E_\pi = \varepsilon_{\pi^*} - \varepsilon_\pi$. The condition of forming a double bond is $\varepsilon_\pi < \varepsilon_{\sigma^*}$ and $\varepsilon_\sigma < \varepsilon_{\pi^*}$, i.e. $(-1/2)E_{\sigma+\pi} < \Delta E_{\text{ST}} < (1/2)E_{\sigma+\pi}$, where $E_{\sigma+\pi} = E_\sigma + E_\pi$. We can expect using PMO (perturbation molecular orbital) theory¹⁸⁾ that when ε_{σ^*} and ε_π are close to each other, effective π - σ^* orbital mixing will lead to significant *trans*-bending (Fig. 1b). The CGMT model predicts that a dimetallene would favor the *trans*-bent geometry if $(1/4)E_{\sigma+\pi} < \Delta E_{\text{ST}} < (1/2)E_{\sigma+\pi}$. Bond dissociation energy (BDE) of the heavy ethylene to two heavy methylenes (H_2E): is estimated to be $\text{BDE} = E_{\sigma+\pi} - 2\Delta E_{\text{ST}}$. The BDE will decrease with increasing ΔE_{ST} , if $E_{\sigma+\pi}$ is constant.

Although the CGMT model has reasonable grounds and is useful to understand the distinct differences in bonding between planar ethylene and *trans*-bent heavy ethylenes, the model should be utilized with several cautions.¹⁹⁾ (1) Because both ΔE_{ST} and $E_{\sigma+\pi}$ are variables depending on element E, the proximity of the π and σ^* levels is determined by the two factors, ΔE_{ST} and $E_{\sigma+\pi}$. Although large ΔE_{ST} values of R_2E : are often taken to be an indication of the *trans*-bent geometry of the $\text{H}_2\text{E}=\text{EH}_2$, the rule cannot be extended to the discussion between different elements; E_σ and E_π for heavier group-14 elements are much smaller than those for carbon. In accord with the CGMT model, tetrasilyldimetallenes $[(\text{H}_3\text{Si})_2\text{E}=\text{E}(\text{SiH}_3)_2]$, E = Si, Ge, and Sn) whose component silylene $(\text{H}_3\text{Si})_2\text{E}$: has smaller ΔE_{ST} than the corresponding H_2E : are shown theoretically to be planar around the E=E bond.¹²⁾ However, although the ΔE_{ST} of F_2C : ($57.6 \text{ kcal mol}^{-1}$)²⁰⁾ is even much larger than that of GeH_2 ($23.1 \text{ kcal mol}^{-1}$),²¹⁾ $\text{F}_2\text{C}=\text{CF}_2$ is a planar molecule, while $\text{H}_2\text{Ge}=\text{GeH}_2$ is *trans*-bent. (2) In the CGMT model, the σ^* orbital participating in the π - σ^* orbital mixing is only $\sigma^*(\text{E}-\text{E})$ orbital, whereas other valence σ^* orbitals in $\text{H}_2\text{E}=\text{EH}_2$, i.e. four $\sigma^*(\text{E}-\text{H})$ orbitals, may contribute to the π - σ^* orbital mixing for the distortion modes of the geometry. A theoretical study has shown that mono-anion of disilene $[\text{H}_2\text{Si}=\text{SiH}_2]^{-\bullet}$ adopts *trans*- and *cis*-bent geometries due to significant mixing between the π^* (SOMO) and a $\sigma^*(\text{Si}-\text{H})$ orbital with proper symmetry representation.^{19c),22)} (3) Applicability of the CGMT model to heavy ethylenes with bulky substituents is less satisfactory because the steric effects are the controlling factor determining the geometry as discussed in the previous section.

Recently, the author has discussed the distortion modes, *trans*- and *cis*-bending and twisting of



Scheme 1. Three possible pathways of *E,Z*-isomerization of disilenes.

$\text{H}_2\text{E}=\text{EH}_2$ (E = C, Si, and Ge) and their anions in detail in terms of a more generalized π - σ^* orbital mixing model using the PMO theory.^{19c)} The model predicts that *trans*- and *cis*-bent geometries of neutral dimetallenes may be more stable than the planar geometry but with very small energy gains, while these geometries should be largely stabilized with significant bent angles and stabilization energies in dimetallene anions. Twisting around the double bonds of dimetallenes may lower the energy of the anions. The above prediction is verified by the potential energy surface calculations at the B3LYP/6-311++G(3df,3pd) level.^{19c)} It should be noted that the π - σ^* orbital mixing underlie the bonding and structure issues of unsaturated compounds of heavy main-group elements, even though the substituent steric effects are often the controlling factor of the geometry as shown in Section 1.3.

1.5. *E,Z*- and formal dyotropic isomerization of disilenes. Thermal *E,Z*-isomerization of alkenes is known to occur through the rotation around the C=C bond but usually with very high activation energy of 40–60 kcal mol^{-1} . On the other hand, at least three distinct pathways should be taken into account for the *E,Z*-isomerization of heavier alkenes as shown in Scheme 1; rotation around Si-Si bond (path 1), dissociation-recombination (path 2), and disilene-silylsilylene interconversion (path 3). While paths 1 and 2 give rise to only *E,Z*-isomerization, path 3 may produce an $\text{A}_2\text{Si}=\text{SiB}_2$ -type isomer in addition.

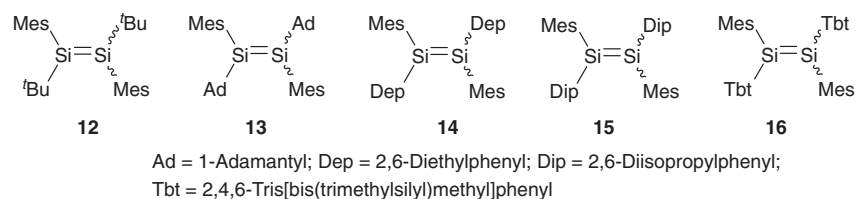
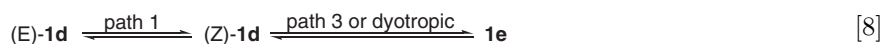
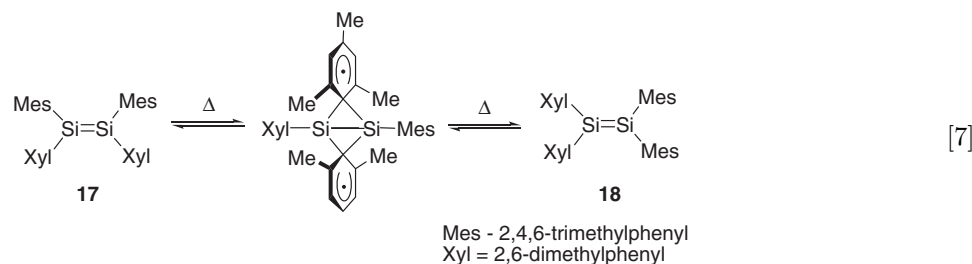


Chart 4.



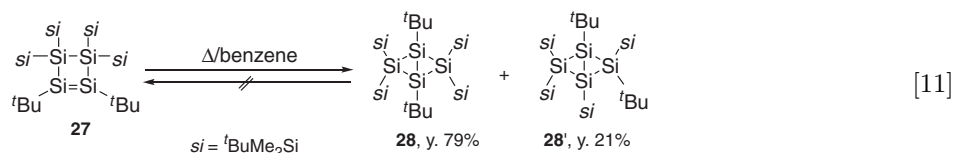
Among disilenes shown in Chart 4, **12–15** are shown to undergo $Z \rightarrow E$ isomerization via path 1 with the activation free energy (ΔG^\ddagger at 350 K) of ca. 26.2–27.4 kcal mol⁻¹.^{4a)} On the other hand, the $Z \rightarrow E$ isomerization of disilene **16** was confirmed to occur via path 2 with the ΔG^\ddagger value of 22.7 kcal mol⁻¹ at 350 K.^{4a),23)} The dissociation of **16** into a pair of the corresponding silylene is evidenced by trapping of the silylene with alkenes and acetylenes. Easy Si=Si double bond cleavage of **16** into the corresponding silylenes suggests that the BDE of the Si=Si bond in **16** is reduced by large steric hindrance among bulky substituents, in addition to the intrinsically small BDE of disilene as expected by the CGMT model (Section 1.4).

Related isomerization of (Z)-ABSi=SiAB-type tetraaryldisilenes into A₂Si=SiB₂-type disilenes and its reverse reaction has been proposed by West *et al.* to occur via a concerted dyotropic mechanism²⁴⁾ rather than path 3.²⁵⁾ Typically, disilene **17** is shown to isomerize to **18** at around 70 °C probably via a bicyclobutane-like transition state or intermediate (eq [7]). The activation free energy for the dyotropic rearrangement is estimated to be even smaller than that for the E, Z -isomerization via path 1 but the activation entropy is much larger in accord with the highly restricted transition state; for **18**→**17**, $\Delta H^\ddagger = 15 \pm 2$ kcal mol⁻¹ and $\Delta S^\ddagger = -36 \pm 4$ cal mol⁻¹ K⁻¹.^{25b)}

The ²⁹SiNMR spectrum of a ca. 2:1 mixture of (E)-**1d** and (Z)-**1d** is remarkably dependent on temperature (eq [8]). Two pairs of signals due to

^tBuMe₂Si and ⁱPr₂MeSi groups are observed independently at 273 K, but coalesce at around 303 K to give two sharp singlets at higher temperature than 330 K, indicating that facile isomerization between (E)- and (Z)-**1d** occurs even at room temperature with the ΔG^\ddagger value of ca. 15.3 kcal mol⁻¹ ($Z \rightarrow E$) at 303 K.^{8b)} Two ²⁹Si signals due to a small amount of contaminated A₂Si=SiB₂ type isomer **1e** is observed to remain sharp in the temperature range of 273–310 K, indicating that a dyotropic or path 3 rearrangement does not participate in the E, Z -isomerization. Because no dissociation of the tetrasilyldisilenes into the corresponding silylenes is observed, the E, Z -isomerization is concluded to occur via the rotation around the Si-Si bond (path 1). The activation free energy for the E, Z -isomerization of **1d** is 10 kcal mol⁻¹ smaller than those of disilenes **12–15**, probably because of effective σ - π conjugation at the twisted transition state of the former.

When pure **1e** is kept at 283 K for 7 days, an equilibrium was established with the ratio of (E)-**1d**, (Z)-**1d**, and **1e** = 1:0.47:0.67 (eq [8]).^{8b),8c)} The activation free energy for the rearrangement from **1e** to (Z)- or (E)-**1d** at 283 K is 17.4 kcal mol⁻¹, which is ca. 2 kcal mol⁻¹ larger than that for the E, Z -isomerization and 7.7 kcal mol⁻¹ smaller than those for the dyotropic rearrangement of tetraaryldisilenes reported by West *et al.*²⁵⁾ A disilene-silylsilylene rearrangement may not be excluded for the formal dyotropic rearrangement between **1e** and **1d**, because of the high 1,2-migratory aptitude of silyl groups.



Cyclotetrasilene **27** having *t*-butyl groups at unsaturated silicon atoms is thermally less stable than the corresponding bicyclotetrasilanes **28** and **28'** (eq [11]). Thus, heating **27** in benzene affords irreversibly a mixture of **28** and **28'**, which are produced via concerted skeletal isomerization and 1,2-silyl migration, respectively (eq [11]).³³ During the isomerization, no evidence is obtained for the intermediary formation of the corresponding 1,3-tetrasiladiene. Irradiation ($\lambda > 420$ nm) of **27** at low temperature gives **28'** quantitatively (eq [12]).³³ Thermal isomerization of **27** to **28** is regarded to be complementary to the concerted isomerization observed among C_4H_6 isomers, because direct electrocyclic isomerization between bicyclobutane and cyclobutene is hard to be observed in the carbon systems.

2.3. Spiropentasiladiene. Spiropentadiene constitutes one of the smallest spiroconjugation systems and has attracted much attention theoretically;³⁴ the two perpendicularly arranged anti-bonding π^* orbitals of spiropentadiene with D_{2d} symmetry interact to each other to split into two π^* orbitals [$(\pi_1^* + \pi_2^*)$ and $(\pi_1^* - \pi_2^*)$] with different energy levels, while the two bonding π orbitals do not interact and remain degenerate (Fig. 2, left). The synthetic study of parent spiropentadiene **29a** and its 1,1'-dichloro substituted one **29b** has shown that they are thermally unstable and only detectable below -100°C by NMR spectroscopy (Chart 5).³⁵ During the reduction of **20** with KC_8 in THF at -78°C (Scheme 2), an interesting spiropentasiladiene **30**, a silicon congener of spiropentadiene, was isolated as a minor but thermally stable compound with mp $216\text{--}218^\circ\text{C}$.³⁶

The remarkable stability of spiropentasiladiene **30** is ascribed partly to much smaller strain energy (SE) of the silicon spiro-ring system than that of the carbon analog, in addition to the kinetic stability due

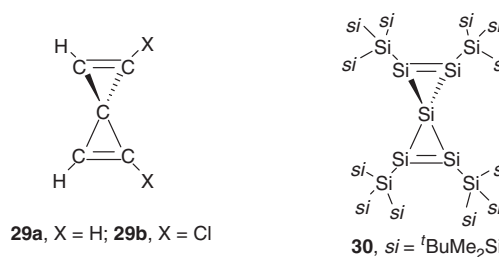


Chart 5.

to steric protection by four bulky tris(*t*-butyldimethylsilyl)silyl groups; the SE value of the parent spiropentasiladiene Si_5H_4 with D_{2d} symmetry (61.1 kcal mol $^{-1}$) calculated using homodesmotic reactions at the B3LYP/6-311++G(3df,2p)//B3LYP/6-31G(d) level is almost a half of that of the corresponding spiropentadiene C_5H_4 (D_{2d} , 114.2 kcal mol $^{-1}$).³⁶ The large SE difference between C_5H_4 and Si_5H_4 is ascribed to the difference in the effects of the introduction of E=E double bonds into a small ring system; although the SE of cyclopropene (55.5 kcal mol $^{-1}$) is almost twice of that of cyclopropane (25.8 kcal mol $^{-1}$), the SE of cyclotrisilene (34.6 kcal mol $^{-1}$) is even smaller than that of cyclotrisilane (35.4 kcal mol $^{-1}$), being in accord with the flexible nature of the Si=Si double bond.

Because **30** is a sole stable spiropentadiene system known among its group-14 congeners, **30** serves as a probe to verify the theoretical spiroconjugation model. The structure of spiropentasiladiene **30** determined by X-ray crystallography shows however that the ring skeleton has D_2 symmetry, where the two cyclopropene rings are not perpendicular to each other with the dihedral angle of 78.25° and the silicon atoms substituted at a cyclotrisilene ring are not coplanar with the ring plane.³⁶ The distortion of a spiropentadiene from D_{2d} to D_2 requires modification

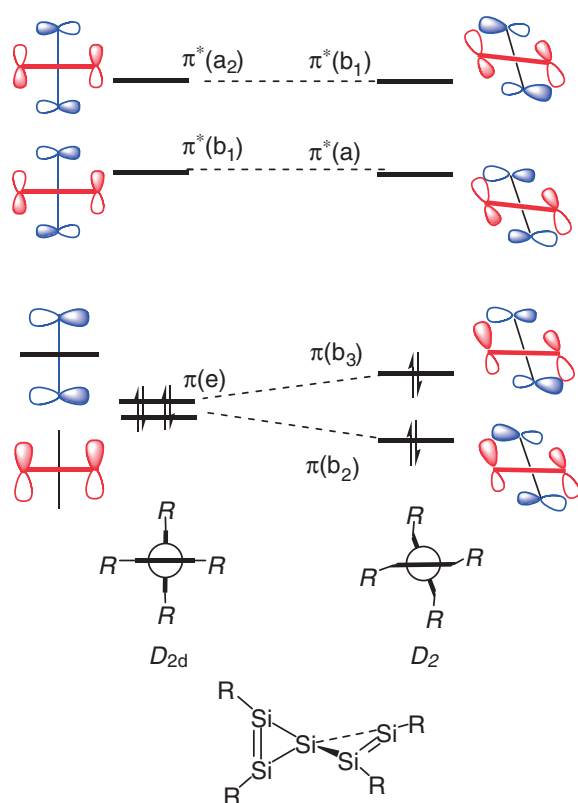


Fig. 2. Schematic MO diagram for spiroconjugation for D_{2d} (left) and D_2 spiropenta(sila)dienes (right).

of the previous theoretical model³⁴⁾ because through-space interaction between two bonding π orbitals is allowed in addition to that between π^* orbitals, as shown in Fig. 2. The modified spiroconjugation model for a D_2 spirocyclic system can be tested by comparing the UV-vis spectrum of **30** with that of reference cyclotrisilene **21**. The UV-vis spectrum of **30** shows four $\pi \rightarrow \pi^*$ bands at $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3$) 560 (2.53), 500 (3.64), 428 (11.7), 383 (18.1), while only one $\pi \rightarrow \pi^*$ band is observed at $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3$) 482 (2.64) for **21** (Fig. 3). The spectral pattern with four distinct $\pi \rightarrow \pi^*$ bands as well as the red shift of the longest wavelength band of **30** is not compatible with the simple model for a D_{2d} spirocyclic system but the modified model for a D_2 spirocyclic system.

3. Trisilaallene and its germanium congeners

In 1999, we synthesized the first isolable dialkylsilylene **31** by the reduction of the corresponding dibromosilane **33**, which was obtained by the reaction of 1,4-dilithiobutane **32**³⁷⁾ with dichlorosilane followed by the bromination, using KC_8 in a good yield (eq [13]).³⁸⁾ Because silylene **31** is divalent

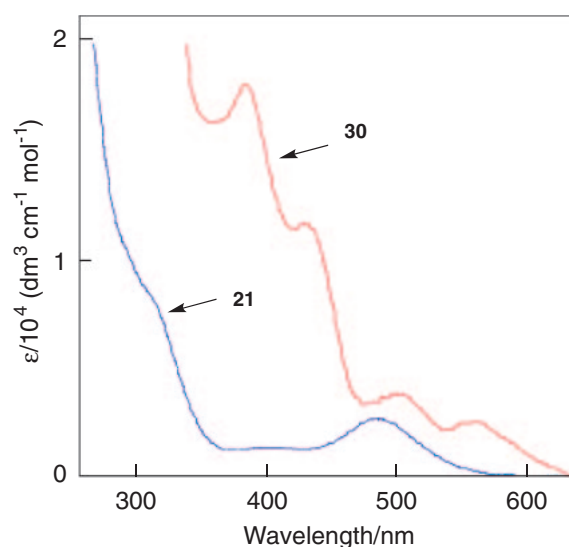


Fig. 3. UV-vis spectra of spiropentasiladiene **30** and cyclotrisilene **21** in hexane.

and highly reactive though it is sterically protected, versatile thermal and photochemical reactions of **31** have been observed.^{6a),39)}

The first compound with cumulative Si=Si double bonds, trisilaallene **34a**, was synthesized starting with stable silylene **31**.⁴⁰⁾ The insertion of silylene **31** into a Si-Cl bond of tetrachlorosilane followed by the reduction with KC_8 affords trisilaallene **34a** as dark-green crystals (eq [14]). Related heavy allenes $\text{R}_2\text{E}=\text{E}'=\text{ER}_2$ (E, E' = Si and Ge) **34b–34d** are synthesized similarly (Chart 6).⁴¹⁾

These heavy allenes are all thermally stable and stored under inert atmosphere but their structural characteristics are remarkably different from those of carbon allenes that have a rigid linear C–C–C skeleton and two orthogonal C–C π bonds.^{19a),40),41)} The geometries of all the synthesized heavy allenes are not linear but bent with the $\text{E}^1\text{–E}^2\text{–E}^3$ bond angles of 122–137°. Typically, the Si=Si double bond distance and the SiSiSi bond angle of trisilaallene **34a** are 2.183(1) Å and 136.49(6)°, which are in good accord with the values calculated theoretically; they are 2.230 Å and 130.2° at the B3LYP/6-31G(d) level,⁴²⁾ and 2.230 Å and 135.7° at the BP86/TZVPP level.⁴³⁾ The optimized geometry of relatively small trisilaallenes, $\text{H}_2\text{Si}=\text{Si}=\text{SiH}_2$ and $\text{Me}_2\text{Si}=\text{Si}=\text{SiMe}_2$, is quite different with a very narrow bend angle of around 70–90° and a small twist angle between two R_2Si plane (R = H, Me)^{40),42),44)} from that of synthesized trisilaallene **34a**, and hence, the structural characteristics of the two types of heavy allenes should be discussed separately.

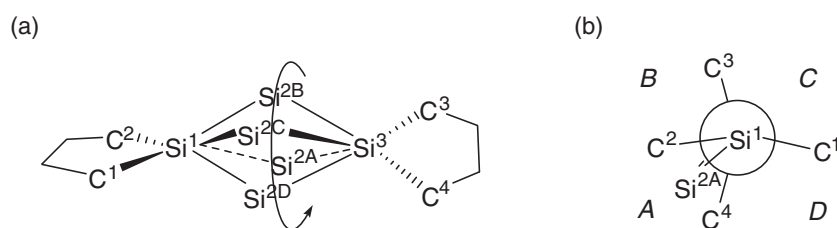
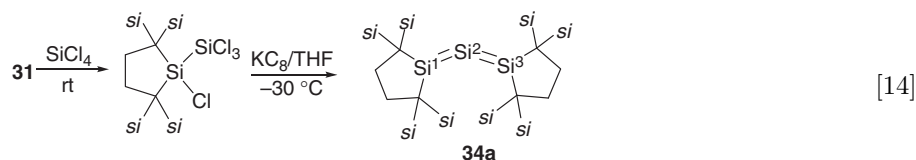
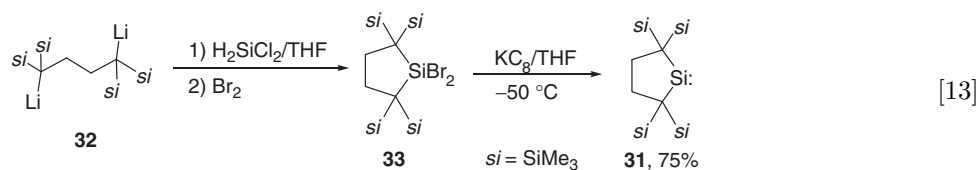


Fig. 4. (a) A schematic representation of bent and fluxional characteristics of trisilaallene skeleton of **34a** determined by X-ray crystallography. Central Si² atom is disordered with occupancy at four positions Si^{2A} to Si^{2D}. (b) A Newmann-like projection along axis through Si¹ and Si³ atoms. The Si^{2A} to Si^{2D} are located in quadrants A to D, respectively, which are separated by two silacyclopentane ring planes. The occupancy factor for Si^{2A} to Si^{2D} depends on temperature as well as the space area of the quadrant. The corresponding dihedral angles are 82.8, 92.1, 92.7, and 92.6° for Si^{2A} to Si^{2D} with the occupancy factors of 0.755, 0.175, 0.0, and 0.070 at -150 °C.

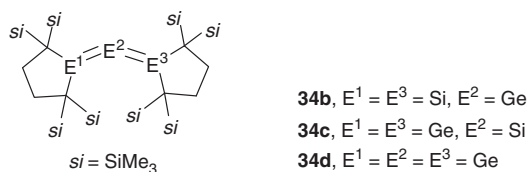


Chart 6.

The bent skeletons of **34a–34d** determined by X-ray crystallography are not rigid but fluxional both in the solid state and in solution (Fig. 4).

The origin of the bent and fluxional skeleton of heavy allenes is ascribed to the Jahn-Teller distortion¹⁸⁾ associated with the effective π - σ^* orbital mixing, as schematically shown in Fig. 4.^{19a)} The π - σ^* distortion (Section 1.4) is caused by the existence of a low-lying σ^* orbital in heavy allenes stemming from the hybridization defects in heavy main group elements (Fig. 5).^{5f),45)} A more detailed discussion for the π - σ^* distortion in heavy allenes is given in a full paper.^{19a)}

The ¹H, ¹³C, and ²⁹Si NMR spectra of **34a–34d** are very simple and show that eight SiMe₃ groups, four ring methylene groups, four ring quaternary carbon atoms, and two allenic terminal silicon atoms

(if they exist) are equivalent, indicating the fluxional nature of the bent allenic structure in solution. The ²⁹Si NMR chemical shifts of the allenic silicons for **34a** are δ 196.9 (terminal) and δ 157.0 (central), which are consistent with those calculated for Me₂Si=Si=SiMe₂ with the bent structure determined by X-ray crystallography using the GIAO method at the B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p) level (δ 205.5 and δ 161.2, respectively).⁴⁰⁾

The heavy allenes show at least two bands in the $\pi \rightarrow \pi^*$ band regions of disilenes and digermenes. The longest band maxima [λ_{\max} /nm (ϵ)] of **34a–34d** are remarkably red shifted from those of tetraalkyldisilenes (λ_{\max} = ca. 390 nm)⁴⁶⁾ and appear at around 584 (700), 599 (1100), 612 (3100), and 630 (5300), respectively, being indicative of significant conjugation between two double bonds of heavy allenes.

4. Other stable disilenes

4.1. Fused bicyclic disilene. Fused bicyclic disilene **35** is synthesized by the reduction of **36** with lithium in THF at room temperature.⁴⁷⁾ Formation of **35** from monocyclic precursor **36** suggests that initial reductive coupling product **37** is highly strained and undergoes facile formal dyotropic rearrangement (Section 1.5) to give **35** as shown in eq [15].

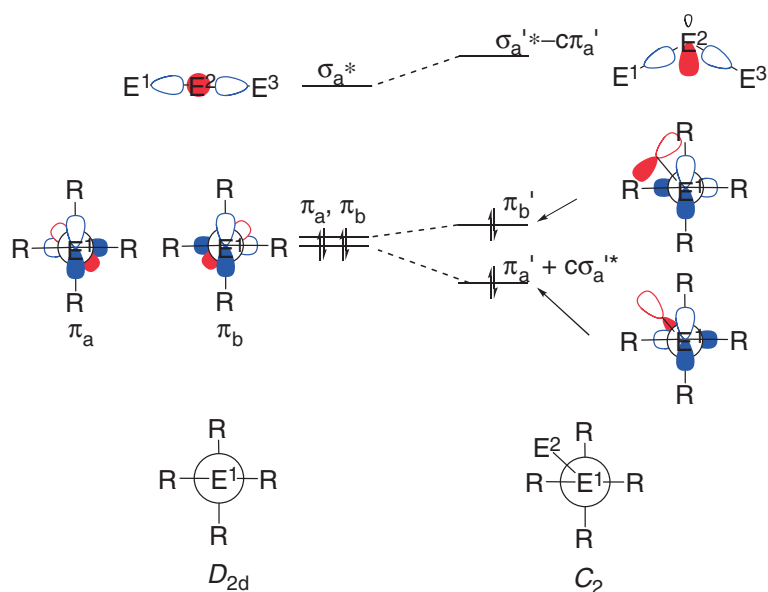
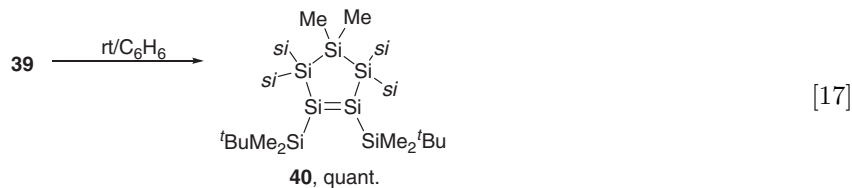
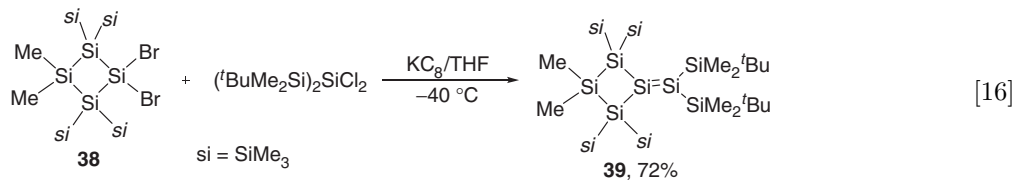
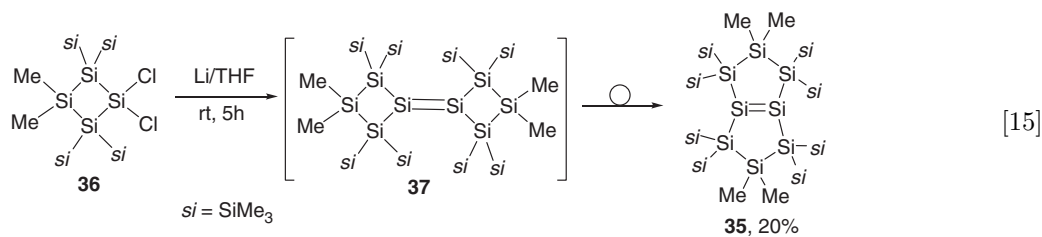
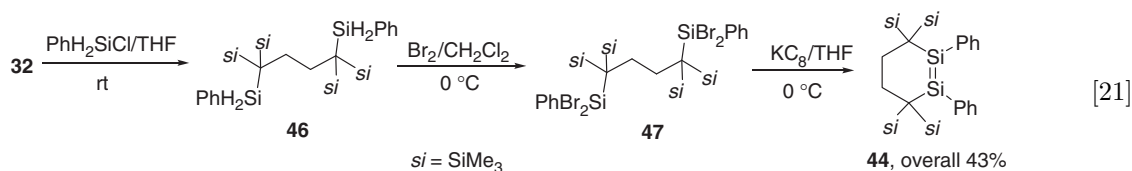
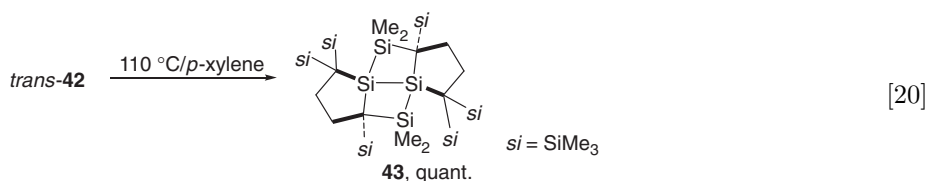
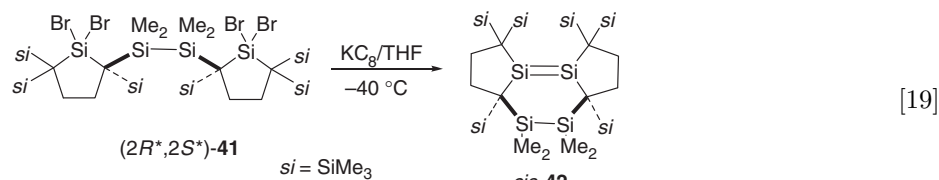
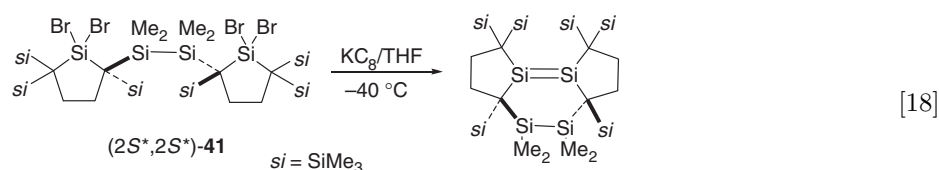


Fig. 5. Schematic π - σ^* orbital mixing diagram for the deformation of a linear D_{2d} allene to a bent C_2 allene. Degeneracy of π orbitals (π_a and π_b) in D_{2d} is removed by the deformation to C_2 allowing the interaction between π_a - σ_a^* interaction. The mixing coefficients c and c' are small positive numbers. Atomic orbitals on E^1 and E^3 and those on E^2 are shown in blue and red, respectively.



Although intermediate **37** is not detected during the reaction (eq [15]), the proposed pathway is supported by a study of a related reaction. Thus, a similar reaction of **38** with $(t\text{BuMe}_2\text{Si})_2\text{SiCl}_2$ at low temperature gives disilene **39** in a high yield (eq [16]). Disilene **39** isomerizes to cyclopentasilene **40** quantitatively at room temperature (eq [17]).⁴⁸⁾ Activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger)

for the first-order isomerization of **39** to **40** are determined to be $24.8 \pm 1.0 \text{ kcal mol}^{-1}$ and $+6.5 \pm 3.2 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively. The positive ΔS^\ddagger is not compatible with the dyotropic rearrangement through a restricted transition state, suggesting preferable disilene-silylsilylene interconversion via 1,2-silyl migration as discussed in Section 1.5.



Fused cyclic disilene **35** features topologically a partial structure of the Si(001) surface up to the third layer. The Si=Si double bond of **35**, whose distance is 2.180(3) Å, adopts rather unusually a slightly *cis*-bent geometry with the bent angle of 3.6°, while all other disilenes whose structures were determined by X-ray analysis are *trans*-bent, twist, or planar. However, because the disilene moiety in the reconstructed Si(001) surface is known to have unsymmetric and significantly *cis*-bent structure,⁴⁹⁾ fused bicyclic disilene **35** is not yet an ideal model for the silicon surface.

4.2. Fused tricyclic disilenes. Dimerization of a silylene to the corresponding disilene and its reverse reaction constitute an important pair of chemical processes in organosilicon chemistry. Tetramesitylsilylene **7**, the first stable silylene, was prepared by the dimerization of the corresponding silylene generated photochemically.²⁾ Disilene **16**²³⁾ and tetrakis(dialkylamino)disilene and a lattice-framework disilene designed by Sakamoto *et al.*⁵⁰⁾ dissociate into the corresponding two silylenes. Because dialkylsilylene **31** is sterically well protected and does not dimerize to the corresponding disilene either in solution or in the solid state, tethering two dialkylsilylene moieties may be possible to give a stable tethered bissilylene. However, the reduction of tetrabromides (2*S*^{*}, 2*S*^{*})-

41 and (2*R*^{*}, 2*S*^{*})-**41** with KC₈ affords unexpectedly fused tricyclic disilenes *trans*-**42** and *cis*-**42**, respectively (eqs [18] and [19]).⁵¹⁾

The geometry around the Si=Si bond in *trans*-**42** is highly distorted with a central twist-boat six-membered ring. The Si=Si bond length of *trans*-**42** (2.2687(7) Å) is much larger than those of usual stable disilenes (Table 2). The Si=Si bond in *trans*-**42** adopts significantly *trans*-bent and twisted geometry with bend angles of 32.9 and 30.9° and a twist angle of 42.5°. Distortion around the Si=Si bond in *cis*-**42** is relatively small with a boat six-membered ring; the Si=Si bond length, the bend angles, and the twist angle are 2.1767(6) Å, 3.9 and 12.4° at the two unsaturated Si atoms, and 3.9°, respectively.

Neither *cis*-**42** nor *trans*-**42** dissociates into the corresponding bissilylene upon heating at 100 °C or upon irradiation with a Xe lamp. Highly distorted *trans*-**42** undergoes unprecedented intramolecular [2_s+2_a] cycloaddition of the Si-Si single bond to the Si=Si double bond at 110 °C to give a tetracyclic compound **43** (eq [20]).

4.3. 1,2-Disilacyclohexene. A novel type of stable six-membered cyclic disilene **44**⁵²⁾ is synthesized as shown in eq [21] using a unique 1,4-dithiobutane **32** that was applied for the synthesis of stable dialkylsilylene **31** (Section 3).³⁷⁾

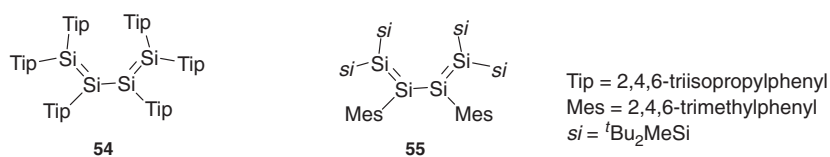
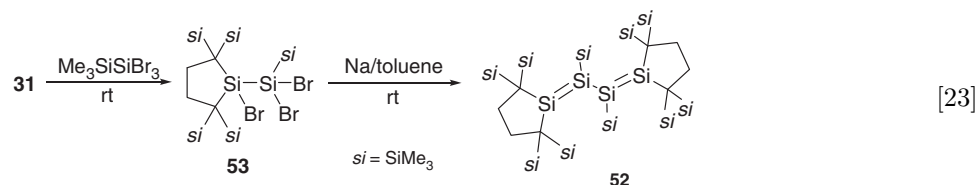
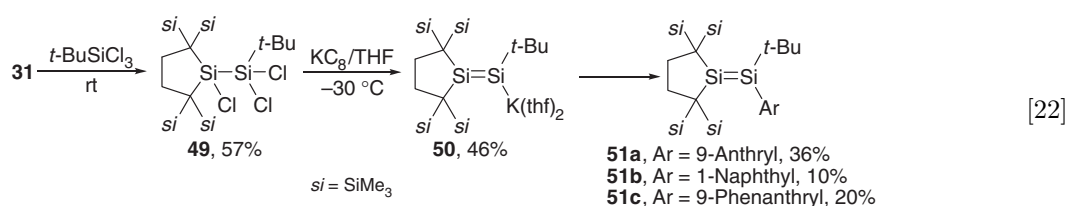


Chart 7.

The X-ray analysis shows that the Si=Si double bond distance of **44** is rather normal with 2.1595(9) Å. The geometry around the double bond is slightly *trans*-bent and the six-membered ring adopts a conformation between an ideal chair and an ideal half-chair, which are known as the most stable conformations in all-carbon cyclohexane and cyclohexene, respectively.

4.4. Aryltrialkyldisilenes. Stable aryldisilenes are usually substituted by two to four aromatic groups, and hence, are not suitable for defining the nature of the electronic interaction between a disilene π and an aromatic π system (π Si- π C interaction). Using stable dialkylsilylene **31** (Section 3)^{38,39} as a key precursor, the synthesis of monoaryl-trialkyldisilenes allowing elucidation of the mode and extent of the π Si- π C interaction has been achieved.⁵³ Prerequisite trialkyldisilene **50** is obtained as single crystals by the reaction of trichlorodisilane **49** with KC₈ in THF.⁵⁴ Disilenes **51a–51c** are synthesized by the reactions of **50** with the corresponding aryl bromides as air-sensitive colored crystals (eq [22]).

Molecular structures of disilenes **51a–51c** determined by X-ray analysis feature *trans*-bent geometry around the Si=Si double bond. The Si=Si bond lengths [2.1754(12), 2.1943(14), and 2.209(2) Å for **51a–51c**] are in the region of those for typical acyclic disilenes (Table 2). Disilene π (π Si) and aromatic π (π C) systems are almost perpendicular to each other with the dihedral angle of 88°, 83°, and 80° for **51a**, **51b**, and **51c**.

No appreciable π Si- π C conjugative interaction is observed in **51a–51c** because of the mutually perpendicular arrangement of the two π systems. However, anthryl-substituted disilene **51c** with low-lying π^* LUMO shows an unprecedented π Si \rightarrow π^* C intramolecular charge transfer (ICT) absorption bands at 520 nm (ϵ 420), suggesting the occurrence of the charge-transfer from a π Si donor to a π C acceptor system in certain circumstances.

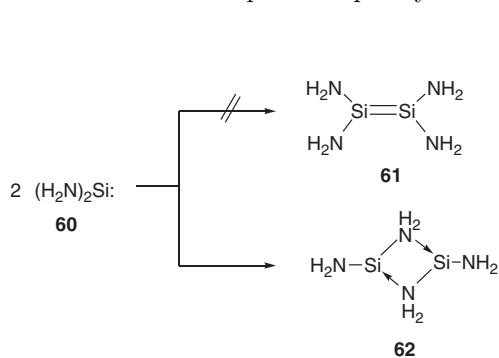
4.5. Tetrasiladiene-1,3-diene. As a conjugated siladiene, tetrasiladiene **52** is synthesized as air-sensitive red crystals in 13% yield by the reaction of silylene **31** with Me₃SiSiBr₃ giving tribromodisilane **53** followed by the reduction with sodium metal in toluene at room temperature (eq [23]).⁵⁵

The Si=Si double bond distances of **52** in a crystal are 2.1980(16) and 2.2168(16) Å and the central Si-Si single bond distance is 2.3400(15) Å. The tetrasiladiene skeleton of **52** is not planar but highly twisted with an anticlinal conformation (the Si1-Si2-Si3-Si4 dihedral angle = 122.56(7)°), while known tetrasiladiene-1,3-dienes **54**⁵⁶ and **55**^{54b} have a synclinal conformation (Chart 7).

The longest wavelength absorption maximum of **52** is observed at 510 nm (ϵ 1200) at 77 K in a 3-methylpentane glass matrix and assignable to a $\pi\rightarrow\pi^*$ transition band. The maximum is comparable to those of **54** (518 nm)⁵⁶ and **55** (531 nm)^{54b} even though no aromatic substituent is in **52**, suggesting significant conjugation between the two π (Si=Si) systems. The ²⁹Si NMR signals of central and

terminal unsaturated Si nuclei of **52** appear at δ 9.3 and δ 210.2. Thermolysis of **52** at 80 °C in benzene gives cyclotrisilene **56** and cyclic silene **57** in high yields (eq [24]). Similarly, photolysis of **52** using a filtered high-pressure mercury arc lamp ($\lambda > 390$ nm) in benzene affords **56** and silacycloheptatriene **58** (eq [25]). Because **57**^{38,57}) and **58**⁵⁸) are known as major products of the thermal and photochemical reactions of silylene **31** in benzene, respectively, the initial step of these reactions should be the cleavage of a Si=Si double bond of **52** into **59** and **31** (eq [26]). Preferential cleavage of the Si=Si double bond to the central Si-Si single bond is a straightforward indication of the smaller bond dissociation energy of the double bond than that of the single bond in **52** as predicted by the CGMT model (Section 1.4).

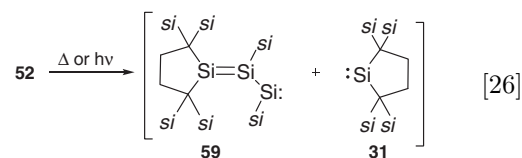
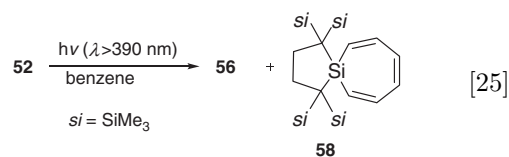
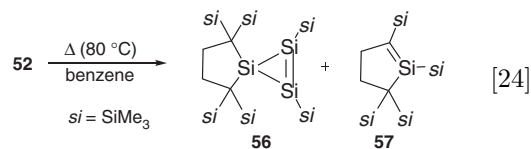
4.6. Tetraaminodisilenes. In accord with the CGMT model (Section 1.4), theoretical calculations have shown that dimerization of diaminosilylene ($(\text{H}_2\text{N})_2\text{Si}:$ (**60**) with high ΔE_{ST} [79.3 kcal mol⁻¹ at the B3LYP/6-311++G(3df,2p)//MP2/6-31G(d) level] does not form the corresponding disilene **61** but a four-membered cyclic bridged dimer **62** (Scheme 5).^{59,60} On the other hand, we have found that diaminosilylene **63** generated by the photolysis of silacyclopropene **64** is marginally stable in solution and dimerizes to the corresponding disilene-type dimer **65** at low temperature (eq [27]).⁶¹ The temperature dependent equilibrium between **63** and **65** is observable UV-vis spectroscopically.



Apparent conflict in the dimerization mode between theoretical diaminosilylene **60** and the experimental diaminosilylene **63** is ascribed to the dependence of the ΔE_{ST} value on the dihedral angle between an n orbital on N and vacant p_π orbital on Si in $(\text{R}_2\text{N})_2\text{Si}:$. The dihedral angle in silylene **63** is significantly increased by the steric effects of bulky isopropyl substituents, and hence, the ΔE_{ST} value is reduced to 54.3 kcal mol⁻¹; the bridged dimer of **63** is higher in energy by 16.0 kcal mol⁻¹ than the Si-Si bonded dimer **65**.⁶⁰ The geometry of tetraaminodisilene **65** calculated at the B3LYP/6-31G(d) level is very unusual with a dramatically long Si=Si distance of 2.472 Å, which is even longer than the Si-Si single bond (2.340 Å in $\text{Me}_3\text{SiSiMe}_3$); **65** is strongly pyramidalized around the silicon atoms with the bend angle of 42.6°.⁶⁰

5. Disilene transition metal complexes

The bonding of an alkene to a transition metal center in a complex is usually understood in terms of alkene-to-metal σ -donation and metal-to-alkene π -back donation, according to the Dewar-Chatt-Duncanson model.⁶² The geometry around C=C double bond depends significantly on the relative importance of σ -donation and π -back donation; the complexes are classified into π -complexes (I) having a major contribution of σ -donation and metallacycles (II) having dominant π -back donation (Chart 8).⁶³



The geometry around the alkene ligand in the π -complex is not very much different from that of the planar free alkene, while that in the metallacycle is significantly distorted and characterized by an elongated C¹–C² bond length (d) and a large bent-back angle (α) defined as the angle between the R¹–C¹–R² (or R³–C²–R⁴) plane and the C¹–C² bond (Chart 8, E = C). Ordinary alkene complexes have an intermediate character between π complex and metallacycle and often shown as a resonance between them. Hereafter, for descriptive purposes in this account, when the character of an alkene or disilene complex is not well known or is not needed to be considered, the structural formula is given as III with a dotted line between M and E=E bond (Chart 8).

It is an interesting issue how the geometry around Si=Si bond is modified when a disilene coordinates to a transition metal. When we started a study in this direction, however, knowledge about the structure of η^2 -disilene metal complexes had been

very limited. Among isolated mononuclear η^2 -disilene transition metal complexes **66a–66c**,⁶⁴⁾ **67a–67b**,^{64b)} and **68a–68b**⁶⁵⁾ (Chart 9), only the structure of tungsten complex **68a**^{65a)} with a character of metallacycle had been determined by X-ray crystallography. The structural issue of the disilene-metal complexes were first discussed theoretically by Sakaki *et al.*⁶⁶⁾ and Gordon *et al.*⁶⁷⁾ The *ab initio* MO calculations for (disilene)platinum complex **69a** show that **69a** features a large bent-back angle ($\alpha = \text{ca. } 25^\circ$), elongated Si–Si bond ($\Delta d = 0.124 \text{ \AA}$) and small Si–Si stretching force constant ($3.08 \text{ mdyn \AA}^{-1}$ for disilene, while $2.63 \text{ mdyn \AA}^{-1}$ for **69a**), and hence, **69a** is characterized as a metallacycle.⁶⁶⁾

Various four-coordinate 16-electron palladium and platinum complexes **70a–70d**⁶⁸⁾ with tetrakis(*t*-butyldimethylsilyl)disilene ligand (**1a**) are synthesized using the reactions of the corresponding dichlorobis(phosphine)metals **71a–71d** with 1,2-dilithiodisilane **72**⁶⁹⁾ (eq [28]).

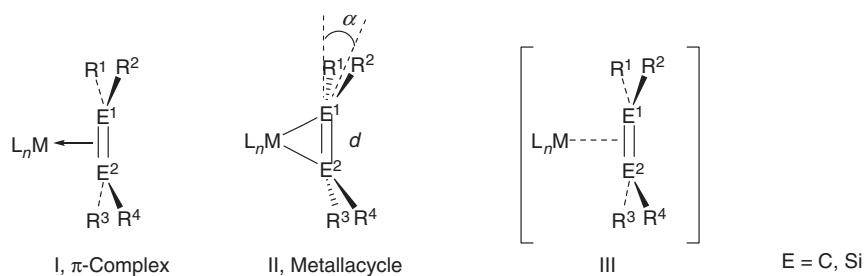


Chart 8.

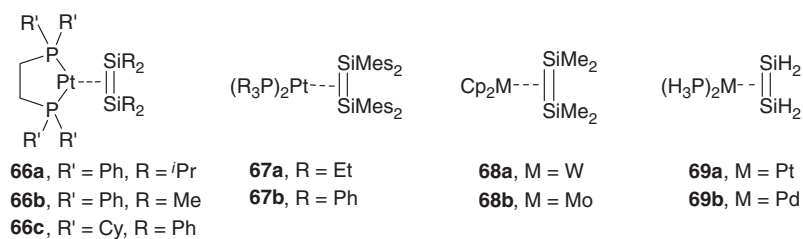
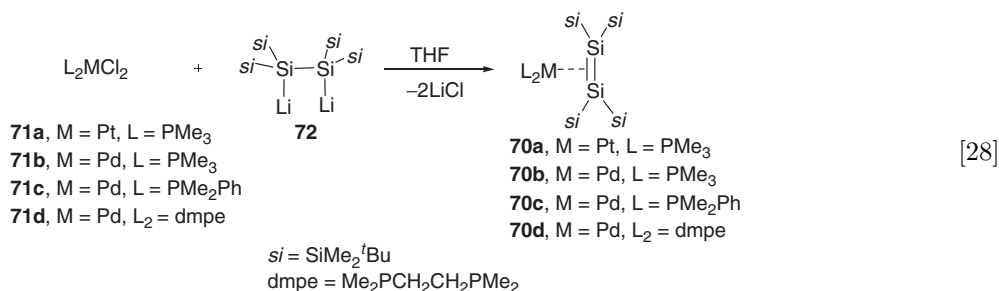
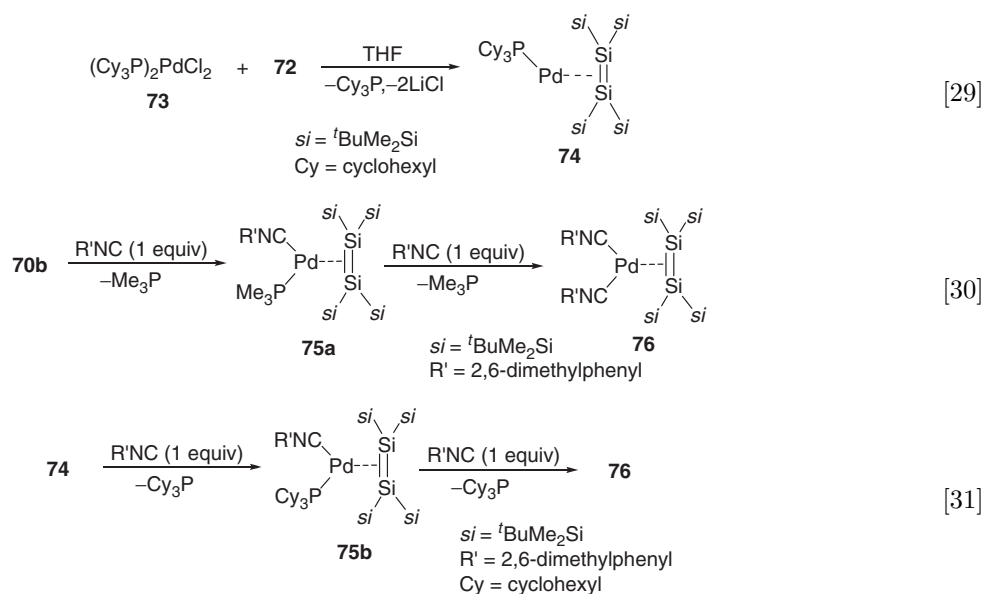


Chart 9.





The reaction of bis(tricyclohexylphosphine)palladium dichloride **73** bearing bulky tricyclohexylphosphine ligands with dilithiodisilane **72** gives rather unusual three-coordinate 14-electron disilene-palladium complex **74** (eq [29]).⁷⁰⁾

Related (disilene)palladium complexes with isocyanide ligands **75a**, **75b**, and **76** are synthesized by the reactions of **70b** and **74** with the corresponding isocyanide (eqs [30] and [31]) in high yields.^{68c)}

Recrystallization of (disilene)metal complexes **70a–70d**, **74**, **75b**, and **76** gives single crystals suitable for X-ray structural analysis. The geometrical characteristics of these complexes are summarized in Table 3.

If the Dewar-Chat-Duncanson model⁶²⁾ is applicable to disilene complexes, the bent-back angle α and bond elongation $\Delta d/d_0$ should decrease with increasing π -complex character of the disilene complexes. The α ($^\circ$) and $\Delta d/d_0$ (%) values for 16-electron Pt complex **70a** are 29.3 and 5.4 and those for Pd complex **70b** are 27.5 and 4.6, respectively. These values are the largest among disilene complexes shown in Table 3 and close to those observed for (disilene)tungsten complex **68a** ($\alpha = 30.2^\circ$ and $\Delta d/d_0 = 3.7\%$) and theoretical values for $(\text{H}_3\text{P})_2\text{M}(\text{Si}_2\text{H}_4)$ ($\text{M} = \text{Pt}$ and Pd),^{66b)} and hence, complexes **70a** and **70b** are characterized as metallacycles, while the π -complex character of **70b** seems slightly larger than that of **70a**. On the other hand, the α and $\Delta d/d_0$ values for 14-electron Pd complex **74** are much smaller than those of the 16-electron complexes.⁷⁰⁾ On this basis, complex **74** is regarded as the complex

having the largest π -complex character among the disilene complexes.

Using α and $\Delta d/d_0$ values, the π -complex character of complexes in Table 3 is evaluated to decrease in the following order: **74** > **76** > **75b** (av.) > **70c** > **70b~70d** > **70a**. The π -back donation in 14-electron disilene complex **74** is the smallest because one basic ligand on palladium is missing. Because π -accepting ability of ligands is expected to increase in the order, $\text{Me}_3\text{P} < \text{PhMe}_2\text{P} < \text{R'NC}$ on the basis of the basicity of the ligands, the π -back donation from the metal will increase in the order, **74** < **76** < **75b** < **70c** < **70b~70d**. Platinum has higher lying occupied d orbitals than palladium, and hence, the π -back donation from Pt would be larger than that from Pd (**70b** < **70a**). The inverse order of the π -back donation is parallel to the observed order of the π -complex character of the disilene complexes, as expected.

Structural parameters of model 14-electron (disilene)palladium complex [**77**, $(\text{Me}_3\text{P})\text{Pd}((\text{H}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiH}_3)_2)$] and 16-electron (disilene)palladium complex [**78**, $(\text{Me}_3\text{P})_2\text{Pd}((\text{H}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiH}_3)_2)$] calculated at the B3LYP/6-31G* for H, C, Si, and P and Lanl2DZ for Pd level⁷⁰⁾ are shown in Chart 11. The unsymmetrical (T-shaped) structure observed for **74** is well reproduced by the optimized unsymmetrical structure (**77U**), while the P–Pd–Si¹ angle for **77U** (114.3°) is significantly smaller than that observed for **74** (128.9°), probably due to the steric effects of bulky trialkylsilyl substituents in the latter.⁷⁰⁾ Unsymmetrical complex **77U** is only

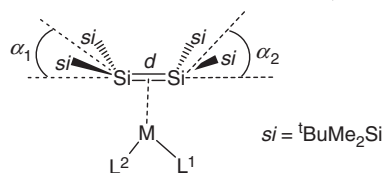
Table 3. Comparison of structural parameters of various (disilene)palladium complexes^a

Chart 10.

Complex ^b	$d^c/\text{\AA}$	$\Delta d/d_0^d$ (%)	α_1 and $\alpha_2^e/^\circ$	$\delta(^{29}\text{Si})^f$
70a , M = Pt, $L^1 = L^2 = \text{PMe}_3$	2.322(2)	5.4	29.3	-79.7
70b , M = Pd, $L^1 = L^2 = \text{PMe}_3$	2.3027(8)	5.2	27.2	-46.5
70c , M = Pd, $L^1 = L^2 = \text{PMe}_2\text{Ph}$	2.2952(13)	4.2	14.4, 26.8 (av 20.6)	-44.8
70d , M = Pd, $L^1L^2 = \text{dmpe}$	2.3180(8)	4.2	27.3	-51.9
75b , M = Pd, $L^1 = \text{R}'\text{NC}$, $L^2 = \text{PCy}_3^g$	2.2861(11)		5.2, 20.6	-39.4, -60.4
	2.2967(11)		3.0, 36.5	
	av 2.291(6)	av 4.0	(av 16.3)	
76 , M = Pd, $L^1 = L^2 = \text{R}'\text{NC}$	2.289(2)	4.0	9.5, 8.9 (av 9.2)	-41.2
74 , M = Pd, $L^1 = \text{PCy}_3$, $L^2 = \text{none}$	2.273(1)	3.2	9.7, 4.4 (av 7.0)	+65.3

a) ref. 68c. b) Cy = Cyclohexyl, dmpe = 1,2-(dimethylphosphino)ethane, R' = 2,6-dimethylphenyl. c) d is the Si=Si distance in complex in \AA . d) $d_0 = d$ for **1a** (2.202(1) \AA); see Table 2. $\Delta d/d_0$ (%) = $(d \text{ for complex} - d_0) \times 100/d_0$. e) Bend angles α_1 and α_2 are defined as angles between the Si=Si bond axis and $s_2\text{Si}$ planes that are *trans* to ligands L^1 and L^2 , respectively. If the complex is symmetric, only one α is shown. f) ^{29}Si NMR chemical shift for unsaturated silicon nuclei. g) Two crystallographically independent molecules are in an asymmetric unit.

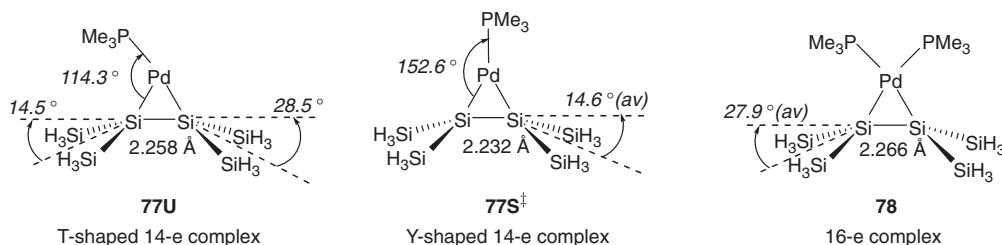


Chart 11.

2.9 kcal mol⁻¹ more stable than symmetrical (Y-shaped) complex **77S**[†] that is found as a transition structure. Due to the intrinsic electron-deficient nature of the central metal of a 14-electron complex, π -back-bonding is much less effective in complex **77** than 16-electron complex **78**.

A new 14-electron three-coordinated (disilene)-palladium complex, **79**, is synthesized by the reaction of cyclic disilene **44** (eq [21]) with $(\text{Cy}_3\text{P})_2\text{Pd}$ (eq [32]).⁵²⁾ Complex **79** is characterized as a Y-shaped tricoordinate complex with roughly symmet-

ric coordination of the phosphine [the two P-Pd-Si angles in **79** are 142.66(2) and 151.48(2)°]. The θ (°) and $\Delta d/d_0$ (%) values for **79** are 6.9 (average) and 1.9, which are both smaller than those for T-shaped **74** (Table 3), being indicative of larger π -complex character of the former. While the substituents around Si=Si bond are different between **74** and **79**, the results support the theoretical prediction that, in a 14-electron three-coordinated disilene complex, Y-shaped complex has larger π -complex character than the corresponding T-shaped complex.

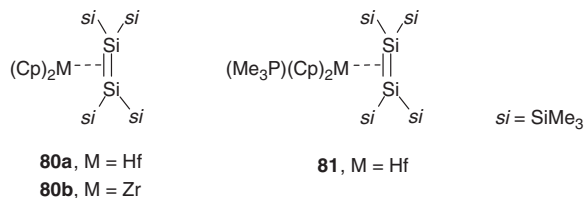
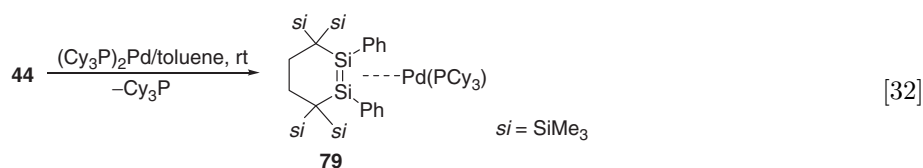


Chart 12.

The ^{29}Si NMR resonance of 16-electron palladium complex **70b–70d** is considerably higher field shifted than the corresponding free disilene (**1a**); $\Delta\delta_{\text{Si}}$ [$\delta_{\text{Si}}(\text{free disilene}) - \delta_{\text{Si}}(\text{complex})$] values for **70b** and **70c** are 188.9 and 186.9. On the other hand, the ^{29}Si chemical shift for 14-electron complex **74** is $\delta +65.3$ with $\Delta\delta_{\text{Si}}$ value of 76.8 (Table 3). The remarkably lower field ^{29}Si chemical shift of **74** would be another indication of its large π -complex character, in view of the difference in the ^{29}Si NMR resonances between hexakis(trialkylsilyl)cyclotrisilanes ($\delta -174$ – -149)⁷¹⁾ and free disilene **1a** ($\delta +142.1$).^{8a)} The ^{29}Si NMR chemical shift for **79** is $\delta 40.2$, which is even higher than that for complex **74** but the $\Delta\delta_{\text{Si}}$ value for **79** (60.7) is significantly smaller than the $\Delta\delta_{\text{Si}}$ value for **74**, which is consistent with the larger π -complex character of **79** estimated by the structural parameters. Recently, Marschner *et al.* have reported more large difference in the ^{29}Si NMR chemical shifts between disilene group-4 metal complexes **80** and **81** (Chart 12) with $\delta 132.8$ for **80a** and $\delta -135.7$ and $\delta -159.7$ for **81**, suggesting remarkable variation in the bonding between disilene and metal.⁷²⁾

Concluding remarks

The chemistry of silicon multiply bonded compounds has rapidly evolved in these three decades. In addition to those discussed in this account, we have extended our studies to $\text{Si}=\text{C}$ (silatriafulvenes⁷³⁾ and silaketeneimines⁷⁴⁾ and $\text{Si}=\text{X}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$ ⁷⁵⁾ and NR ⁷⁶⁾ compounds. Many silicon unsaturated compounds with novel types of bonding and structure including silabenzene,⁷⁷⁾ disilaacetylene,⁷⁸⁾ tetrasilacyclobutadiene,⁷⁹⁾ and silanone⁸⁰⁾ have been brought forth by other research groups. Their structural characteristics have been found often to be quite

unique and far from the analogical extension of those of the carbon congeners.

The origin of the remarkable difference in the bonding and structure between carbon and heavier group-14 element compounds is usually ascribed to the less effective hybridization between s and p orbitals (hybridization defect) in the latter, in association with the fact that the difference in the radii between 2s and 2p orbitals of carbon is exceptionally small compared with that between valence ns and np orbitals of the heavier main group elements.^{5f),45)} Although there is no doubt that the hybridization defect principle underlies the unusual properties of the heavier group-14 element compounds, it is hard to say currently that the principle is connected straightforwardly or logically to the unusual properties. As shown in this article, the π - σ^* orbital mixing may be one of convincing rationales or concepts intervening between the hybridization defect and the unusual properties. Discovering and evaluating new such concepts will lead to construct a systematic and useful structural theory of heavier main-group elements.

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Profile

Mitsuo Kira was born in Higashiosaka City, Osaka in 1943. He graduated from Kyoto University, Faculty of Engineering in 1967 and started his research carrier at the laboratory of Prof. Makoto Kumada. After moving to Tohoku University, Faculty of Science, he received his D. Sc. degree from Tohoku University in 1974 under the guidance of Prof. Hideki Sakurai. He was appointed research associate, associate professor, and then full professor at Tohoku University during 1970–2007. He was an Alexander von Humboldt Research Fellow in the group of Prof. Hans Bock, Frankfurt University, Germany during 1977–1978 and a team leader at Photodynamics Research Center, Sendai, The Institute of Physical and Chemical Research (RIKEN) during 1990–1998. After retiring from Tohoku University in 2007, he has held guest professorships in Tohoku University, Open University in Japan, and Key Laboratory of Organosilicon Chemistry and Material Technology of Chinese Ministry of Education, Hangzhou Normal University, China. His research interests include the chemistry of silicon and germanium compounds, physical organic chemistry, and organic photochemistry with particular focus on structure and reactivity of silicon unsaturated compounds including silylenes and disilenes, oligo- and polysilanes, hypercoordinate silicon compounds, and giant organosilicon compounds. He has been the recipient of The Chemical Society of Japan Award (2005), Wacker Silicone Award (2005), Japanese Medal of Honor with Purple Ribbon (2007), The Society of Silicon Chemistry, Japan Award (2009), and F. S. Kipping Award from the American Chemical Society (2012) and was elected Fellow of The Chemical Society of Japan (2008).

