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SYNTHESIS OF 1,2-DIALKYNYLDISILANES INCORPORATED IN 10-MEMBERED-RING SYSTEM

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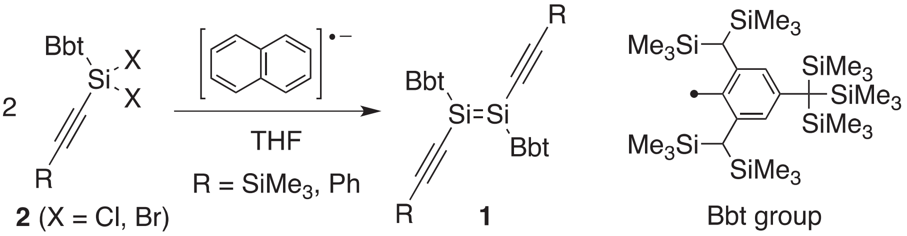
Abstract – The reduction of a bis(dichloroethynylsilane) bridged by *o*-xylylene by lithium naphthalenide afforded *trans*- and *cis*-isomers of novel 10-membered-cyclic disilanes. Their structures were characterized by X-ray crystallographic analysis, showing the strain around the C≡C bonds and the close distances between two ethynylene moieties.

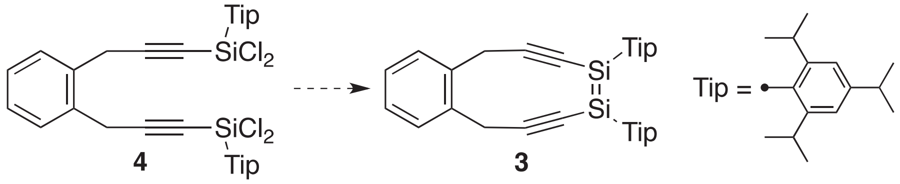
Dedicated to Dr. Professor Isao Kuwajima, Professor emeritus of Tokyo Institute of Technology on the occasion of his 77th birthday

INTRODUCTION

Disilenes are silicon–silicon double-bond compounds, the first example of which was reported by West *et al*. in 1981.[1] Since then, a number of disilenes that are kinetically stabilized by bulky substituents have been reported.[2] Recently, several π-conjugated systems between the Si=Si unit and the connected aryl groups have been reported, which exhibited optically and electrochemically unique properties.[3] From the viewpoint of elucidation of the π-conjugation between the Si=Si and C≡C units, we have succeeded in the synthesis and isolation of the first stable silicon analogues of (*E*)-enediyne, (*E*)-1,2-dialkynyldisilenes **1**, by the reductive coupling of the corresponding dihalosilanes **2** (Scheme 1).[4] The experimental and theoretical results indicated that the Si=Si unit conjugated with two alkynyl groups. On the other hand, (*Z*)-isomers are expected to show through-space interaction between two alkynyl groups in addition to the through-bonds interaction observed similarly in the (*E*)-isomers, resulting in the different electronic properties from those of (*E*)-isomers. However, the generation of the (*Z*)-1,2-dialkynyldisilenes could not be observed under those synthetic conditions. In order to synthesize the (*Z*)-isomers selectively, we attempted the introduction of *o*-xylylene bridge between two ethynyl units leading to the synthesis of (*Z*)-1,2-dialkynyldisilene **3** (Scheme 2).



Scheme 1

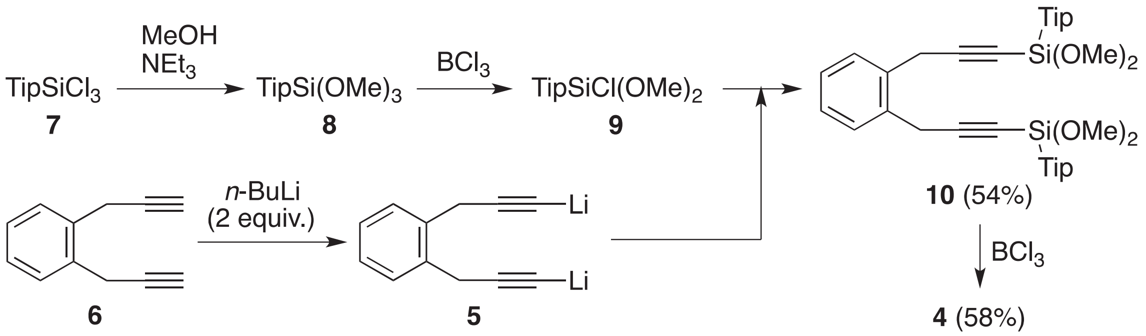


Scheme 2

RESULTS AND DISCUSSION

For the synthesis of disilenes, the reduction of dihalosilanes is known as one of the efficient methods.[2] Actually, those methods were applicable toward the synthesis of **1**, where the reduction of dichloro- or dibromosilanes **2** by lithium naphthalenide gave **1** in moderated yields. Accordingly, the bis(dichlorosilane) **4** was designed as the precursor of (*Z*)-dialkynyldisilene **3** (Scheme 2).

Bis(dichlorosilane) **4** was synthesized as shown in Scheme 3. At first, we attempted the reaction of dilithio compound **5**,[5] which was prepared by the treatment of **6**[6] with *n*-butyllithium, with $TipSiCl_3$ **7**.[7] Although the formation of **4** was indicated by the results of ^1H NMR measurement, the isolation of **4** from this reaction mixture was difficult due to its high sensitivity toward moisture. The attempted reaction of $TipSi(OMe)_3$ **8**, which was prepared by the treatment of **7** with methanol in the presence of triethylamine, with **5** was unsuccessful leading to the recovery of the starting material. Partial chlorination of **8** by boron trichloride was found to give $TipSiCl(OMe)_2$ **9** as a main product along with ca. 10% of starting material **8** and $TipSiCl_2(OMe)$. The reaction of this mixture with **5** afforded bis(dimethoxysilane) **10** in 54% yield. Compound **10** had enough stability to be handled in the air and was purified by HPLC and recrystallization to be isolated. Following chlorination of **10** proceeded almost quantitatively to give **4** in 58% isolated yield (after recrystallization). Compound **4** was characterized by NMR spectroscopy together with elemental analysis, and the structure of **4** was finally determined by X-ray crystallographic analysis (Figure 1). The two $TipSi(Cl_2)C{\equiv}C–$ moieties were situated at opposite sides each other in the crystalline state.



Scheme 3

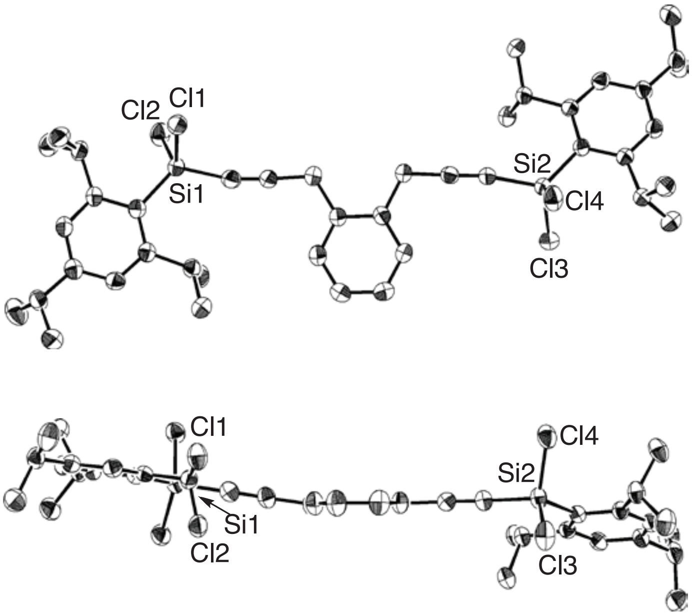
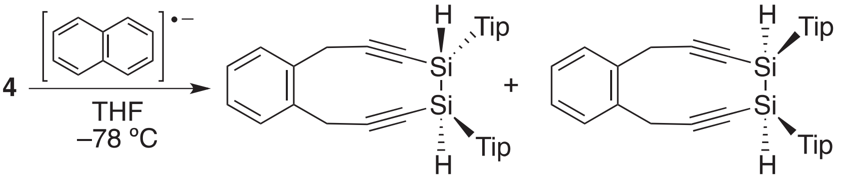


Figure 1. Thermal ellipsoid plots of compound **4** (50% probability) from front (a) and side (b). Hydrogen atoms were omitted for clarity.

The reduction of **4** was examined by using lithium naphthalenide under several conditions (various concentrations and ways of adding substrates). However, each reaction afforded a complicated mixture, the ^{29}Si NMR spectra of which showed no signal characteristic of a disilene in low field region.[2] HPLC analysis of the mixture suggested that the main component should be oligomeric materials. Finally, the 10-membered-cyclic products, *trans*- and *cis*-**11**, were isolated from the mixture in low yields. The yield of **11** was up to 11% by the method of simultaneous addition of **4** and lithium naphthalenide. On the contrary to our expectation, the chlorine atoms on the silicon atoms were fully replaced by the hydrogen atoms, which were probably derived from solvent and/or benzylic protons of **4**.



	trans-**11**	*cis*-**11**
13 mM	3%	trace
1.3 mM	3%	6%
adding simultaneously	6%	5%

Scheme 4

The structures of *trans*- and *cis*-**11** were shown in Figure 2, and the selected bond lengths and angles were summarized in Figure 3 together with the theoretically optimized structures for real molecules **11** and model compound **12** (Chart 1) bearing hydrogen atoms instead of Tip groups for comparison. The optimized structures calculated at M06-2X/6-31G(d) level showed good agreement with the observed ones, and their details were described later. In both cases of *trans*- and *cis*-**11**, the bridging *o*-xylylene units were found to flip toward C≡CSiSiC≡C cores. This trend was reproduced by the optimized structures of **11** and **12**. In *cis*-isomer **11**, interestingly, the *o*-xylylene moiety flipped toward the same side from C≡CSiSiC≡C core as two Tip groups probably due to the more condensed packing in the crystalline state. In the gas-phase calculations at M06-2X/6-31G(d) level, the energy difference between two configurations, *cis*-**11a** and *cis*-**11b** (Chart 1) was 0.0 kcal/mol. In the ^{1}H NMR of *trans*-**11**, the signal assignable to the Si–H was observed as a singlet, suggesting their free flipping in solution at room temperature.

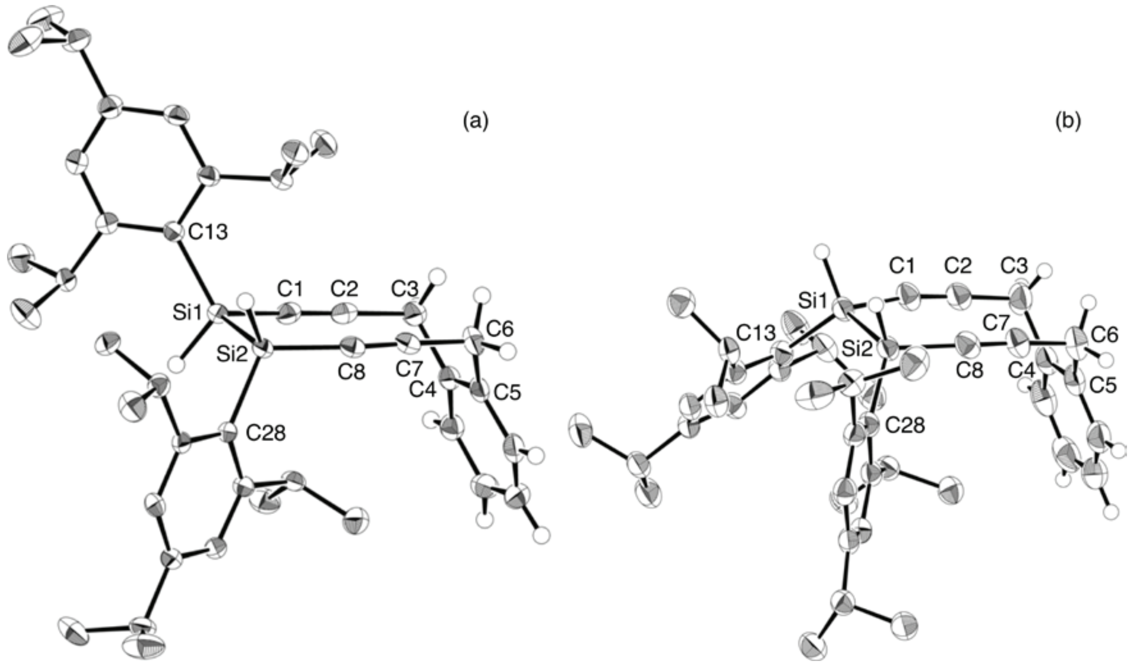
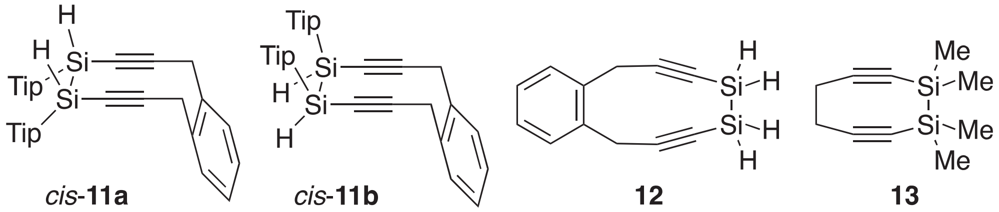


Figure 2. Thermal ellipsoid plots of *trans*-**11** (a) and *cis*-**11** (b) (50% probability). Hydrogen atoms on the Tip groups were omitted for clarity.

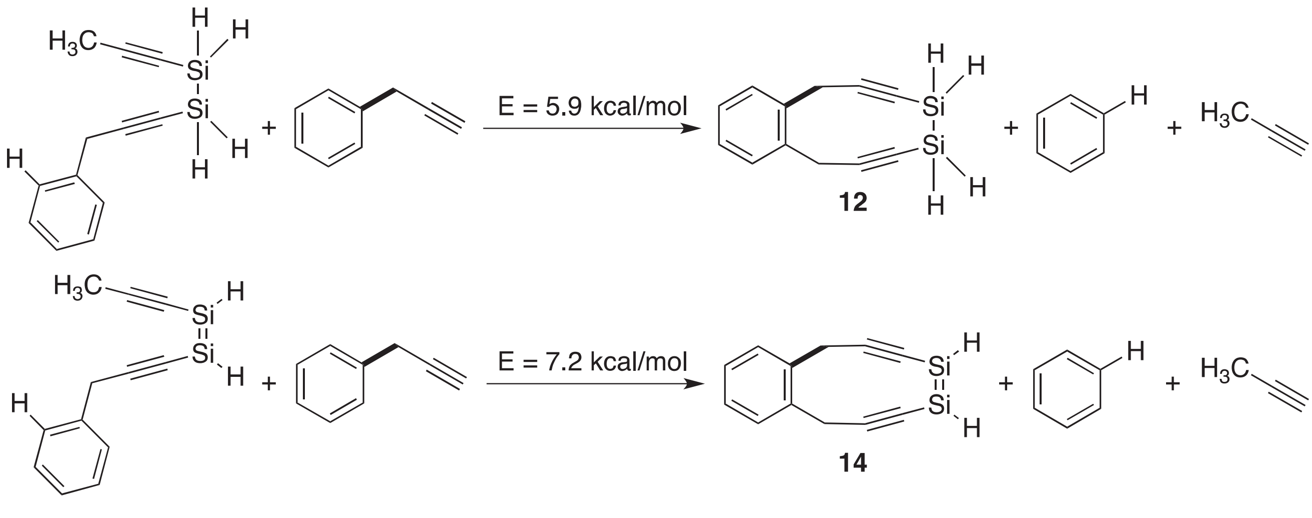


cis-**11a** *cis*-**11b** **12** **13**

Chart 1

The structural parameters of **12** were similar to those of *trans*-**11**, suggesting the negligible steric effect in *trans*-**11**. On the other hand, those of *cis*-**11**, especially the distances between two ethynylene moieties, were different from those of *trans*-isomer, *e.g.*, C1···C8: 3.345(4) (*trans*)/3.202(5) (*cis*) and C2···C7: 3.281(4) (*trans*)/3.182(5) (*cis*) Å. This is likely interpreted in terms of the steric repulsion between two Tip groups in *cis*-**11** as follows. The C13–Si1–Si2/C28–Si2–Si1 angles in *cis*-**11** [118.34(8)/121.37(9)°] were much larger than those in *trans*-**11** [114.63(9)/108.06(9)°], these changes [Figure 4, arrow (a)] induced the movement (b) in Figure 4. As a result, Si2–Si1–C1 angle [99.99(9)°] in *cis*-**11** was smaller than that in *trans*-**11**. While those distances were larger than the smallest values in cyclic 1,2-diethynyldisilanes structurally characterized so far [**13** (Scheme 4),[8] C1···C8: 3.155, C2···C7: 2.672 Å], those were one of the closest distances. The ethynylene moieties in *trans*- and *cis*-**11** were highly strained, and the angles of Si–C1–C2/Si2–C8–C7 were 160.7(3)/164.6(3)° (*trans*) and 163.0(2)/168.7(3)° (*cis*), respectively. These values were within the range of the Si–C≡C angles of cyclic 1,2-diethynyldisilanes (smallest one is 155.8(1)/156.3(1)° observed in **13**).

In order to estimate the ring strains in compounds **11** and **3**, the calculations on isodesmic reactions of model compounds **12** and **14** were performed together with prop-2-yn-1-ylbenzene (Scheme 5) at M06-2X/6-31G(d) level. In both cases, the energy differences were 6-7 kcal/mol, which values were not so large and close to the strain energies for cyclopentane and cycloheptane.[9] Judging from these results, the ring strains did not affect the low yield of the product very much.



Scheme 5

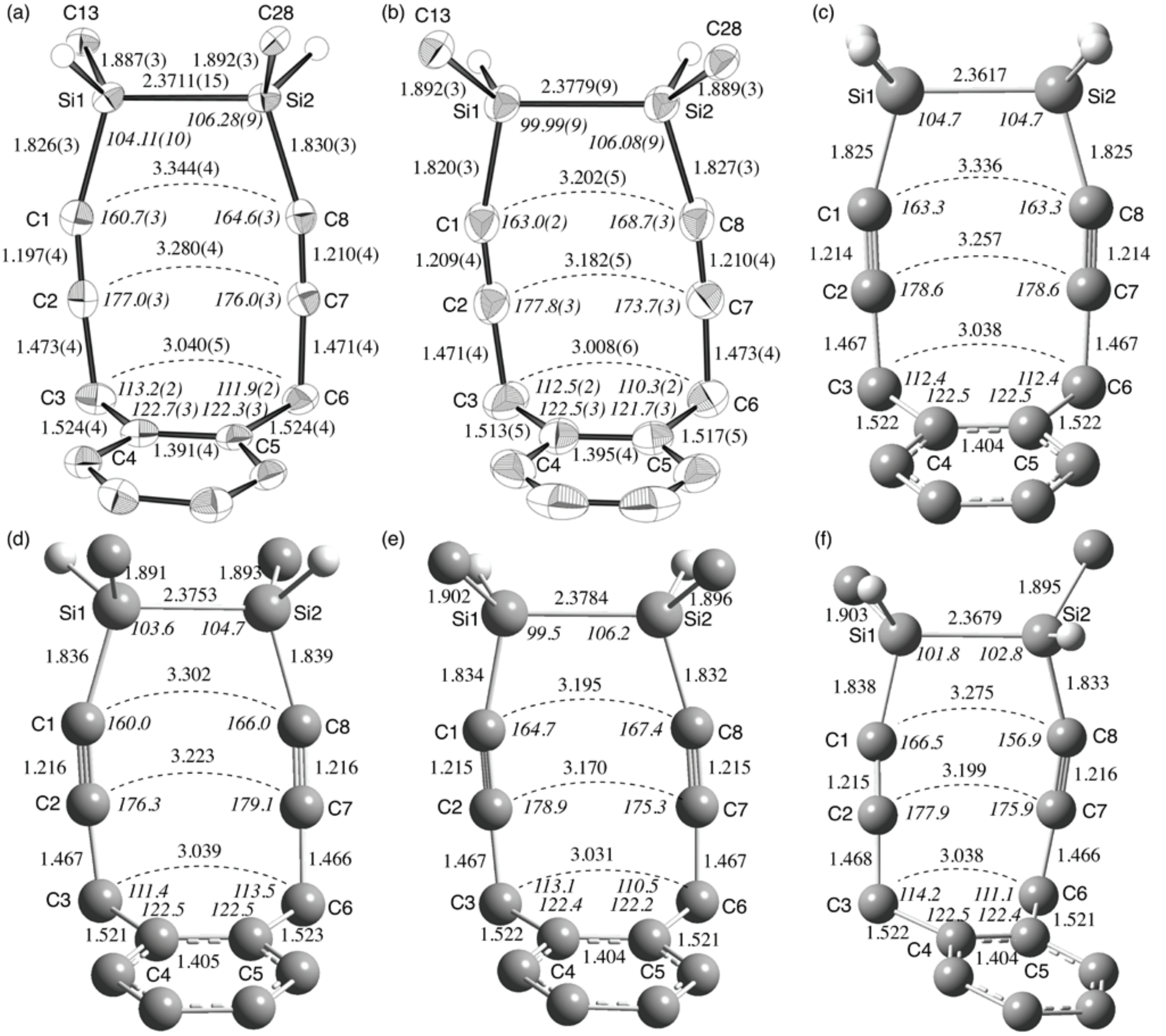


Figure 3. Selected bond lengths (Å, plain) and angles (deg, *italic*) in *trans*-**11** (a), *cis*-**11** (b), and the optimized structures for **12** (c), *trans*-**11** (d), *cis*-**11a** (e), and *cis*-**11b** (f) calculated at M06-2X/6-31G(d) level. Tip groups were omitted for clarity.

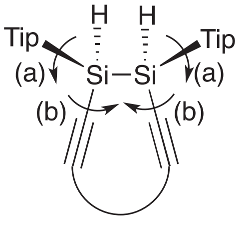


Figure 4

Molecular orbitals of *trans*-**11**, *cis*-**11a**, and **12** were shown in Figure 5. In the model compound **12**, the HOMO and LUMO apparently expanded to whole of the 10-membered ring and *o*-phenylene moiety. The HOMO showed the effective σ-π conjugation between the Si–Si bond and C≡C bonds, which corresponded to the HOMO–4's in *trans*-**11** and *cis*-**11a**. The dominant component of HOMOs of **11** was σ(Si–Si)-π(aryl) conjugation along with small contribution of ethynyl moieties.

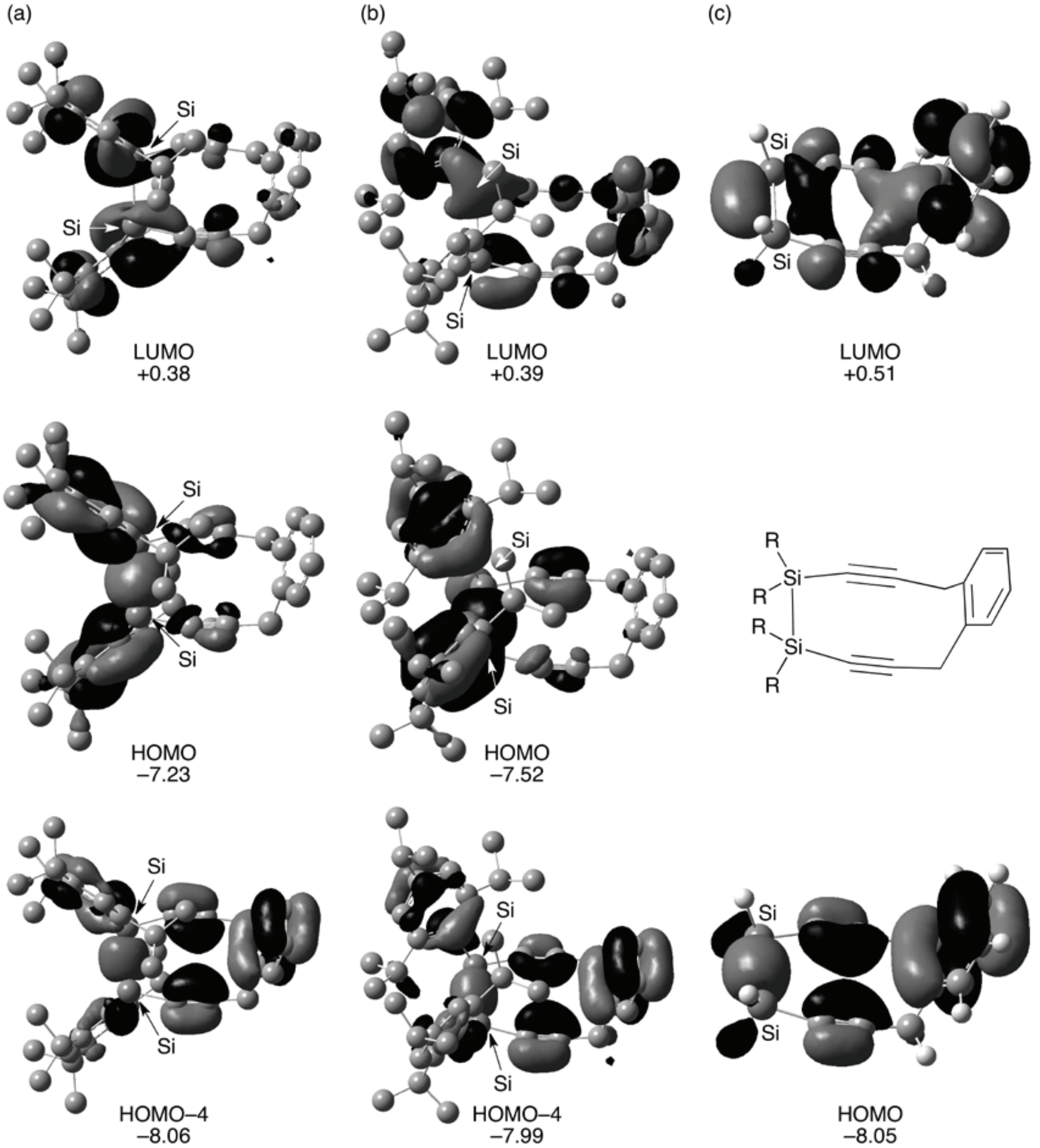


Figure 5. Molecular orbitals (isovalue = 0.03) and energies (eV) for *trans*-**11** (a), *cis*-**11a** (b), and **12** (c). Hydrogen atoms on compounds **11** were omitted for clarity.

As a result, novel 10-membered-cyclic disilanes **11** were found to have unique orbitals expanded to the whole rings. The introduction of Si=Si instead of Si–Si in **11** is expected to exhibit more effective π-electronic conjugation, and the transformation of compounds **11** into cyclic disilenes is now in progress.

EXPERIMENTAL

General procedures. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (GlassContour

Company).[10] ^{1}H NMR (300 MHz), ^{13}C NMR (76 MHz), and ^{29}Si NMR (59 MHz) spectra were measured in C_6D_6 with a JEOL JNM-AL300 spectrometer. In ^{1}H NMR, signal due to C_6D_5H (7.15 ppm) was used as references, and that due to C_6D_6 (128 ppm) was used in ^{13}C NMR. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. ^{29}Si NMR was measured with NNE and INEPT techniques using $SiMe_4$ as an external standard. GPLC (gel permeation liquid chromatography) was performed on an LC-908, LC-918, or LC-908-C60 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform). All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 1,2-Di(prop-2-yn-1-yl)benzene (**6**)[6] and trichloro(2,4,6-triisopropylphenyl)silane (**7**)[7] were prepared by following the procedures reported previously. All theoretical calculations were carried out using the Gaussian 09[11] programs.

Synthesis of trimethoxy(2,4,6-triisopropylphenyl)silane (8). To mixture of MeOH (200 mL) and triethylamine (30 mL) was added a *n*-hexane solution (100 mL) of trichloro(2,4,6-triisopropylphenyl)silane **7** (10.7 g, 31.8 mmol) at 0 ºC. After stirring at 0 ºC for 1.5 h, the solvents were removed under reduced pressure. *n*-Hexane was added to the residue, and the resulting suspension was filtered through Celite® to remove inorganic salts to give **8** (9.94 g, 30.6 mmol, 96%). **8**: viscous liquid; ^{1}H NMR (300 MHz, C_6D_6, δ in ppm) 1.21 (d, J = 7.0 Hz, 6H), 1.36 (d, J = 6.7 Hz, 12H), 2.79 (sept, J = 7.0 Hz, 1H), 3.48 (s, 9H), 3.88 (sept, J = 7.0 Hz, 2H), 7.21 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, δ in ppm) 24.0 (CH_3), 25.6 (CH_3), 33.0 (CH), 34.8 (CH), 50.3 (CH_3), 121.6 (CH), 123.7 (C), 151.3 (C), 157.7 (C); ^{29}Si NMR (59 MHz, C_6D_6, δ in ppm) –59.3; HRMS(FAB), *m*/*z* calcd for ($[M–H]^+$): 323.2037, found: 323.2042.

Synthesis of 1,2-bis{3-[dimethoxy(2,4,6-triisopropylphenyl)silyl]prop-2-yn-1-yl}benzene (10). To a *n*-hexane solution (60 mL) of **8** (2.08 g, 6.42 mmol) was added boron trichloride (1.0 M heptane solution, 3.2 mL, 3.2 mmol) at 0 ºC, and the mixture was stirred at 0 ºC for 40 h. The solvents were removed under reduced pressure to give the mixture of chloro(dimethoxy)silane [$TipSi(OMe)_2Cl$] **9** mainly with ca. 10% of starting material **8** and $TipSiCl_2(OMe)$. The mixture was used for the next reaction without further purification. To a THF solution (178 mL) of 1,2-di(prop-2-yn-1-yl)benzene **6** (407 mg, 2.60 mmol) was added *n*-butyllithium (1.61 M in *n*-hexane, 3.3 mL, 5.3 mmol) at –78 ºC, and the mixture was stirred at –78 ºC for 1 h. The resulting solution was added to a THF solution (25 mL) of the mixture containing **9** at 0 ºC, and the mixture was warmed up to room temperature overnight. The solvents were removed under reduced pressure. *n*-Hexane was added to the residue, and the resulting suspension was filtered through Celite® to remove inorganic salts. The reaction mixture was purified by GPLC (eluent: $CHCl_3$) to afford **10** (1.53 g, 0.207 mmol, 54%). **9**: ^{1}H-NMR (300 MHz, C_6D_6, δ in ppm)

1.18 (d, *J* = 7.0 Hz, 6H) 1.33 (d, *J* = 6.7 Hz, 12H), 2.74 (sept, *J* = 7.0 Hz, 1H), 3.48 (s, 6H), 3.89 (sept, *J* = 6.7 Hz, 2H), 7.18 (s, 2H). **10**: pale yellow viscous liquid; ^{1}H NMR (300 MHz, C_6D_6, rt, δ in ppm) 1.21 (d, *J* = 7.0 Hz, 12H), 1.38 (d, *J* = 6.7 Hz, 24H), 2.77 (sept, *J* = 7.0 Hz, 2H), 3.38 (s, 4H), 3.61 (s, 12H), 4.15 (sept, *J* = 6.7 Hz, 4H), 6.98 (dd, 2H, *J* = 5.6, 3.5 Hz), 7.21 (s, 4H), 7.37 (dd, 2H, *J* = 5.6, 3.5 Hz); ^{13}C NMR (75 MHz, C_6D_6, rt, δ in ppm) 23.9 (*C*H$_2$), 24.0 (*C*H$_3$), 25.4 (*C*H$_3$), 32.9 (*C*H), 34.8 (*C*H), 50.9 (*C*H$_3$), 84.1 (*C*), 104.4 (*C*), 121.7 (*C*H), 125.5 (*C*), 127.7 (*C*H), 128.1 (*C*H), 133.9 (*C*), 151.6 (*C*), 157.5 (*C*); ^{29}Si NMR (59 MHz, C_6D_6, rt, δ in ppm) –42.9; HRMS (FAB) *m/z* calcd for $C_{46}H_{67}O_4Si_2$ ($[M+H]^+$): 739.4578, found: 739.4577; Anal. Calcd for $C_{46}H_{66}O_4Si_2$: C, 74.74; H, 9.00%. Found: C, 74.81; H, 8.95%.

Synthesis of 1,2-bis{3-[dichloro(2,4,6-triisopropylphenyl)silyl]prop-2-yn-1-yl}benzene (4). To a *n*-hexane solution (150 mL) of **10** (938 mg, 1.26 mmol) was added boron trichloride (1.0 M heptane solution, 5.1 mL, 5.1 mmol) at 0 ºC, and the mixture was stirred at 0 ºC for 3.5 h. The solvents were removed under reduced pressure. Toluene was added to the residue, and the resulting suspension was filtered through Celite® to remove inorganic salts. The filtrate was re-precipitated from *n*-hexane to afford **4** (550 mg, 0.73 mmol, 58%). **4**: colorless crystals; mp 124 ºC (decomp); ^{1}H NMR (300 MHz, C_6D_6, rt, δ in ppm) 1.13 (d, *J* = 7.0 Hz, 12H), 1.27 (d, *J* = 6.7 Hz, 24H), 2.67 (sept, *J* = 7.0 Hz, 2H), 3.23 (s, 4H), 4.25 (sept, *J* = 6.7 Hz, 4H), 6.95 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.12 (s, 4H), 7.22 (dd, *J* = 5.7, 3.4 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, rt, δ in ppm) 23.7 (*C*H$_3$), 23.9 (*C*H$_2$), 25.0 (*C*H$_3$), 33.6 (*C*H), 34.7 (*C*H), 85.3 (*C*), 108.7 (*C*), 122.6 (*C*H), 124.9 (*C*), 128.0 (*C*H), 129.3 (*C*H), 132.9 (*C*), 153.5 (*C*), 156.8 (*C*); ^{29}Si NMR (59 MHz, C_6D_6, rt, δ in ppm) –42.0; Anal. Calcd for $C_{42}H_{54}Cl_4Si_2$: C, 66.65; H, 7.33%. Found: C, 66.77; H, 7.33%.

Reduction of 4 (concentration of 4: 13 mM). To a solution of **4** (102 mg, 0.134 mmol) in THF (10 mL) was added lithium naphthalenide (0.29 M, 1.85 mL, 0.536 mmol) at –78 ºC. The reaction mixture was allowed to warm slowly to –5 ºC, where stirring was continued for 2.5 h. The solvent was removed under reduced pressure. Hexane was added to the residue and the resulting suspension was filtered through Celite® in order to remove all inorganic salts. The reaction mixture was separated by GPLC ($CHCl_3$) to afford oligomeric products (88 mg) and the mixture of *trans*- and *cis*-**11**. The following PTLC (CH_2Cl_2:*n*-hexane = 1:1) gave *trans*-**11** (3.1 mg, 0.0050 mmol, 3%) and *cis*-**11** (n.d., <1%).

Reduction of 4 (concentration of 4: 1.3 mM). To a solution of **4** (99.4 mg, 0.131 mmol) in THF (100 mL) was added lithium naphthalenide (0.28 M, 1.9 mL, 0.532 mmol) at –78 ºC. The reaction mixture was allowed to warm up slowly to –5 ºC, where stirring was continued for 2.5 h. The solvent was removed under reduced pressure. *n*-Hexane was added to the residue and the resulting suspension was filtered through Celite® in order to remove all inorganic salts. The reaction mixture was separated by GPLC ($CHCl_3$) to afford oligomeric products (51.8 mg) and the mixture of *trans*- and *cis*-**11**. The following PTLC (CH_2Cl_2:*n*-hexane = 1:1) gave *trans*-**11** (2.4 mg, 0.0039 mmol, 3%) and *cis*-**11** (4.7 mg, 0.0076 mmol, 6%).

Reduction of 4 (adding simultaneously). A 0.30 M THF solution (1.77 mL) of lithium naphthalenide (0.531 mmol) and a solution of **4** (100 mg, 0.132 mmol) in THF (1.77 mL) were added simultaneously from separate gas-tight syringes to 60 mL of THF at –78 ºC. The reaction mixture was allowed to warm slowly to –20 ºC, where stirring was continued for 4 h. The solvent was removed under reduced pressure. *n*-Hexane was added to the residue and the resulting suspension was filtered through Celite® in order to remove all inorganic salts. The reaction mixture was separated by GPLC ($CHCl_3$) to afford oligomeric products (51.8 mg) and the mixture of *trans*- and *cis*-**11**. The following PTLC (CH_2Cl_2:*n*-hexane = 1:1) gave *trans*-**11** (4.5 mg, 0.0073 mol, 6%) and *cis*-**11** (4.2 mg, 0.0068 mmol, 5%).

Compound data for *trans*-11. colorless crystals; mp 151 ºC (decomp.); ^{1}H-NMR (300 MHz, C_6D_6, rt, δ in ppm) 1.10 (d, J = 6.6 Hz, 12H), 1.16 (dd, J = 6.9, 1.3 Hz, 12 H), 1.32 (d, J = 6.6 Hz, 12 H), 2.72 (sept, J = 6.9 Hz, 2 H), 3.33 (d, J = 1.3 Hz, 4 H), 3.57 (sept, J = 6.6 Hz, 4H), 5.31 (s, 2H), 6.86-6.87 (m, 2H), 6.96-6.97 (m, 2H), 7.13 (s, 4H); ^{13}C NMR (C_6D_6, rt, δ in ppm) 24.0 (CH_3), 24.1 (CH_3), 24.7 (CH_3), 24.9 (CH_3), 25.7 (CH_2), 34.8 (CH), 34.9 (CH), 83.1 (C), 111.0 (C), 121.5 (CH), 125.3 (C), 127.9 (CH), 131.1 (CH), 135.8 (C), 151.2 (C), 156.7 (C); ^{29}Si NMR (59 MHz, C_6D_6, rt, δ in ppm) –63.6; HRMS (FAB) *m*/*z* calcd for $C_{42}H_{55}Si_2$ ($[M–H]^+$): 615.3842, found: 615.3834.

Compound data for *cis*-11. colorless crystals; mp 153 ºC (decomp.); ^{1}H NMR (300 MHz, C_6D_6, rt, δ in ppm) 0.99 (d, J = 6.5 Hz, 12H), 1.10 (d, J = 6.8 Hz, 12 H), 1.12 (d, J = 6.8 Hz, 12 H), 2.66 (sept, J = 6.8 Hz, 2 H), 3.15 (d, J = 17.1 Hz, 2H), 3.43 (d, J = 17.1 Hz, 2H), 3.46 (sept, J = 6.8 Hz, 4H), 5.51 (s, 2H), 6.85 (dd, 2H, J = 5.5, 3.4 Hz), 6.96 (dd, 2H, J = 5.5, 3.4 Hz), 6.99 (s, 4H). ^{13}C NMR (75 MHz, C_6D_6, rt, δ in ppm) 23.9 (CH_3), 24.3 (CH_3), 24.7 (CH_3), 26.0 (CH_2), 34.5 (CH), 34.7 (CH), 84.1 (C), 112.4 (C), 121.5 (CH), 123.3 (C), 127.9 (CH), 130.9 (CH), 135.8 (C), 151.0 (C), 156.5 (C); ^{29}Si NMR (59 MHz, C_6D_6, rt, δ in ppm) –65.5; HRMS (FAB) *m*/*z* calcd for $C_{42}H_{55}Si_2$ ($[M–H]^+$): 615.3842, found: 615.3846.

General procedure for X-ray crystallographic analysis of compounds 4, *trans*-11, and cis-11. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71070 Å). A single crystal suitable for X-ray analysis was mounted on a glass fiber. The structures were solved by a direct method (SHELXS-97)[12] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[12] All hydrogen atoms except for Si–H were placed using AFIX instructions, while all other atoms were refined anisotropically. Deposition numbers CCDC-1012315 (**4**), 1012317 (*trans*-**11**), and 1012316 (*cis*-**11**). Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. X-Ray crystallographic data

	trans-**11**	*cis*-**11**	**4**
Empirical formula	$C_{42}H_{56}Si_2$	$C_{42}H_{56}Si_2$	$C_{42}H_{54}Cl_4Si_2$
Formula weight	617.05	617.05	756.83
Temperature (K)	103(2)	103(2)	103(2)
Crystal dimensions (mm)	0.15 x 0.05 x 0.05	0.20 x 0.05 x 0.05	0.30 x 0.10 x 0.10
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1$/a (#14)	$Pna2_1$ (#33)	*P*-1 (#2)
a (Å)	12.288(6)	19.4795(3)	11.1010(7)
b (Å)	17.401(8)	21.1949(4)	13.5386(9)
c (Å)	17.936(9)	8.8915(2)	13.9937(12)
α (°)	90	90	77.746(7)
β (°)	98.649(5)	90	89.200(4)
γ (°)	90	90	88.854(3)
V (Å^3)	3791(3)	3671.00(12)	2054.7(3)
Z	4	4	2
D_{calc} (g·cm^{-3})	1.081	1.116	1.223
μ (mm^{-1})	0.120	0.124	0.375
θ range (°)	2.22 to 25.25	1.92 to 25.25	1.83 to 25.25
Independent reflections	6827	6602	7381
R_{int}	0.0813	0.0730	0.0556
Completeness to θ (%)	99.4	99.7	99.0
No. of parameters	417	417	445
Goodness of fit	1.102	1.063	1.050
Final R indices [I>2σ(I)]	0.0654	0.0474	0.0529
R indices (all data)	0.1361	0.1190	0.1509
Absolute structure parameter	–	0.16(11)	–
Largest diff. peak (e·Å^3)	0.300	0.220	0.398
Largest diff. hole (e·Å^3)	–0.314	–0.188	–0.424

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