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Organosilicon Chemistry

Two Pentasilahousanes Fused Together

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Abstract: The organosilicon cluster **1** with two pentasilahousanes fused together was synthesized by the reduction of 1,1,3-trichlorocyclotetrasilane. This reaction involves dimerization and rearrangement of the silicon skeleton. The structure and properties of **1** were studied by X-ray crystallographic and spectroscopic analyses.

Organosilicon clusters with unique structures have been studied intensively for the last few decades. Their studies are important because 1) organosilicon clusters can be regarded as partial structures of bulk crystalline or amorphous silicon and 2) organosilicon clusters containing a large number of silicon atoms may open new organosilicon chemistry.[1] Various types of silicon analogues of polyhedranes have been reported.[2–4] Nowadays, organosilicon clusters expand into more complicated and sophisticated ones such as decasilaadamantane,[5] pentasila[1.1.1]propellane,[6] persila[*n*]staffanes,[7] organosilicon clusters with bicyclo[1.1.0]tetrasilane substructures,[8] and others.[9] The construction of organosilicon clusters is still challenging, and one of the most fundamental approaches is reductive oligomerization of polyhalosilanes. For example, $(t\text{Bu}_3\text{Si})_6\text{Si}_8$ (**I**),[8a] an isomer of hexasilabenzene **II**,[10] and charge-separated cyclotetrasiladiene **III**,[11] were synthesized by the reduction of 1,1,2,3,4-pentaiodocyclotetrasilane, 1,1,2-trichlorocyclotrisilane, and tribromosilane, respectively (Figure 1). Compounds **I**–**III** are intriguing from the viewpoints of the unique skeletons, the characteristic configurations around the silicon atoms, and/or peculiar Si–Si bonds. In addition, some organosilicon clusters such as **I** and **II** have unsubstituted silicon vertexes, for which Scheschkewitz and co-workers have recently proposed the term "siliconoids".[3b]

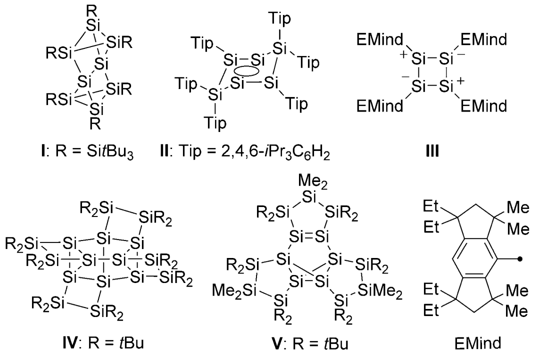
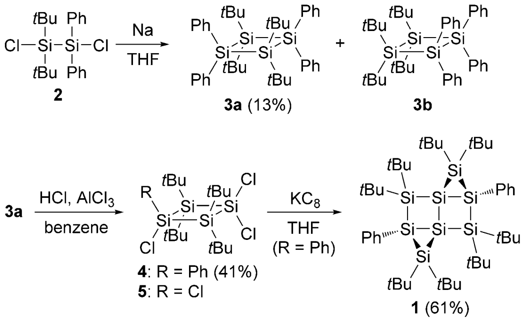

I: R = Si*t*Bu$_3$ **II**: Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$ **III**
IV: R = *t*Bu **V**: R = *t*Bu EMind

Figure 1. Organosilicon clusters synthesized by the reductive oligomerization of polyhalosilanes.

We have recently reported the synthesis of cyclotetrasilane-fused octasilacuneane **IV**[12] and cyclopentasilane-fused hexasilabenzvalene **V**[13] by the reduction of 1,1,2,2-tetrachlorocyclotetrasilane and 1,1,2,2-tetrachlorocyclopentasilane, respectively. Compounds **IV** and **V** are the first examples of octasilacuneane and hexasilabenzvalene derivatives, respectively. They have unsubstituted silicon atoms with highly deformed trigonal monopyramidal structures. These results prompted us to examine the reduction of different types of polyhalocyclooligosilanes to form unknown organosilicon clusters. We report herein the synthesis, structure, and properties of $t\text{Bu}_8\text{Ph}_2\text{Si}_8$ (**1**), an organosilicon cluster with two pentasilahousanes fused together by the reduction of 1,1,3-trichlorocyclotetrasilane **4**.

The synthetic route to **1** is outlined in Scheme 1. The Wurtz-type coupling of dichlorodisilane **2**[12] with sodium in THF gave a mixture of cyclotetrasilanes **3a** and **3b**.[14] The head-to-tail adduct **3a** was isolated in 13% yield after washing with ethanol and purification by column chromatography on silica gel. The careful chlorodephenylation of **3a** with hydrogen chloride and aluminum chloride gave a mixture of 1,1,3-trichlorocyclo-



2 **3a** (13%) **3b**
4: R = Ph (41%)
5: R = Cl
1 (61%)

Scheme 1. Synthesis of **1**.

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tetrasilane **4** and 1,1,3,3-tetrachlorocyclotetrasilane **5**.[15,16] Purification by column chromatography on silica gel gave **4** in 41% yield. The reduction of **4** with potassium graphite afforded **1** in 61% yield as pale yellow crystals. The formation of **1** involves dimerization and rearrangement of the silicon skeleton (vide infra).

The X-ray crystallographic analysis of **1** showed the unique tetracyclic silicon skeleton with two cyclotrisilane rings and two cyclotetrasilane rings with all-*anti* configuration (Figure 2).[16] Compound **1** has a twofold axis through a midpoint of the Si2–Si2* bond. The cyclotetrasilane rings have a slightly folded structure with the fold angle of 6.4 and 7.1°. They also have a slightly rhombic structure: the Si1-Si2-Si2* (96.31(4)°) and Si2-Si4-Si1* (95.03(3)°) bond angles are large, and the Si2-Si1-Si4* (84.40(3)°) and Si4-Si2-Si2* (83.87(3)°) bond angles are small. The Si–Si bond lengths range from 2.3642(9) to 2.3812(9) Å except for the short Si2–Si3 bond (2.3179(9) Å) and the long Si2–Si4 bond (2.4005(9) Å). The bridgehead Si2 and Si4 atoms exhibit deformed trigonal monopyramidal geometries with the sum of three Si-Si-Si bond angles of 356.5 and 357.8°, respectively (Figure 3). Similar structures have previously been reported in silicon clusters such as I,[8] IV,[12] and V.[13] This deformation implies that the Si2 orbital of the Si2–Si3 bond has increased s character, whereas the Si2 orbital of the Si2–Si4 bond has increased p character. In addition, the Si4 orbital of the Si2–Si4 bond has increased p character. As a result, the Si2–Si3 bond becomes short, whereas the Si2–Si4 bond becomes long.

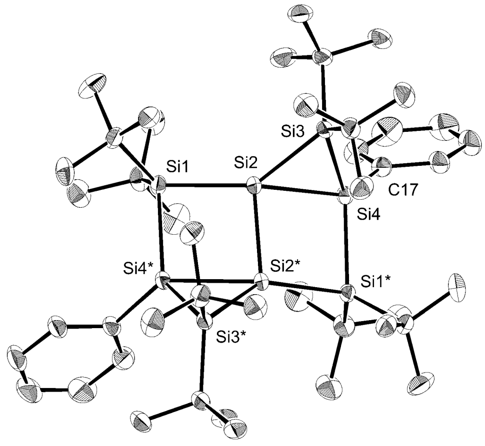


Figure 2. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and included hexane are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.3642(9), Si1–Si4* 2.3812(9), Si2–Si3 2.3179(9), Si2–Si4 2.4005(9), Si2–Si2* 2.369(1), Si3–Si4 2.3703(9); Si2-Si1-Si4* 84.40(3), Si1-Si2-Si3 142.20(4), Si1-Si2-Si4 145.09(4), Si1-Si2-Si2* 96.31(4), Si3-Si2-Si4 60.28(3), Si3-Si2-Si2* 118.00(3), Si4-Si2-Si2* 83.87(3), Si2-Si3-Si4 61.59(3), Si2-Si4-Si3 58.13(3), Si2-Si4-Si1* 95.03(3), Si2-Si4-C17 134.58(8), Si3-Si4-Si1* 127.73(4), Si3-Si4-C17 114.84(8), Si1*-Si4-C17 115.18(8).

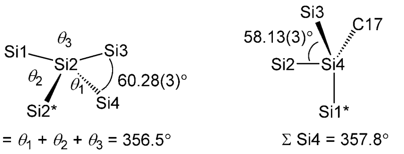


Figure 3. Geometries around the deformed silicon atoms of **1**.

The dihedral angles between the cyclotrisilane and cyclotetrasilane rings and between the two cyclotetrasilane rings are 129.4 and 145.2°, respectively. These values are much larger than those of tricyclo[3.1.0.0^{2,4}]hexasilane **6** (113.54°)[17] and bicyclo[2.2.0]hexasilane **7** (119.3°) (Figure 4).[18] To obtain insight into the large dihedral angles, theoretical calculations of **1** and the derivative of **1**, in which all *tert*-butyl groups are replaced by methyl groups (represented as $\mathbf{1}_{\mathrm{calc}}$ and $\mathbf{1}_{\mathrm{Me}}$, hereafter) were carried out at the B3LYP/6-311G(3d) level for silicon atoms and at the B3LYP/6-31G(d) level for carbon and hydrogen atoms. The optimized structure of $\mathbf{1}_{\mathrm{calc}}$ well reproduces the X-ray structure except that all Si–Si bond lengths are slightly longer (see Figure S22 and Table S4 in the Supporting Information). The dihedral angles between the cyclotrisilane and cyclotetrasilane rings of $\mathbf{1}_{\mathrm{Me}}$ (116.6°) is smaller than that of $\mathbf{1}_{\mathrm{calc}}$ (128.3°) and similar to those of **6** and **7**, indicating that the large dihedral angle of **1** is due to the steric hindrance between *tert*-butyl groups. The dihedral angle between the two cyclotetrasilane rings of $\mathbf{1}_{\mathrm{Me}}$ (135.3°) is still larger. This large dihedral angle may be related with the Si1-Si2-Si3 bond angles. If the dihedral angle became smaller, the large Si1-Si2-Si3 bond angle (142.20(4)°) would become larger. To prevent an unusually large Si(1)-Si(2)-Si(3) bond angle, the dihedral angle should be large.

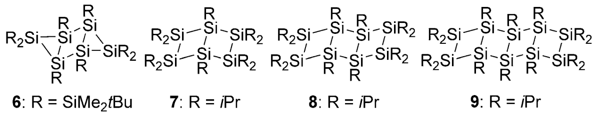


Figure 4. Compound **6** and ladder oligosilanes **7**–**9**.

In the ^{1}H and ^{13}C NMR spectra of **1**, four sets of *tert*-butyl signals and one set of phenyl signals are observed, supporting the C_2 symmetry of **1**. The ^{29}Si NMR spectrum exhibits four signals at $\delta = -84.5$ (Si2), -48.0 (Si4), -20.1 (Si3), and 26.1 (Si1) ppm.[19] The three signals observed in the upfield region are ascribed to the ^{29}Si nuclei of the cyclotrisilane ring. The ^{29}Si chemical shift of the Si2 nucleus ($\delta = -84.5$ ppm) is similar to those of **IV** ($\delta = -71.8$, -62.4, and -56.6 ppm).[12] The others are normal compared with those of cyclotrisilanes and cyclotetrasilanes with *tert*-butyl and phenyl groups.[20]

In the UV/Vis spectrum of **1**, the broad absorption tailing to about 450 nm was observed with a few shoulders at 247, 267, 303, and 376 nm (Figure 5). The absorption without clear bands is similar to that of **IV**[12] and is in contrast with those of ladder oligosilanes **7**–**9**, which show the lowest energy absorption as a distinctive band.[21] Thus, this result suggests that **1** shows the electronic properties as an organosilicon cluster. The TD-DFT calculation of $\mathbf{1}_{\mathrm{calc}}$ shows that the lowest energy

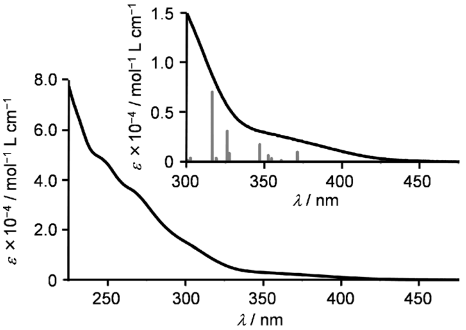
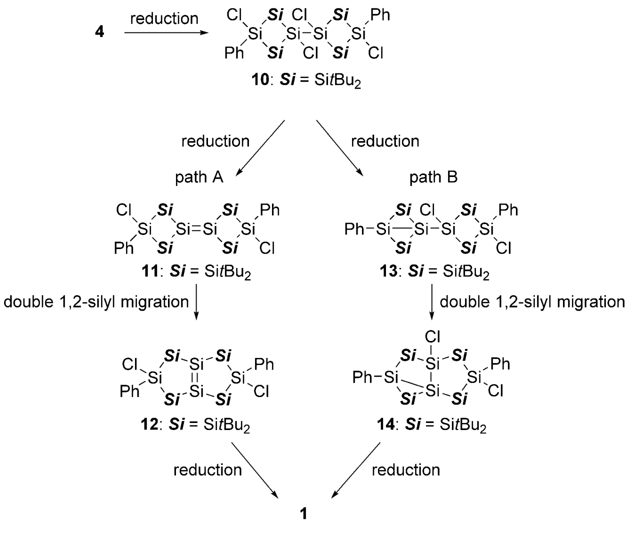


Figure 5. UV/Vis spectra of **1** in hexane at room temperature with transitions calculated at the B3LYP/6-31+G(2d,p) level (gray bars).

absorption band at 376 nm is due to the HOMO–LUMO transition ($\lambda_{calcd} = 371$ nm, $f = 0.0130$). The major contribution to the HOMO is σ conjugation of Si–Si bonds, that is, an out-of-phase interaction among σ orbitals along the Si2*–Si1*–Si4–Si3–Si2–Si2*–Si3*–Si4*–Si1–Si2 bonds (Figures S23 and S24). The major contribution to the LUMO is pseudo π* orbitals of the cyclotrisilane rings, consisting of the σ* orbitals of six Si–Si and Si–C bonds attached to the cyclotrisilane rings. It is interesting to compare the lowest energy absorption maximum of **1** with those of related compounds. The lowest energy absorption maximum of **1** (λ_{max} 376 nm) is larger than those of **6** (λ_{max} 320 nm),[17] **7** (λ_{max} 310 nm),[21b] and **8** (λ_{max} 345 nm).[21] It is close to that of **9** (λ_{max} 380 nm),[21b] in which two terminal cyclotetrasilane rings are fused into bicyclo[2.2.0]hexasilane.

Possible reaction mechanisms of the formation of **1** from **4** are shown in Scheme 2. On the basis of the previous reports on the double 1,2-silyl migration during the formation of bicyclo[3.3.0]octasil-1(5)-ene[22,23] and $(tBu_3Si)_6Si_9Cl_2$,[8b] the following reaction pathways are conceivable. Initially, bis(cyclotetrasilanyl) **10** is formed by the reductive coupling of **4** at the less crowded and more reactive silicon atom with two chlorine atoms. Path A includes the formation of disilene **11** by the reduction of **10**, followed by the ring expansion by double 1,2-silyl migration to give **12**. Further reduction of **12** leads to the formation of two cyclotrisilane rings by the cleavage of the Si=Si double bond to give **1**. On the other hand, path B includes the formation of **13** by the reduction of **10**, followed by the double 1,2-silyl migration to give **14**. Further reduction of **14** gives **1**. Although it is difficult to determine whether the reaction proceeds by path A or path B at this moment, we believe path B may be favorable because of the steric congestion around the internal Si–Cl bonds. In addition, the coefficients of the σ* orbitals of the terminal Si–Cl bonds in the LUMO of **10** are somewhat larger than those of the internal ones (Figure S25), implying high reactivity of the terminal Si–Cl bonds compared with the internal ones.[24]



Scheme 2. Possible reaction mechanisms of the formation of **1**.

In summary, we have synthesized the organosilicon cluster **1** with two pentasilahousanes fused together by the reduction of 1,1,3-trichlorocyclotetrasilane **4** via dimerization and rearrangement of the silicon skeleton. The X-ray crystallography, spectroscopy, and theoretical calculations revealed the unique structure and properties of **1**, such as the bridgehead silicon atoms with the deformed trigonal monopyramidal geometries and the σ conjugation of the three-dimensional organosilicon cluster. Further studies on the synthesis of unique organosilicon clusters are currently under way.

Acknowledgements

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Keywords: organosilicon clusters · pentasilahousane · σ conjugation · theoretical calculations · trigonal monopyramidal geometry

[1] For reviews on cyclic oligosilanes and silicon cage compounds, see: a) E. Hengge, R. Janoschek, *Chem. Rev.* **1995**, *95*, 1495–1526; b) A. Sekiguchi, H. Sakurai, *Adv. Organomet. Chem.* **1995**, *37*, 1–38; c) A. Sekiguchi, S. Nagase in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 119–152; d) E. Hengge, H. Stüger in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 2177–2216.

[2] For tetrasilatetrahedranes, see: a) N. Wiberg, C. M. M. Finger, K. Polborn, *Angew. Chem.* **1993**, *105*, 1140–1142; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1054–1056; b) M. Ichinohe, M. Toyoshima, R. Kinjo, A. Sekiguchi, *J. Am. Chem. Soc.* **2003**, *125*, 13328–13329.

[3] For hexasilaprismanes, see: a) A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **1993**, *115*, 5853–5854; b) K. Abersfelder, A. Russell, H. S. Rzepa, A. J. P. White, P. R. Haycock, D. Scheschkewitz, *J. Am. Chem. Soc.* **2012**, *134*, 16008–16016.

[4] For octasilacubanes, see: a) H. Matsumoto, K. Higuchi, Y. Hoshino, H. Koike, Y. Naoi, Y. Nagai, *J. Chem. Soc. Chem. Commun.* **1988**, 1083–1084; b) K. Furukawa, M. Fujino, N. Matsumoto, *Appl. Phys. Lett.* **1992**,

60, 2744–2745; c) A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **1992**, *114*, 6260–6262; d) H. Matsumoto, K. Higuchi, S. Kyushin, M. Goto, *Angew. Chem.* **1992**, *104*, 1410–1412; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1354–1356; e) K. Furukawa, M. Fujino, N. Matsumoto, *J. Organomet. Chem.* **1996**, *515*, 37–41; f) M. Unno, T. Matsumoto, K. Mochizuki, K. Higuchi, M. Goto, H. Matsumoto, *J. Organomet. Chem.* **2003**, *685*, 156–161.

[5] J. Fischer, J. Baumgartner, C. Marschner, *Science* **2005**, *310*, 825.

[6] D. Nied, R. Köppe, W. Klopper, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, *132*, 10264–10265.

[7] T. Iwamoto, D. Tsushima, E. Kwon, S. Ishida, H. Isobe, *Angew. Chem.* **2012**, *124*, 2390–2394; *Angew. Chem. Int. Ed.* **2012**, *51*, 2340–2344.

[8] a) G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem.* **2005**, *117*, 8096–8099; *Angew. Chem. Int. Ed.* **2005**, *44*, 7884–7887; b) T. M. Klapötke, S. K. Vasisht, P. Mayer, *Eur. J. Inorg. Chem.* **2010**, 3256–3260.

[9] a) D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 3014–3016; *Angew. Chem. Int. Ed.* **2005**, *44*, 2954–2956; b) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem.* **2011**, *123*, 8082–8086; *Angew. Chem. Int. Ed.* **2011**, *50*, 7936–7939.

[10] K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, *327*, 564–566.

[11] K. Suzuki, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *Science* **2011**, *331*, 1306–1309.

[12] S. Ishida, K. Otsuka, Y. Toma, S. Kyushin, *Angew. Chem.* **2013**, *125*, 2567–2570; *Angew. Chem. Int. Ed.* **2013**, *52*, 2507–2510.

[13] A. Tsurusaki, C. Iizuka, K. Otsuka, S. Kyushin, *J. Am. Chem. Soc.* **2013**, *135*, 16340–16343.

[14] Wurtz-type coupling of **2** with lithium in THF resulted in the selective formation of the head-to-head adduct **3b**.[12] The reason for the different reactivity between sodium and lithium is unclear at present.

[15] When hydrogen chloride was bubbled rapidly, **5** was obtained selectively. See the Supporting Information.

[16] CCDC-999894 (**1**), CCDC-999895 (**4**), and CCDC-999896 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] T. Iwamoto, K. Uchiyama, C. Kabuto, M. Kira, *Chem. Lett.* **2007**, *36*, 368–369.

[18] H. Matsumoto, H. Miyamoto, N. Kojima, Y. Nagai, M. Goto, *Chem. Lett.* **1988**, 629–632. The dihedral angle was calculated by using the atomic coordinates reported in this paper.

[19] The GIAO calculation of $\mathbf{1}_{\text{calc}}$ at the B3LYP/6–311+G(2d,p) level predicts the ^{29}Si chemical shifts at $\delta=-62.4$ (Si2), -32.2 (Si4), -19.5 (Si3), and 39.8 (Si1) ppm.

[20] For example, ^{29}Si signals of cyclotrisilanes have been reported to be observed at $\delta=-4.0$ ppm for $(t\text{Bu}_2\text{Si})_3$,[25a] $\delta=-34.81$ ppm for *cis,cis*-$[(i\text{PrMe}_2\text{C})\text{PhSi}]_3$,[25b] and $\delta=-41.25$ and -35.98 ppm for *cis,trans*-$[(i\text{PrMe}_2\text{C})\text{PhSi}]_3$.[25b] ^{29}Si signals of di-*tert*-butyl-substituted silicon nuclei of cyclotetrasilanes have been reported to be observed at $\delta=31.7$ and 41.8 ppm for $t\text{Bu}_7\text{Si}_4\text{H}$,[26a] $\delta=32.0$ ppm for *trans*-$t\text{Bu}_6\text{Si}_4\text{H}_2$,[26a] $\delta=37.3$ ppm for $t\text{Bu}_2(t\text{Bu}_2\text{MeSi})_3\text{Si}_4\text{Br}_3$,[26b] $\delta=24.7$ ppm for *trans*-$t\text{Bu}_6\text{Si}_4\text{Br}_2$,[26c] $\delta=16.0$ ppm for $t\text{Bu}_4\text{Si}_4\text{Cl}_4$,[12] $\delta=20.4$ ppm for $t\text{Bu}_4i\text{Pr}_2\text{Ph}_2\text{Si}$,[26d] $\delta=23.5$ ppm for **3a**, $\delta=29.9$ ppm for **3b**,[12] $\delta=18.0$ ppm for **4**, and $\delta=16.3$ ppm for **5**.

[21] a) S. Kyushin, M. Kawabata, Y. Yagihashi, H. Matsumoto, M. Goto, *Chem. Lett.* **1994**, 997–1000; b) S. Kyushin, H. Matsumoto, *Adv. Organomet. Chem.* **2003**, *49*, 133–166.

[22] H. Kobayashi, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.* **2005**, *127*, 15376–15377.

[23] Iwamoto and co-workers demonstrated the direct observation of the ring expansion from silylenecyclotetrasilane to cyclopentasilene. Theoretical calculations showed that the reaction proceeds via the ring expansion giving cyclic silylene followed by the migration of a silyl group. See: T. Iwamoto, Y. Furiya, H. Kobayashi, H. Isobe, M. Kira, *Organometallics* **2010**, *29*, 1869–1872.

[24] We have recently succeeded in the synthesis of 1,1′-bi(2,2,4,4-tetra-*tert*-butyl-3,3-dimethylcyclotetrasilanylidene) (**15**), which has *tert*-butyl groups instead of trimethylsilyl groups of Iwamoto and Kira's compound.[22] No reaction occurred when a solution of **15** in toluene was refluxed for 12 h. The structural similarity between **11** and **15** may exclude the possibility of the isomerization of **11** to **12** (path A). The synthesis and properties of **15** will be reported in future.

[25] a) M. Weidenbruch, *Chem. Rev.* **1995**, *95*, 1479–1493; b) M. Unno, H. Masuda, H. Matsumoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2449–2458.

[26] a) S. Kyushin, H. Sakurai, H. Matsumoto, *J. Organomet. Chem.* **1995**, *499*, 235–240; b) A. Sekiguchi, T. Matsuno, M. Ichinohe, *J. Am. Chem. Soc.* **2001**, *123*, 12436–12437; c) S. Kyushin, H. Kawai, H. Matsumoto, *Organometallics* **2004**, *23*, 311–313; d) T. Kuribara, S. Kyushin, *Acta Crystallogr. Sect. E* **2013**, *69*, o149.

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