

Consecutive disilanylsilylene to silyldisilene rearrangements

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Abstract

Thermolysis of 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivatives **1** in the presence of 2,3-dimethylbutadienes gave the trapping products of the corresponding bissilylene, disilanylsilylene, and a tetrasila-1,3-butadiene, via a consecutive disilanylsilylene to silyldisilene rearrangement.

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1. Introduction

Silylenes are significant, highly reactive organosilicon compounds [1]. The chemistry of silylenes has enjoyed a few decades of explosive growth, and recently, stable silylenes have been reported [2]. The reactions of silylenes are: (a) insertion of O–H, N–H, Si–Si, Si–O, and Si–X (halogen) bonds, (b) addition to carbon–carbon π -bonds, (c) dimerization to disilenes, and (d) silylene to disilene rearrangements. Among these, the dimerization of silylenes and the rearrangement reactions are interesting, because these reactions provide disilenes, which are silicon–silicon double bonded compounds [3]. Indeed, West et al. obtained the first isolable disilene, tetramesityldisilene, in 1981, based on the dimerization of dimesitylsilylene [4]. The isomerization of disilanylsilylenes to silyldisilenes using thermal and photochemical pathways has been also discussed (Scheme 1). For example, the thermolysis of a 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivative in the presence of 2,3-dimethylbutadienes gives a silylene adduct and a disilene adduct [5]. However, a limited number of

reactions utilizing this reaction have been available until now.

We have recently reported on the first example of the generation and consecutive intramolecular dimerization of two silylenes in a molecule to form a cyclic disilene [6], and we have extended this cumulative silylene system to oligosilanes. In this report, we describe the consecutive disilanylsilylene to silyldisilene rearrangement of two silylenes in tetrasilane-1,1,4,4-tetrayl. This reaction shows evidence for the transient existence of a tetrasila-1,3-butadiene. Recently, the chemistry of tetrasila-1,3-butadiene has attracted great interest. Kira and co-workers have reported on the dehalogenation reaction of 2,2,3,3-tetrabromotetrasilane and 2,2-dibromotetrasilane yielding a tetrasila[1.1.0]bicyclobutane, which undergoes interconversion with a tetrasilacyclobutene [7]. Weidenbruch et al. have reported on a kinetically stable hexaaryltetrasilabuta-1,3-diene [8]. In addition, Sekiguchi and co-workers have reported on a stable tetrasila-1,3-butadiene, based the reaction of 1,1-dilithiosilane with 1,1,2,2-tetrachlorodisilane derivatives [9].

2. Results and discussion

We reported some years ago on the isomerization of disilanylsilylenes to silyldisilenes (and vice versa) using thermal and photochemical pathways, which can be applied

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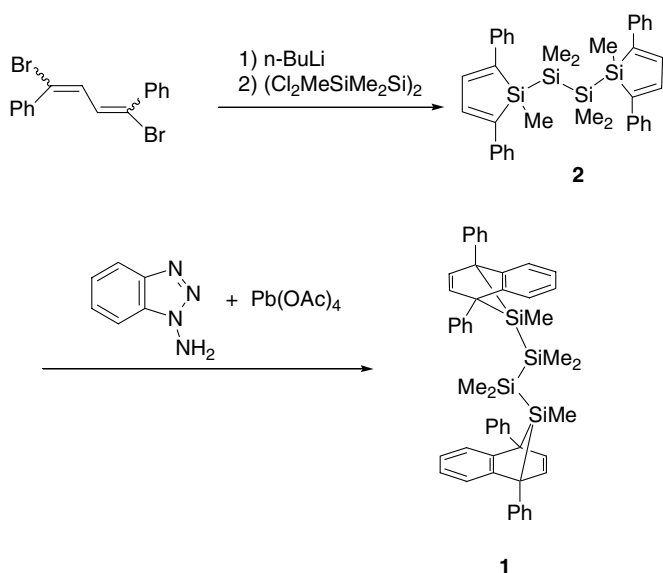
E-mail address: sanji@res.titech.ac.jp (T. Sanji).



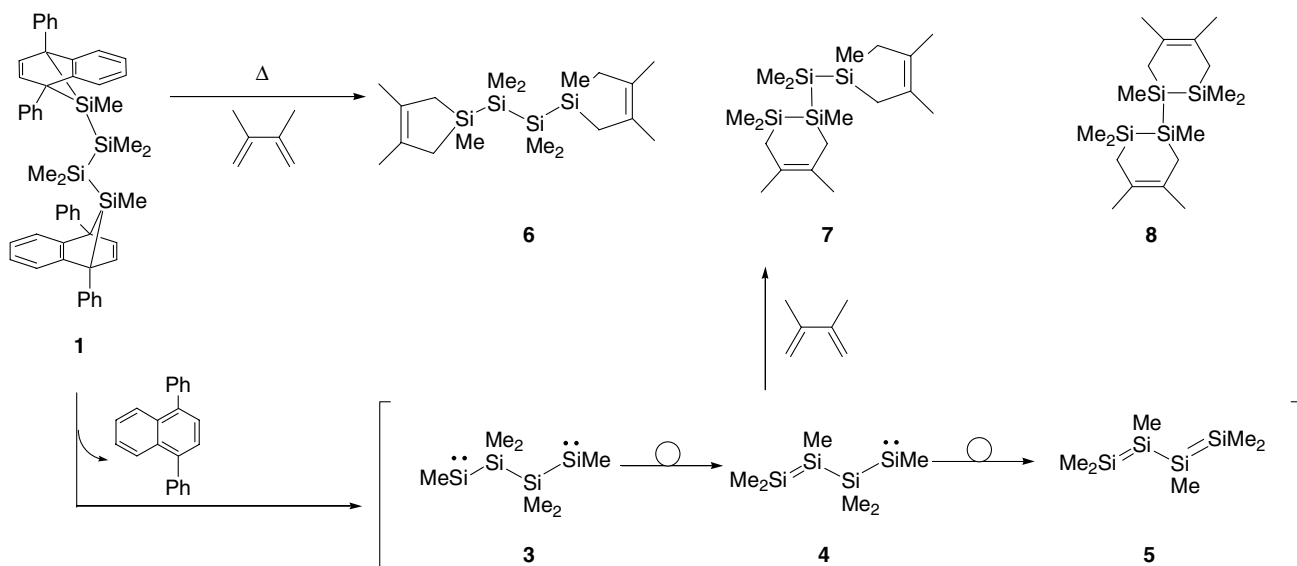
Scheme 1.

to generate oligosilenes [5]. Thus, we have adopted this strategy to form tetrasilane-1,1,4,4-tetrayl compounds, and expected the formation of tetrasilane-1,3-butadiene based on a thermal disilanylsilylene to silyldisilene rearrangement.

To generate the required tetrasilane-1,1,4,4-tetrayl compound, 1,4-bissilylene, **1** was synthesized as the precursor, because 2,3-benzo-1,4-diphenyl-7-silanorbornadiene deriv-



Scheme 2.

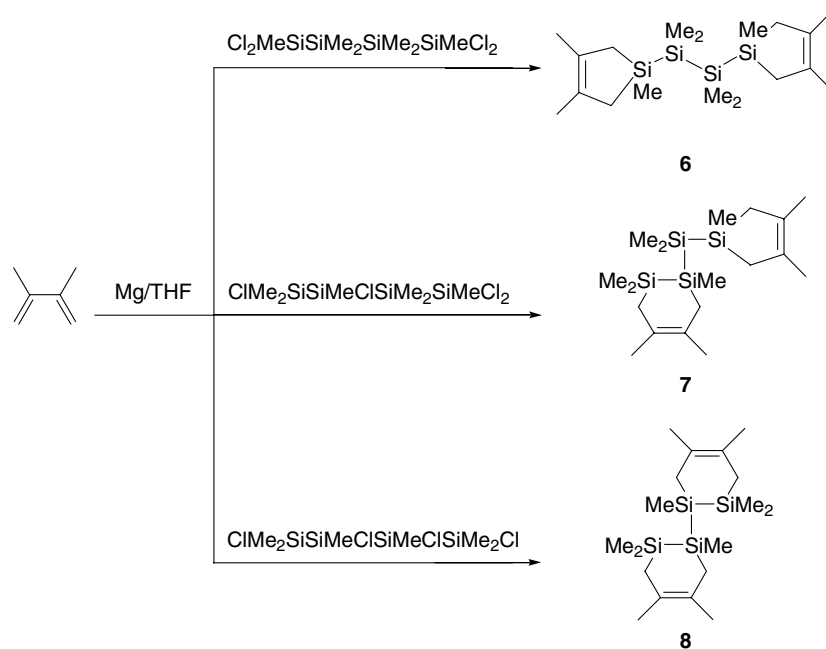


Scheme 3.

atives were presumed to be useful silylene generators [10]. Very recently, an attempted generation of a related 1,2-bis-silylene has been reported [11]. The synthetic procedure of the parent compound **1** was prepared in a manner similar to that reported [5,10], as shown in Scheme 2. The reaction of 1,4-dithio-1,4-diphenyl-1,3-butadiene with 1,1,4,4-tetrachlorotetrasilane gave **2** in 47% yield. The [4 + 2] cycloaddition between **2** and benzyne prepared in situ by the reaction of 1-aminobenzotriazole and lead tetracetate gave the silanorbornadiene **1** in 72% yield. The precursor **1** was fully characterized using several spectroscopic techniques.

The thermolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene in a sealed tube at 220 °C for 2 h gave adducts **7** and **8** in addition to the expected bissilylene adduct **6** (Scheme 3). These products were isolated and characterized using GCMS, and ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The structures of compounds **6**, **7**, and **8** were further confirmed by comparing the spectroscopic data obtained from authentic samples that were independently prepared by the reaction of the corresponding tetrachlorotetrasilanes with 2,3-dimethyl-1,3-butadiene and magnesium, as shown in Scheme 4.

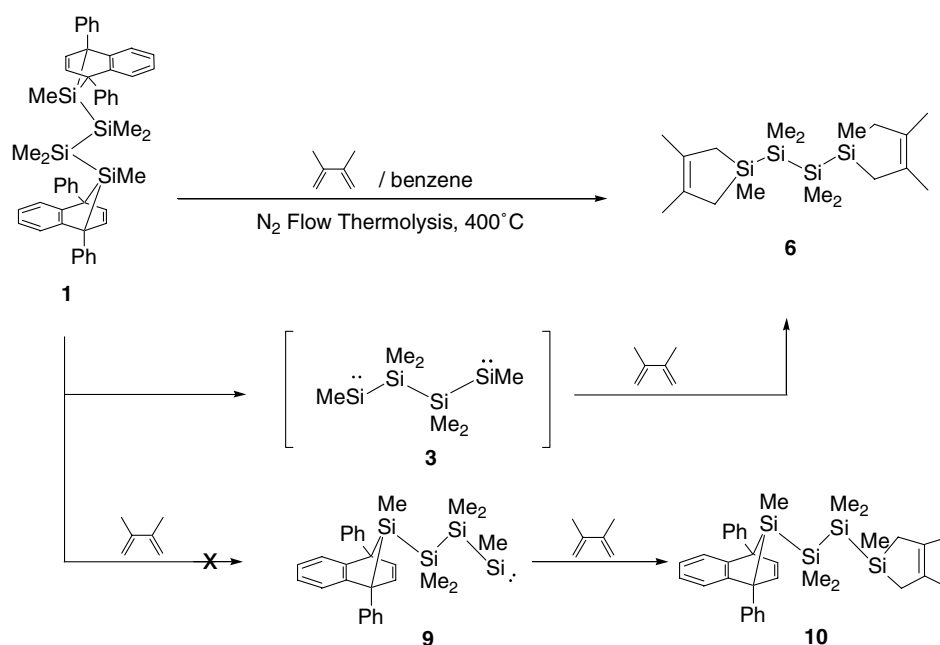
The formation of **6** provides evidence for the formation of the transient tetrasilane-1,1,4,4-tetrayl **3**, 1,4-bissilylene, upon thermolysis, which undergoes cycloaddition to 2,3-dimethyl-1,3-butadiene. The tetrasilane-1,1,4,4-tetrayl **3** also underwent isomerization. Thus, compound **7** is produced via isomerization of **3** to a disilanylsilylene **4** followed by addition to 2,3-dimethyl-1,3-butadiene. The disilene part of **4** forms the six-membered part of **7** by a Diels–Alder-type reaction, and the silylene part of **3** forms the five-membered moiety of **7**. The silylene to disilene rearrangement is very facile, based on quantum calculations [12]. In addition to these compounds, a remarkable product **8** was obtained from the



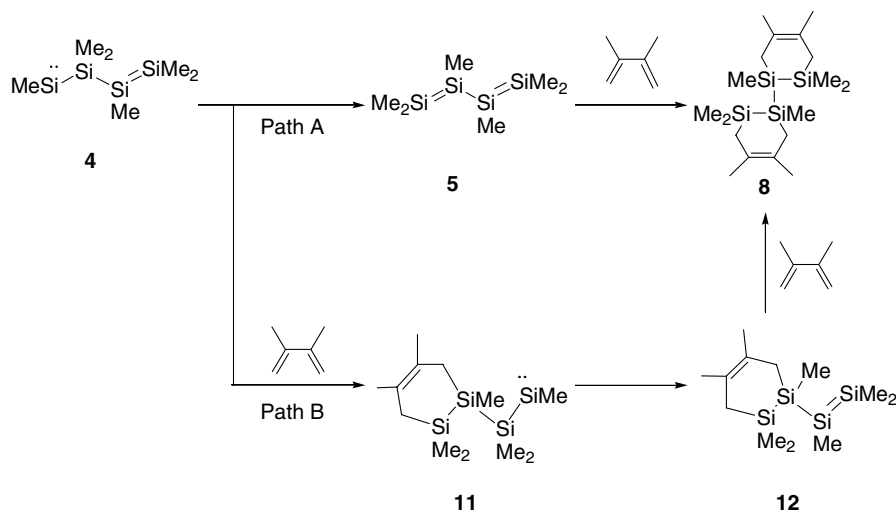
Scheme 4.

thermolysis of **1**. Compound **8** has two six-membered parts, and its formation suggests that a double Diels–Alder reaction occurred. The most reasonable pathway for the formation of **8** is the further silylsilylene to disilene rearrangement of **4** to form a tetrasilacyclobutene **5**, which undergoes a Diels–Alder reaction with 2,3-dimethyl-1,3-butadiene. Under this set of conditions, a very small amount of trapping products, corresponding to the mass numbers of tetrasilacyclobutene or tetrasilacyclobutane, were also observed using GCMS.

To elucidate the reaction pathway, N_2 flow thermolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene at 400°C was examined (Scheme 5). Under these conditions, the reaction gave only **6**, but not **10** with a 10% conversion of **1**. This suggests the formation of the transient 1,4-bissilylene **3** could be responsible upon thermolysis, which then undergoes cycloaddition to 2,3-dimethyl-1,3-butadiene to form **6**. After the disilanylsilylene to silyldisilene rearrangement from **3** to **4** (Scheme 6, Path A), the subsequent rearrangement to **5** gave **8**. However, it is possible that the



Scheme 5.



Scheme 6.

disilene part of **4** may undergo a reaction with 2,3-dimethyl-1,3-butadiene to form **11**, followed by rearrangement to **12**, which is then trapped with 2,3-dimethyl-1,3-butadiene to give **8** (Scheme 6, Path B). This reaction pathway cannot be excluded completely. Although further study is required, a plausible mechanism is shown in Scheme 3 involving the stepwise formation of **4** and **5** from **3**. If this is the case, then the product ratio should depend on the relative amounts of the precursor and the trapping reagent. In fact, the ratio of **6**, **7**, and **8** depended upon the relative ratio of **1** to 2,3-dimethyl-1,3-butadiene, supporting the stepwise rearrangement from **3** to **5**. For example, at high ratios of [1]/[2,3-dimethyl-1,3-butadiene] (e.g., 1/73), the thermolysis of **1** afforded **6**, **7**, and **8** in a ratio of 1:1.7:0.8, but at a lower ratios of [1]/[2,3-dimethyl-1,3-butadiene] (e.g., 1/50), compounds **6**, **7**, and **8** were detected in a ratio of 1:2.5:1.9.

3. Summary

We examined the consecutive disilanylsilylene to silyldisilene rearrangement of two silylenes in a tetrasilane-1,1,4,4-tetrayl compound. The thermal reaction of the 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivative **1** in the presence of 2,3-dimethylbutadiene gave the trapping products of the corresponding bisilylene, disilanylsilylene, and a tetrasilane-1,3-butadiene. This reaction may open a new way to form cumulative silylenes, and silicon–silicon double-bonded compounds.

4. Experimental

4.1. General procedures

¹H (300 MHz), ¹³C (75 MHz), and ²⁹Si (59 MHz) NMR spectra were measured using a Bruker DPX 300 spectrometer. CDCl₃ or C₆D₆ was used as the solvent, with the residual chloroform ($\delta = 7.24$ ppm; ¹³C = 77.0 ppm)

benzene ($\delta = 7.15$ ppm; ¹³C = 128.0 ppm), and Me₄Si used as an internal standard. The GLC data were recorded on Shimadzu GC-8A and GC-17A chromatographs. The GPC data were obtained using a JEOL LC-908 chromatograph equipped with Shodex AC 80M and 804 columns using toluene as the eluent. The GC mass spectra were measured at an ionization potential of 70 eV using Shimadzu GC-MS QP2000A and a Finnigan MAT GCQ mass spectrometers. High-resolution mass spectra were obtained using a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. All of the experiments were carried out under an argon atmosphere.

4.2. Synthesis of compound 2

To 100 mL of an ether solution of 1,4-dibromo-1,4-diphenyl-1,6-butadiene (15.0 g, 41.2 mmol) at 0 °C, a hexane solution of *n*-butyllithium (83.2 mmol) was added dropwise over a period of 30 min. The mixture was then stirred for 2 h, and then warmed to room temperature. A THF solution (150 mL) of 1,1,4,4-tetrachloro-1,2,2,3,3,4-hexamethyltetrasilane (7.07 g, 20.5 mmol) at room temperature was then added. The mixture was stirred for a period of 12 h, and then heated under reflux for 2 h. After addition of ethanol and water to the solution, the products were extracted with ether. The combined organic layer was washed successively with water, sat. NH₄Cl solution, and sat. NaCl solution, and then evaporated after being dried over anhydrous Na₂SO₄. Recrystallization from benzene/hexane gave **2** as yellow crystals (5.83 g, 9.56 mmol) in 47% yield.

2: M.p. = 163–164 °C; ¹H NMR (CDCl₃, 300 MHz) δ –0.16 (s, 12H), 0.69 (s, 6H), 7.19–7.34 (m, 24H); ¹³C NMR (CDCl₃, 75 MHz) δ –3.47, –2.83, 128.33, 128.51, 130.27, 139.92, 141.33, 149.10; ²⁹Si NMR (CDCl₃, 59 MHz) δ –41.00, –12.18; UV (hexane) $\lambda_{\text{max}} = 376$ nm ($\epsilon = 3.1 \times 10^4$); HRMS m/z for C₃₈H₄₂Si₄, calc. = 610.2364, found = 610.2372.

4.3. Synthesis of 1,2-[1,1'-bis(2,3-benzo-1,4-diphenyl-7-silanorbornadienyl)]-1,1,2,2-tetramethyldisilane (**1**)

To 20 mL of a dichloromethane solution of 1,2-[1,1'-bis(1-methyl-2,5-diphenyl-1-silacyclopentadienyl)]-1,1,2,2-tetramethyldisilane (266 mg, 0.437 mmol) and 1-amino-benzotriazole (201 mg, 1.50 mmol) at 0 °C, a dichloromethane solution (7.5 mL) of lead tetraacetate (90%, 809 mg, 1.83 mmol) was added over a period of 3 min. The mixture was subjected to flash chromatography through a short column (3.5 × 5 cm²) packed with silica gel. Benzene was used as an eluent. After removal of the solvent, crystallization from hexane/benzene afforded pale yellow crystals of 1,2-[1,1'-bis(2,3-benzo-1,4-diphenyl-7-silanorbornadienyl)]-1,1,2,2-tetramethyldisilane **1** (239 mg, 72%).

1: Pale yellow crystals; m.p. = 218–219 °C (decomp.); ¹H NMR (CDCl₃, 300 MHz) δ -0.41 (s, 12H), 0.08 (s, 6H), 6.79–6.92 (m, 8H), 7.03 (s, 4H), 7.19–7.37 (m, 20H); ¹³C NMR (CDCl₃, 75 MHz) δ -3.75, 1.10, 57.8, 121.79, 123.95, 125.79, 127.88, 128.66, 135.51, 139.37, 148.91; ²⁹Si NMR (CDCl₃, 59 MHz) δ -42.43, 83.21; HRMS *m/z* for C₅₀H₅₀Si₄, calc. = 762.2990, found = 762.3007.

4.4. Thermal reaction of **1** in the presence of 2,3-dimethyl-1,3-butadiene

A typical experiment was as follows. A benzene solution (0.5 mL) of **1** (43 mg, 0.056 mmol) and 2,3-dimethyl-1,3-butadiene (338 mg, 4.12 mmol) contained in a sealed evacuated tube was heated to 220 °C for a period of 2 h. After co-thermolysis, the products **6**, **7**, and **8** were formed in the ratio 1:1.7:0.8 from GLC analysis of the pyrolysate. The volatile materials were removed under reduced pressure, and the mixture of **6**, **7**, and **8** and 1,4-diphenylnaphthalene were obtained using preparative GLC and/or HPLC. The yields of **6**, **7**, and **8** were determined to be ca. 9.8%, 16.7%, and 7.9%, respectively.

Authentic samples **6**, **7**, and **8** were independently prepared as follows.

Synthesis of 6. Lithium (85 mg, 12 mmol) and 2,3-dimethyl-1,3-butadiene (1.0 g, 12 mmol) was added to a THF solution (20 mL) of magnesium chloride (570 mg, 6.0 mmol) and naphthalene (150 mg, 1.2 mmol) at room temperature. The mixture was stirred for a period of 4 h, and then 1,1,4,4-tetrachloro-1,2,2,3,3,4-hexamethyltetrasilane (720 mg, 2.1 mmol) was added to the mixture at -78 °C. After stirring for a period of 30 min, the mixture was warmed to room temperature and stirred for an additional 2 h. On addition of water to the solution, the mixture was extracted with ether. The combined organic layer was then washed successively with water, sat. NH₄Cl solution, and sat. NaCl solution, and dried over anhydrous Na₂SO₄. After evaporation, Kugelrohr distillation gave **6** (680 mg, 1.86 mmol) in 89% yield.

6: Colorless oil; b.p. = 144–146 °C/0.02 mmHg (Kugelrohr distillation); ¹H NMR (C₆D₆, 300 MHz) δ 0.24 (s,

12H), 0.25 (s, 6H), 1.57 (dd, *J* = 17 and 50 Hz, 8H), 1.75 (s, 12H); ¹³C NMR (C₆D₆, 75 MHz) δ -5.61, -2.96, 19.45, 25.26, 130.97; ²⁹Si NMR (C₆D₆, 59 MHz) δ -44.98, -7.64; GC-MS (70 eV) *m/z* (%) 366 (10, M⁺), 241 (100), 73 (12); HRMS *m/z* for C₁₈H₃₈Si₄, calc. = 366.2051, found = 366.2037.

Synthesis of 7. This was prepared from the reaction of 1,1,3,4-tetrachloro-1,2,2,3,4,4-hexamethyltetrasilane in 77% yield. **7**: colorless oil; bp = 130–150 °C/0.05 mmHg (Kugelrohr distillation); ¹H NMR (CDCl₃, 300 MHz) δ 0.12 (s, 3H), 0.15 (s, 3H), 0.21 (s, 3H), 0.24 (s, 3H), 0.25 (s, 3H), 0.26 (s, 3H), 1.44 (s, 2H), 1.50–1.71 (m, 8H), 1.75 (bs, 12H); ¹³C NMR (CDCl₃, 75 MHz) δ -7.45, -5.44, -5.21, -3.55, -3.00, -1.95, 19.45, 21.56, 22.31, 22.38, 25.29, 124.09, 124.47, 131.01; ²⁹Si NMR (CDCl₃, 59 MHz) δ -47.40, -45.38, -14.16, -7.70; GC-MS (70 eV) *m/z* (%) 366 (56, M⁺), 241 (41), 183 (100); HRMS *m/z* for C₁₈H₃₈Si₄, calc. = 366.2051, found = 366.2054.

Synthesis of 8. This was prepared from the reaction of 1,2,3,4-tetrachloro-1,1,2,3,4-hexamethyltetrasilane in 12% yield. **8** (a mixture of diastereomers): colorless oil; b.p. = 140–150 °C/0.02 mmHg (Kugelrohr distillation); ¹H NMR (C₆D₆, 300 MHz) δ 0.13, 0.18, 0.19, 0.20, 0.23 (s, 18H), 1.52–1.68 (m, 4H), 1.75 (s, 3H), 1.77 (s, 3H); ¹³C NMR (C₆D₆, 75 MHz) δ -7.26, -3.62, -2.02, -1.82, 21.65, 21.89, 22.30, 22.37, 22.48, 25.19, 124.11, 124.14, 124.52, 124.56; ²⁹Si NMR (C₆D₆, 59 MHz) δ -48.18, -47.86, -14.38, -14.27; GC-MS (70 eV) *m/z* (%) 366 (100, M⁺), 183 (36), 73 (24); HRMS *m/z* for C₁₈H₃₈Si₄, calc. = 366.2051, found = 366.2022.

Acknowledgements

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