



Synthesis of silicon-functionalized 7-silanorbornadienes and their thermolysis and photolysis

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ABSTRACT

A series of 7-silanorbornadienes were prepared and characterized by X-ray crystallographic analysis. 2,3-Benzo-7-mesityl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1a**) was prepared by the [4+2] cycloaddition reaction of 1-mesityl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (**4**) with benzyne. 7-Hydro **1a** was converted into 7-chloro-substituted silanorbornadiene **1b**. Treatment of **1b** with lithium phenylamide and lithium phenylthiolate gave 7-phenylamino-substituted silanorbornadiene **1c** and 7-phenylthio-substituted silanorbornadiene **1d**, respectively. Reductive lithiation of **1b** with lithium naphthalenide afforded 7-lithiated silanorbornadiene **1f**, which reacted with chlorotrimethylsilane to give 7-trimethylsilyl-substituted silanorbornadiene **1e**. Stereochemistry at the bridging silicon during these transformations was determined by X-ray crystallographic analysis. Thermolysis of **1** produced corresponding silylenes **5**, which were trapped with triethylsilane to give disilanes **6**. Photolysis of **1** except **1c** also afforded corresponding silylenes **5**. Theoretical calculation of the models of silanorbornadienes was performed at the MP2/6-31+G(d, p) level.

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1. Introduction

7-Silanorbornadienes are attractive species because they show unique reactivity that is attributed to their heavily strained skeletons [1]. Thermolysis and photolysis of 7-silanorbornadienes generate corresponding silylenes with elimination of arenes. For example, hydro-silanorbornadiene [1e] and silyl-silanorbornadienes [1f,1g] gave corresponding hydrosilylene and silylsilylenes, respectively. (7-Methyl-7-silanorbornadienyl)FeCp(CO)₂ [1h] and (7-alkyl-7-silanorbornadienyl)MLn (alkyl = methyl or ethyl, MLn = CpRu(CO) or CpNi(CO)) [1i] produced silylenes bearing transition metals. Thus, silicon-functionalized silanorbornadienes are expected to serve as precursors of silicon-functionalized silylenes.

Recently, we preliminarily reported the preparation and structures of a series of silicon-functionalized silanorbornadienes **1** [2]. Herein, we described the full details of **1** including their preparation, structures, and stereochemistry. We also disclosed the generation and trapping of silicon-functionalized silylenes by thermolysis and photolysis of **1**.

2. Results and discussion

2.1. Synthesis of silicon-functionalized 7-silanorbornadienes

2.1.1. 7-Hydro-substituted **1a**

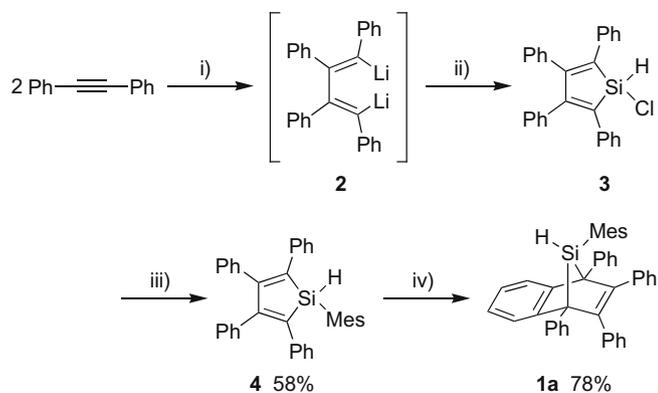
2,3-Benzo-7-mesityl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1a**) was prepared in a manner similar to the reported procedure (Scheme 1) [3]. Diphenylacetylene was treated with lithium in Et₂O to produce 1,4-dilithio-tetraphenylbutadiene **2**. The reaction of **2** with trichlorosilane in Et₂O afforded air-sensitive 1-chloro-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (**3**). Without isolation, crude **3** was reacted with mesitylmagnesium bromide in THF to afford 1-mesityl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (**4**) in 58% yield. The [4+2] cycloaddition reaction of **4** with benzyne, which was prepared in situ by the reaction of *o*-bromofluorobenzene with magnesium, gave 7-hydro-substituted **1a** in 78% yield as the sole diastereoisomer.

2.1.2. 7-Chloro-substituted **1b**

The reaction of **1a** with refluxing carbon tetrachloride in the presence of palladium dichloride (30 mol%) for 48 h successfully afforded 7-chloro-substituted **1b** in 90% yield as the sole diastereoisomer (Scheme 2) [4]. Attempts to chlorinate **1a** by other conventional methods (CuCl₂, CuCl₂/CuI) were unsuccessful [5].

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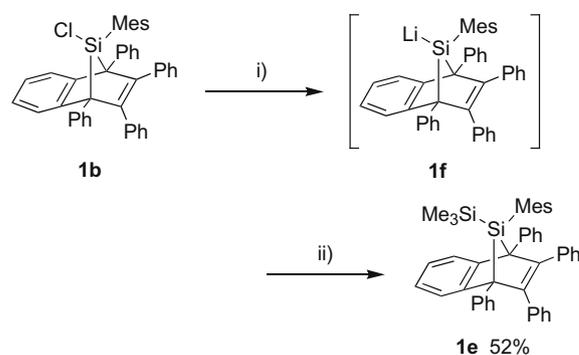
E-mail address: kawachi@sci.hiroshima-u.ac.jp (A. Kawachi).



Mes = 2,4,6-trimethylphenyl

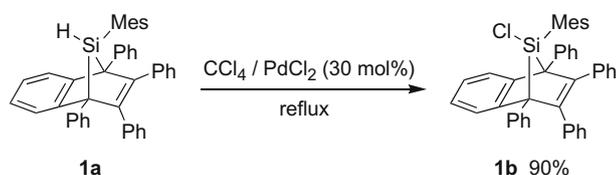
i) Li, Et₂O, r.t. ii) HSiCl₃, liq. N₂ bath to r.t. iii) MesMgBr, THF, r.t.
iv) *o*-C₆H₄FBBr / Mg, THF, r.t.

Scheme 1.

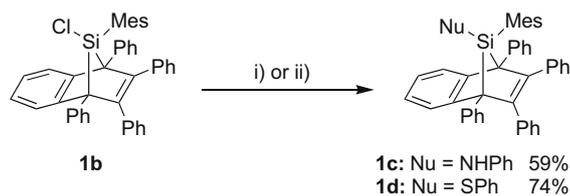


i) Lithium naphthalenide, THF–benzene (4/1), –78 °C.
ii) Me₃SiCl, –78 °C to r.t.

Scheme 4.



Scheme 2.



i) PhNHLi, THF–benzene (4/1), r.t. ii) PhSLi, THF–benzene (4/1), r.t.

Scheme 3.

2.1.3. Nucleophilic transformations of 7-chloro-substituted **1b**

Treatment of **1b** with lithium phenylamide in THF–benzene for 3 h at room temperature gave 7-phenylamino-substituted **1c** in 59% yield as the sole diastereoisomer (Scheme 3). The reaction of **1b** with lithium phenylthiolate in THF–benzene for 16 h at room temperature afforded 7-phenylthio-substituted **1d** in 74% yield as the sole diastereoisomer.

2.1.4. Electrophilic transformations of 7-chloro-substituted **1b**

The exposure of **1b** to 4 equivalents of lithium naphthalenide in THF–benzene at –78 °C for 4 h produced 7-lithio **1f** (Scheme 4) [6,7]. The ²⁹Si NMR resonance of **1f** could not be observed even at low temperatures in spite of several trials. The reduction of **1b** with lithium 4,4'-di-*tert*-butylbiphenylide under the same conditions was unsuccessful. 7-Lithio **1f** reacted with chlorotrimethylsilane to form 7-silyl-substituted **1e** in 52% yield as the sole diastereoisomer.

2.2. Structures of **1a**, **1b**, **1c**, and **1e**

The structures of **1** were determined by X-ray crystallographic analysis (Figs. 1–4) [8]. Crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization from CDCl₃/

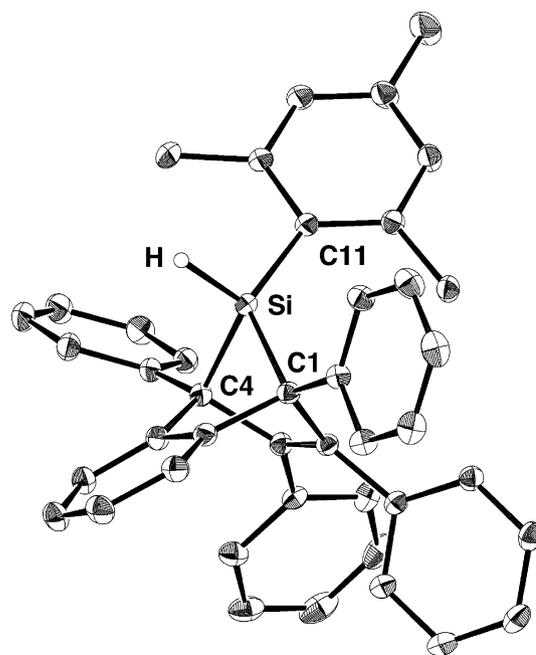


Fig. 1. Molecular structure of **1a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for the hydrogen attached to the silicon are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–H, 1.50(2); Si–C1, 1.9295(15); Si–C4, 1.9345(17); Si–C11, 1.8892(17); C1–Si–H, 108.9(7); C4–Si–H, 111.4(8); C11–Si–H, 107.2(8); C1–Si–C4, 81.96(7); C1–Si–C11, 127.48(6); C4–Si–C11, 117.77(7).

hexane. It was revealed that the functional groups at the bridging silicon are *syn* with respect to the annulated benzene ring in all of the present cases.

The selected bond lengths and angles of **1** are given in Table 1. Si–X bond lengths fall in the range of typical silicon–heteroatom bond lengths (Si–H, 1.47–1.50 Å; Si–Cl, 2.02–2.05 Å; Si–N, 1.70–1.76 Å; Si–Si, 2.33–2.37 Å) [9]. Endocyclic Si–C(1) and Si–C(4) bonds are longer than the exocyclic Si–C(11) bond. C(1)–Si–C(4) angles are significantly smaller than those in the ideal tetrahedral geometry at silicon atom (109.5°). The sum of C–Si–C bonds ($\Sigma(\text{C–Si–C})_3$) increases with increasing electronegativities of the atoms bonded to the silicon atom except for 7-phenylamino derivative **1c** [10].

2.3. Stereochemistry

The chlorination reaction of **1a** proceeded with retention of configuration at the silicon. The stereochemistry is consistent with the

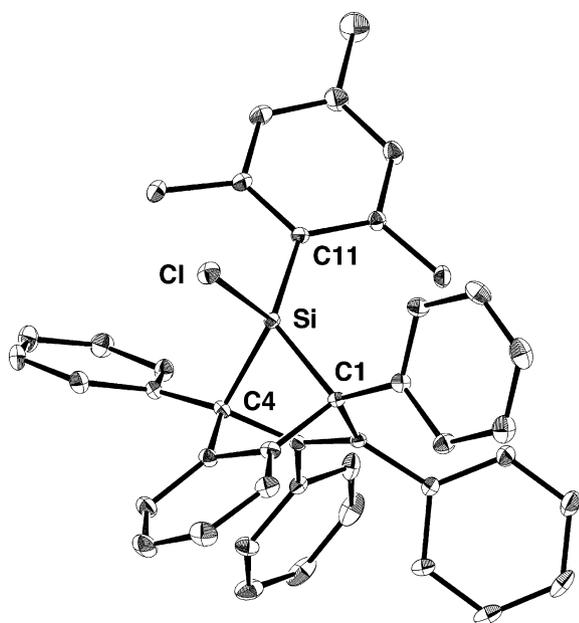


Fig. 2. Molecular structure of **1b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–Cl, 2.0826(8); Si–C1, 1.919(2); Si–C4, 1.937(2); Si–C11, 1.893(2); Cl–Si–C1, 105.89(7); Cl–Si–C4, 113.38(7); Cl–Si–C11, 105.65(8); C1–Si–C4, 82.42(10); C1–Si–C11, 129.50(9); C4–Si–C11, 118.56(9).

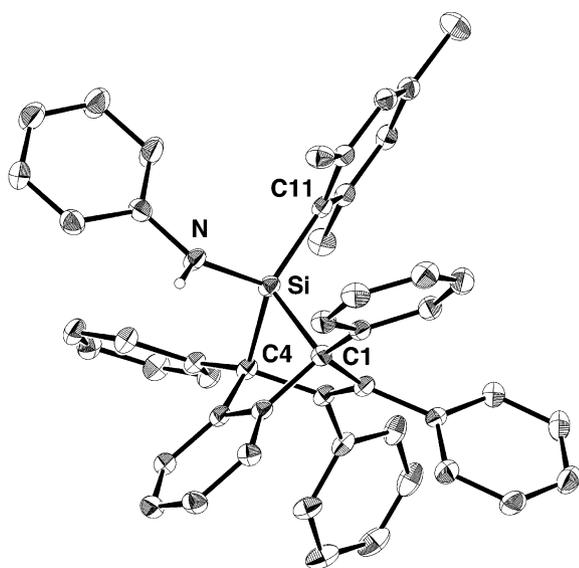


Fig. 3. Molecular structure of **1c** with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for the hydrogen attached to the nitrogen atom are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–N, 1.725(2); Si–C1, 1.929(3); Si–C4, 1.942(3); Si–C11, 1.886(3); N–Si–C1, 110.31(12); N–Si–C4, 109.52(12); N–Si–C11, 110.90(12); C1–Si–C4, 81.86(11); C1–Si–C11, 115.28(11); C4–Si–C11, 125.53(12).

trend that reactions involving intermediary silyl radicals proceed with predominant retention of configuration at the silicon [11]: Sommer et al. reported that optically active 1-naphthylphenylmethylsilane underwent retention of configuration at the asymmetric silicon [11b].

The nucleophilic substitution reaction of **1b** proceeded with retention of configuration at the silicon. Although nucleophilic displacements of chlorosilanes usually lead to inversion at the silicon, the stereochemistry tends to be retained when the silicon is included in a strained ring [11a]. For instance, 1-chloro-1,2-di-

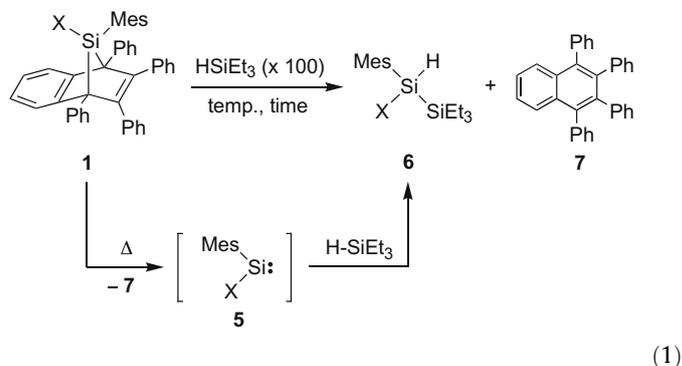
methyl-1-silacyclobutane reacts with nucleophiles with predominant retention of configuration regardless of the nature of the nucleophiles [12].

The lithiation of **1b** and the subsequent reaction of the resulting **1f** with electrophiles take place with net retention of configuration at the silicon. This is consistent with the trend that reductive lithiations of chlorosilanes and subsequent reactions with electrophiles proceed with net retention of configuration at the silicon [13]. Oestreich et al. reported that the optically active chlorosilane, 1-chloro-2-methylphenyl-1,2,3,4-tetrahydro-1-silanaphthalene, reacted with lithium 4,4'-di-*tert*-butylbiphenylide to give the corresponding silyllithium that was trapped as a protonated compound with retention of configuration at the silicon [13e].

2.4. Generation of silicon-functionalized silylenes by thermolysis of **1**

Next, we performed thermolysis of silicon-functionalized silanorbornadienes **1** in order to generate corresponding silicon-functionalized silylenes by elimination of naphthalene [14]. Heating of 7-hydro-substituted **1a** in refluxing hydrocarbon solvents, such as benzene, toluene, or *p*-xylene, in the presence of 10 equivalents of triethylsilane as the silylene-trapping agent afforded no silylene-trapped products. Then, thermolysis of 7-silanorbornadienes **1** was performed in a sealed pressure-resistant glass container at 250 °C for 2 h in the presence of 100 equivalents of triethylsilane that acted as both a silylene-trapping agent and a solvent. We confirmed that **1** was consumed completely after the reaction. The results are summarized in Eq. (1) and Table 2.

Thermolysis of **1** except **1d** produced corresponding silylenes with elimination of **7**, the former of which were trapped as **6** (Table 2, entries 1–3, 5). Whereas **1d** gave a small amount of disilane **6d** at 250 °C for 2 h, thermolysis of **1d** at a lower temperature for a shorter reaction time successfully afforded **6d** in 48% yield (Table 2, entry 4).



2.5. Generation of silicon-functionalized silylenes by photolysis of **1**

Photolysis of 7-silanorbornadienes **1** was performed in the presence of 10 equivalents of triethylsilane using a high-pressure mercury lamp ($\lambda = 313$ nm) [14]. The results are summarized in Eq. (2) and Table 3.

The photolysis of 7-hydro-substituted **1a** and 7-phenylthio-substituted **1d** resulted in the formation of disilane **6a** in 46% yield and **6d** in 35% yield, together with **7** (Table 3, entries 1, 5). In the case of 7-chloro-substituted **1b**, the formation of disilane **6b** was confirmed by analyzing ^1H NMR spectra: the yield of **6b** was estimated to be 53% by ^1H NMR analysis using cyclodecane as the internal standard (Table 3, entry 2). For isolation, **6b** in the reaction mixture was treated with phenyllithium in Et_2O to generate phenyldisilane **8** in 43% yield (Scheme 5). In contrast to these, photolysis of 7-phenylamino-substituted silanorbornadiene **1c** afforded no silylene-trapped product under the same reaction conditions,

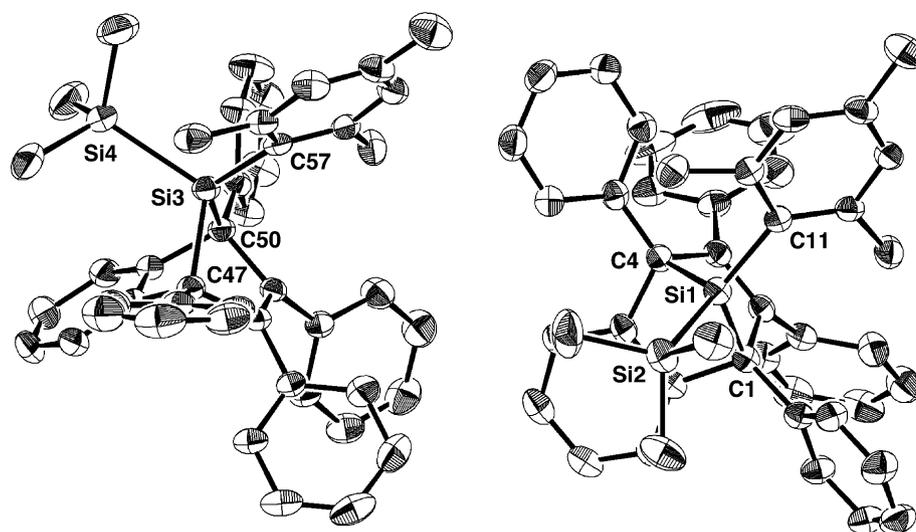
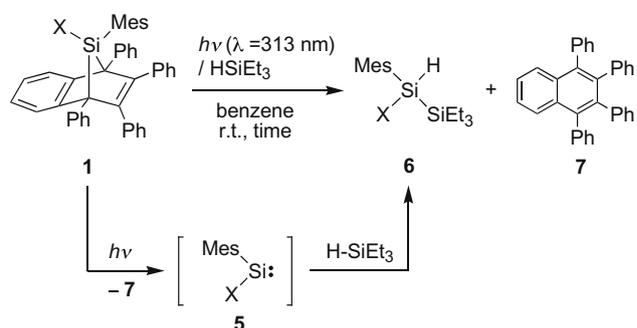


Fig. 4. Molecular structure of **1e** with thermal ellipsoids at the 30% probability level. There are two independent molecules in the unit cell. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2, 2.3956(11); Si3–Si4, 2.3852(12); Si1–C1, 1.930(3); Si3–C47, 1.954(3); Si1–C4, 1.940(3); Si3–C50, 1.951(3); Si1–C11, 1.904(3); Si3–C57, 1.896(3); Si2–Si1–C1, 107.10(8); Si4–Si3–C47, 114.88(9); Si2–Si1–C4, 118.71(9); Si4–Si3–C50, 109.43(9); Si2–Si1–C11, 111.74(8); Si4–Si3–C57, 110.99(9); C1–Si1–C4, 81.11(12); C47–Si3–C50, 80.51(11); C1–Si1–C11, 123.52(12); C47–Si3–C57, 114.44(12); C4–Si1–C11, 112.04(11); C50–Si3–C57, 123.65(12).

although **7** was obtained in good yield (Table 3, entry 3). Although photolysis of **1c** was performed in the presence of 100 equivalents of triethylsilane, no **6c** was formed (Table 3, entry 4). Photolysis of **1c** in the presence of 2,3-dimethyl-1,3-butadiene, which is also a good silylene-trapping agent, under the same reaction conditions was also unsuccessful. It was confirmed that **6c**, which was prepared in another route, was not photolabile: **6c** in benzene-*d*₆ remained unchanged after irradiation for 24 h in the presence of **7**. Thus, it is anticipated that the N–H functionality in **1c** or **5c** could not tolerate the present reaction condition. Photolysis of **1e** resulted in a low yield of **6e**, which was probably due to photosen-

sitivity of the formed trisilane skeleton in **6e** (Table 3, entries 6, 7) [14g,14h].



(2)

Table 1
Selected bond lengths (Å) and angles (°) of 7-silanorbornadienes **1**.

X =	H (1a)	Cl (1b)	NHPh (1c)	SiMe ₃ (1e)
Si–X	1.50(2)	2.0826(8)	1.725(2)	2.3965(11) 2.3852(12)
Si–C(1)	1.9295(15)	1.919(2)	1.929(3)	1.930(3) 1.951(3)
Si–C(4)	1.9345(17)	1.937(2)	1.942(3)	1.940(3) 1.954(3)
Si–C(11)	1.8892(17)	1.893(2)	1.886(3)	1.904(3) 1.896(3)
C(1)–Si–C(4)	81.96(7)	82.42(10)	81.86(11)	81.11(12) 80.51(11)
X–Si–C(11)	107.2(8)	105.65(8)	110.90(12)	111.74(8) 110.99(9)
∑(C–Si–C) ₃	327.2	330.5	322.7	316.7 318.6

Table 2
Thermolysis of silanorbornadienes **1**.

Entry	X	Temperature (°C)	Time (h)	Isolated yield (%)	
				6	7
1	H (a)	250	2	44	53
2	Cl (b)	250	2	70	86
3	NHPh (c)	250	2	53	97
4	SPh (d)	180	1	48	97
5	SiMe ₃ (e)	250	2	42	55

2.6. Theoretical study

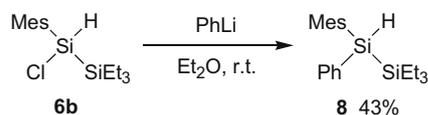
We performed calculations of a series of model compounds, that is, silanorbornadienes **1'** (X = H (**a**), Cl (**b**), NH₂ (**c**), SH (**d**), SiH₃ (**e**)) at the MP2/6-31+G(d, p) level [15]. The selected bond lengths and angles in the optimized structures of **1'** are shown in Table 4. The obtained structures of **1'** are almost in agreement with the corresponding crystal structures of **1**. The values of ∑(C–Si–C)₃ increased with increasing electronegativities of the heteroatoms

Table 3
Photolysis of silanorbornadienes **1**.^a

Entry	X	HSiEt ₃ (eq.)	Time (h)	Isolated yield (%)	
				6	7
1	H (a)	10	38	46	62
2	Cl (b)	10	40	53 ^b	79
3	NHPh (c)	10	106	0	51
4	NHPh (c)	100	225	0	90
5	SPh (d)	10	96	35	74
6	SiMe ₃ (e)	10	127	6 ^b	47
7	SiMe ₃ (e)	100	114	17 ^b	70

^a Photolysis was carried out with a high-pressure mercury lamp.

^b Estimated by use of cyclodecane as the internal standard in ¹H NMR measurement.



Scheme 5.

(Si < H < S < Cl) bonded to the silicon, except for amino-substituted **1'c** [10].

We also performed calculations for the model compounds of silylenes (**5'**) and disilanes (**6'**) and examined the relative energies for the formation of **5'** from **1'** (Eq. (3)) and the insertion reaction of **5'** into a Si–H bond of trimethylsilane (Eq. (4)). The relative energies are summarized in Table 5. Whereas the formation of **5'a** and **5'e** involves an endothermic reaction, that of **5'b**, **5'c**, and **5'd** involves an exothermic one. The stability of **5'b**, **5'c**, and **5'd** can be explained in terms of the $\pi\pi$ – $p\pi$ conjugation between the lone pair on the heteroatoms (Cl, N, and S) and the vacant orbital at the silicon center. The insertion reaction of **5'** into the Si–H bond in Me₃SiH is highly exothermic in all of the cases. Thus, in **5'a** and **5'e**, endothermic silylene formation is compensated by the highly exothermic silylene insertion reaction. The calculation also showed that the formation and insertion of amino-substituted silylene **5'c** are energetically favorable.

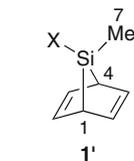
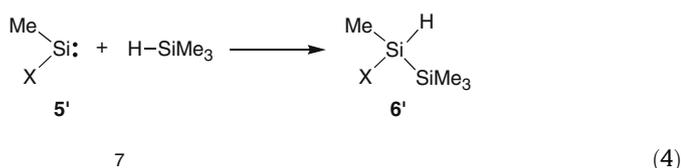
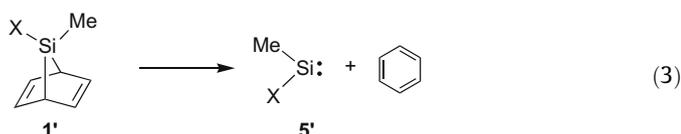


Table 4

Selected bond lengths (Å) and angles (°) of models **1'** optimized at MP2/6-31+G(d, p) level.

X =	H (1'a)	Cl (1'b)	NH ₂ (1'c)	SH (1'd)	SiH ₃ (1'e)
Si–X	1.484	2.078	1.725	2.145	2.362
Si–C(1)	1.936	1.930	1.947	1.943	1.943
Si–C(4)	1.936	1.930	1.947	1.943	1.943
Si–C(11)	1.879	1.874	1.879	1.877	1.886
C(1)–Si–C(4)	79.8	80.4	79.3	79.7	79.3
X–Si–C(11)	109.3	105.5	105.8	104.2	111.8
∑(C–Si–C) ₃	316.8	320.2	315.9	317.7	313.9

Table 5

Relative energies of Eqs. (3) and (4) (kcal/mol).

X =	H (a)	Cl (b)	NH ₂ (c)	SH (d)	SiH ₃ (e)
Eq. (3)	+4.4	–2.2	–8.0	–4.5	+3.6
Eq. (4)	–46.8	–38.8	–28.0	–35.6	–47.9
(3) + (4)	–42.4	–40.8	–36.0	–40.1	–44.3

3. Conclusion

7-Hydro-substituted silanorbornadiene **1a** was prepared and converted into chloro-substituted **1b**. The Si–Cl functionality in **1b** was converted into Si–N (**1c**) and Si–S (**1d**) functionalities by nucleophilic substitution reactions and into the Si–Li (**1f**) functionality by reductive lithiation. These transformations proceeded with net retention of configuration at the silicon. The thermolysis and photolysis of **1** revealed that silicon-functionalized 7-silanorbornadienes **1** can serve as precursors of silicon-functionalized silylenes **5**. Although the reason remains unclear, trapping of amino-substituted silylene **5c** was experimentally unsuccessful, whereas calculations showed that the model reaction was energetically favorable.

4. Experimental

4.1. General procedure

¹H (400 MHz), ¹³C (100 MHz), and ²⁹Si (79.4 MHz) NMR spectra were recorded with a JEOL EX-400 or AL-400 spectrometer. ¹H and ¹³C chemical shifts were referenced to internal CDCl₃ (¹H δ = 7.26; ¹³C δ = 77.00) and benzene-*d*₆ (¹H δ = 7.20; ¹³C δ = 128.0). ²⁹Si chemical shifts were referenced to external tetramethylsilane (δ = 0). Mass spectra (EI) were measured at 70 eV with a JEOL SX-102A mass spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. UV–Vis spectra were recorded with a Shimadzu UV-1650PC spectrophotometer. Melting points were measured with a Yanaco Micro Melting Point Apparatus and were uncorrected. Elemental analyses were performed with a Perkin–Elmer 2400CHN elemental analyzer at our laboratory. Recycling reverse-phase liquid chromatography was performed with a JAI LC-928 instrument equipped with a JAIGEL ODS-AP column. Reverse-phase column chromatography was performed using Wakogel 50C18 (particle size; 38–63 μm) (Wako Pure Chemical Industries Ltd.). Reverse-phase thin-layer chromatography was performed on plates of RP-18 F254s (Merck). Column chromatography on silica gel was performed using Kieselgel 60 (230–400 mesh) (Merck). Thin-layer chromatography was performed on plates of Silica gel 60/Kieselgel F254 (Merck). Photolysis was carried out with a high-pressure mercury lamp (Riko-kagaku Sangyo Co. Ltd.).

Chlorotrimethylsilane was treated with small pieces of sodium under nitrogen atmosphere to remove dissolved HCl, and the supernatant was used. Lithium (ribbon), magnesium shavings, palladium(II) dichloride, aniline, and diphenylacetylene were purchased from Aldrich Co. *n*-Butyllithium (*n*-BuLi) in hexane was purchased from Katayama Chemical Co. Inc. Methyl-lithium (MeLi) in diethyl ether and phenyllithium (PhLi) in cyclohexane-diethyl ether were purchased from Kanto Chemical Co. Inc. Benzenethiol, triethylsilane, 2,3-dimethyl-1,3-butadiene, and cyclodecane were purchased from Tokyo Chemical Industry Co. Ltd. Iodomethane was purchased from Kishida Chemical Co. Ltd. Acetonitrile, benzene, carbon tetrachloride, hexane, iodomethane, and triethylsilane were distilled over calcium hydride under nitrogen atmosphere. 2,3-Dimethyl-1,3-butadiene was distilled over sodium borohydride under nitrogen atmosphere. Tetrahydrofuran and diethyl ether were distilled over sodium diphenylketyl under nitrogen atmosphere, or dehydrated solvents (<10 ppm for THF and <50 ppm for Et₂O; Kanto Chemical Co. Inc.) were dried through a Solvent Dispensing System (Glass Contour) under nitrogen atmosphere. All reactions were carried out under inert gas atmosphere.

4.2. Synthesis

4.2.1. Preparation of 2,3-benzo-7-mesityl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1a**)

A solution of *o*-bromofluorobenzene (0.88 mL, 7.9 mmol) in THF (5 mL) was added dropwise to a stirred suspension of 1-mesityl-2,3,4,5-tetraphenylsilacyclopentadiene (2.02 g, 4.00 mmol) and magnesium shavings (191 mg, 8.00 mmol) in THF (35 mL) over 5 min at room temperature. The reaction mixture was stirred for 48 h at the same temperature to afford a dark brown mixture. The mixture was filtered through filter paper and the filtrate was concentrated in vacuo. The residue (4.36 g) was diluted with dry dichloromethane (ca. 10 mL) and filtered through filter paper. The filtrate was concentrated to two-thirds of its original volume and allowed to stand at -18°C for 24 h to give a white precipitate. The precipitate (3.46 g) was washed with dry CH_3CN (30 mL \times 1) and dried in vacuo to yield **1a** (1.82 g, 78% yield) as a white solid. Recrystallization of **1a** from CDCl_3 /hexane afforded colorless crystals: m.p. 223–224 $^{\circ}\text{C}$ (decomposed); ^1H NMR (CDCl_3 , δ) 2.19 (s, 6H, *o*- CH_3 in mesityl group), 2.23 (s, 3H, *p*- CH_3 in mesityl group), 5.01 (s, 1H, Si-H), 6.72 (s, 2H, *m*-H in mesityl group), 6.89–7.00 (m, 8H, phenyl protons), 7.04–7.09 (m, 4H, phenyl protons), 7.10–7.14 (m, 8H, phenyl protons), 7.18 (dd, 2H, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, benzo protons), 7.60 (dd, 2H, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, benzo protons); ^{13}C NMR (CDCl_3 , δ) 21.25, 24.64, 59.85, 122.45, 123.99, 125.32, 125.95, 126.32, 127.09, 127.59, 128.48, 129.88, 130.56, 137.54, 137.78, 140.61, 145.58, 147.07, 148.02; ^{29}Si NMR (CDCl_3 , δ) 32.94 (d, $^1J_{\text{SiH}} = 206$ Hz); UV-Vis (CH_2Cl_2 , λ_{max}) 289 nm (sh). Anal. Calc. for $\text{C}_{43}\text{H}_{36}\text{Si}$: C, 88.92; H, 6.25. Found: C, 88.79; H, 6.62%.

4.2.2. Preparation of 2,3-benzo-7-chloro-7-mesityl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1b**)

A suspension of **1a** (1.16 g, 2.00 mmol) and palladium(II) dichloride (110 mg, 0.600 mmol) in carbon tetrachloride (14.0 mL, 145 mmol) was heated to reflux for 48 h to afford a black reaction mixture. The mixture was concentrated in vacuo. The residue (1.45 g) was diluted with dry dichloromethane (100 mL) and filtered through dry florisisil pad. The filtrate was concentrated in vacuo. The obtained pale yellow solid (1.23 g) was washed with dry CH_3CN (20 mL \times 1) and dried in vacuo to give **1b** (1.11 g, 90% yield) as a white solid. Recrystallization of **1b** from CDCl_3 /hexane afforded colorless crystals: m.p. 252–253 $^{\circ}\text{C}$ (decomposed); ^1H NMR (CDCl_3 , δ) 2.08 (s, 6H, *o*- CH_3 in mesityl group), 2.24 (s, 3H, *p*- CH_3 in mesityl group), 6.29–6.45 (m, 2H, phenyl protons), 6.75 (s, 2H, *m*-H in mesityl group), 6.80–7.04 (m, 8H, phenyl protons), 7.09–7.22 (m, 12H, phenyl and benzo protons), 7.54 (dd, 2H, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, benzo protons); ^{13}C NMR (CDCl_3 , δ) 21.15, 25.57, 61.70, 123.37, 124.40, 125.34, 125.74, 126.33, 127.14, 127.57, 128.96, 130.11, 131.27, 135.97, 137.37, 140.91, 145.53, 146.87, 147.52; ^{29}Si NMR (CDCl_3 , δ) 30.29; UV-Vis (CH_2Cl_2 , λ_{max}) 290 nm (sh); Anal. Calc. for $\text{C}_{43}\text{H}_{35}\text{ClSi}$: C, 83.94; H, 5.73. Found: C, 83.88; H, 5.79%.

4.2.3. Preparation of 2,3-benzo-7-mesityl-1,4,5,6-tetraphenyl-7-(*N*-phenylamino)-7-silanorbornadiene (**1c**)

(1) A solution of *n*-BuLi in hexane (1.6 M, 1.4 mL, 2.2 mmol) was added to a solution of aniline (0.20 mL, 2.2 mmol) in THF (12 mL) and benzene (4 mL) over 5 min at 0°C . The reaction mixture was stirred for 4 h at 0°C to afford an orange solution of lithium phenylamide. (2) A suspension of **1b** (1.23 g, 2.00 mmol) in THF (12 mL) and benzene (4 mL) was added dropwise to the prepared solution of lithium phenylamide over 15 min at 0°C . The mixture was then stirred for 2 h at room temperature to afford a red mixture. Chlorotrimethylsilane (0.30 mL, 2.4 mmol) was added to the reaction mixture at 0°C and the mixture was stirred for 1 h at room temperature to produce a yellow mixture. The yellow mixture

was concentrated in vacuo. The residue was washed with hexane (20 mL) and then with CH_3CN (15 mL \times 1) to give **1c** (784 mg, 59% yield) as a white solid. Recrystallization of **1c** from CDCl_3 /hexane afforded colorless crystals: m.p. 192–193 $^{\circ}\text{C}$ (decomposed); ^1H NMR (CDCl_3 , δ) 1.87 (s, 3H, *p*- CH_3 in mesityl group), 2.22 (s, 6H, *o*- CH_3 in mesityl group), 3.93 (s, 1H, N-H), 6.22–6.24 (m, 2H, phenyl protons), 6.28–6.55 (m, 2H, phenyl protons), 6.57–6.65 (m, 3H, *m*-H in mesityl group and phenyl protons), 6.82–7.09 (m, 20H, phenyl protons), 7.22 (dd, 2H, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, benzo protons), 7.55 (dd, 2H, $^3J_{\text{HH}} = 5.6$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, benzo protons); ^{13}C NMR (CDCl_3 , δ) 21.05, 24.08, 60.80, 118.30, 119.11, 123.80, 124.29, 124.63, 125.12, 126.08, 127.12, 127.58, 127.65, 128.61, 128.83, 130.90, 138.00, 138.68, 140.34, 144.82, 146.25, 146.36, 148.54; ^{29}Si NMR (CDCl_3 , δ) 20.92; UV-Vis (CH_2Cl_2 , λ_{max}) 286 nm (sh); Anal. Calc. for $\text{C}_{49}\text{H}_{41}\text{NSi}$: C, 87.59; H, 6.15; N, 2.08. Found: C, 87.22; H, 6.15; N, 2.48%.

4.2.4. Preparation of 2,3-benzo-7-mesityl-1,4,5,6-tetraphenyl-7-(phenylthio)-7-silanorbornadiene (**1d**)

(1) A solution of *n*-BuLi in hexane (1.58 M, 1.15 mL, 1.80 mmol) was added to a solution of benzenethiol (0.18 mL, 1.8 mmol) in THF (10 mL) over 5 min at 0°C . The reaction mixture was stirred for 3 h at 0°C to afford a colorless solution of lithium phenylthiolate. (2) The prepared solution of lithium phenylthiolate was added dropwise to a suspension of **1b** (923 mg, 1.50 mmol) in THF (10 mL) and benzene (5 mL) over 20 min at 0°C . The mixture was then stirred for 15 h at room temperature to produce a colorless mixture. Iodomethane (0.12 mL, 2.0 mmol) was added to the reaction mixture at 0°C and the mixture was stirred for 1 h at room temperature, affording a pale yellow mixture. The mixture was concentrated in vacuo. The residue was washed with dry CH_3CN (25 mL \times 1) to give **1d** as a white solid (764 mg, 74% yield); m.p. 150.5–152.5 $^{\circ}\text{C}$ (decomposed); ^1H NMR (CDCl_3 , δ) 1.87 (s, 6H, *o*- CH_3 in mesityl group), 2.15 (s, 3H, *p*- CH_3 in mesityl group), 6.36 (br, 2H, phenyl protons), 6.53 (s, 2H, *m*-H in mesityl group), 6.70–6.81 (m, 2H, phenyl protons), 6.81–6.92 (m, 5H, phenyl protons), 6.92–7.08 (m, 6H, phenyl protons), 7.08–7.20 (m, 8H, benzo and phenyl protons), 7.32–7.45 (m, 6H, benzo and phenyl protons); ^{13}C NMR (CDCl_3 , δ) 20.90, 25.08, 61.46, 123.81, 124.74, 125.41, 125.89, 126.24, 127.14, 127.39, 127.84, 128.60, 129.17, 130.46, 131.43, 131.46, 133.81, 137.50, 138.63, 140.22, 145.72, 147.94, 148.42; ^{29}Si NMR (CDCl_3 , δ) 45.46; UV-Vis (CH_2Cl_2 , λ_{max}) 283 nm (sh); Anal. Calc. for $\text{C}_{49}\text{H}_{40}\text{SiS}$: C, 85.42; H, 5.85. Found: C, 85.70; H, 5.69%.

4.2.5. Preparation of 7-lithio **1f** and trapping with Me_3SiCl to form 2,3-benzo-7-mesityl-7-trimethylsilyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1e**)

(1) A suspension of lithium ribbon (8 mg, 1 mmol) and naphthalene (167 mg, 1.30 mmol) was stirred in THF (2 mL) at room temperature for 6 h, resulting in a dark green solution of lithium naphthalenide. The solution was diluted further with 2 mL of THF. (2) A suspension of **1b** (186 mg, 0.300 mmol) in THF (2 mL) and benzene (4 mL) was added dropwise to the prepared solution of lithium naphthalenide over 15 min at -78°C . The reaction mixture was stirred for 4 h at -78°C to afford a dark blue solution of 7-lithio derivative **1f**. (3) Chlorotrimethylsilane (0.32 mL, 2.6 mmol) was added to the solution at -78°C . The reaction mixture was stirred for 1 h at -78°C and then allowed to warm to room temperature. The reaction mixture was stirred for another 30 min at room temperature and was concentrated in vacuo thereafter. The residue was diluted with dry hexane (5 mL) and filtered through filter paper. The filtrate was concentrated in vacuo. The pale yellow residue (266 mg) was washed with dry CH_3CN (3 mL \times 1) and dried in vacuo to give **1e** (102 mg, 52% yield) as a white solid. Recrystallization of **1e** from CDCl_3 /hexane afforded colorless crystals: m.p.

243–244 °C (decomposed); ¹H NMR (CDCl₃, δ) –0.30 (s, 9H, SiMe₃), 2.07 (s, 6H, *o*-CH₃ in mesityl group), 2.23 (s, 3H, *p*-CH₃ in mesityl group), 6.17–6.28 (m, 2H, phenyl protons), 6.71 (s, 2H, *m*-H in mesityl group), 6.78–7.22 (m, 20H, phenyl protons), 7.72 (dd, 2H, ³J_{HH} = 5.6 Hz, ⁴J_{HH} = 3.2 Hz, benzo protons); ¹³C NMR (CDCl₃, δ) 1.37, 21.11, 25.06, 63.16, 123.15, 123.77, 125.28, 125.59, 126.88, 127.05, 128.36, 129.48, 129.61, 130.49, 132.11, 138.08, 138.49, 138.88, 144.64, 148.21, 149.92; ²⁹Si NMR (CDCl₃, δ) –15.91 (Si–SiMe₃), 56.17 (Si–SiMe₃); UV–Vis (CH₂Cl₂, λ_{max}) 288 nm (sh), 309 nm (sh); Anal. Calc. for C₄₆H₄₄Si₂: C, 84.61; H, 6.79. Found: C, 84.23; H, 6.90%.

4.2.6. Thermolysis of 7-silanorbornadienes **1**: General procedure for trapping experiment of silylenes **5** with HSiEt₃

A mixture of **1** and 100 equivalents of degassed triethylsilane in a pressure-resistant glass container was refluxed at 250 °C for 2 h or at 180 °C for 1 h. The obtained mixture was concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation or recycling reverse-phase liquid chromatography using CH₃CN as eluent, giving disilane **6**.

4.2.7. 1,1,1-Triethyl-2-mesityldisilane (**6a**) [14a]

The isolation of **6a** was carried out by recycling reverse-phase liquid chromatography using CH₃CN as eluent (*R_f* = 0.30): colorless oil (44% yield); ¹H NMR (C₆D₆, δ) 0.71 (q, 6H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 0.99 (t, 9H, Si–CH₂–CH₃, ³J_{HH} = 8.0 Hz), 2.16 (s, 3H, *p*-CH₃ in mesityl group), 2.46 (s, 6H, *o*-CH₃ in mesityl group), 4.46 (s, 2H, Si–H, ¹J_{SiH} = 184 Hz), 6.81 (s, 2H, *m*-H in mesityl group); ¹³C NMR (C₆D₆, δ) 4.93, 8.31, 21.29, 24.62, 126.54, 128.55, 138.53, 144.25; ²⁹Si NMR (C₆D₆, δ) –82.09 (SiH), –5.52 (SiEt₃).

4.2.8. 1-Chloro-2,2,2-triethyl-1-mesityldisilane (**6b**) [14a]

The isolation of **6b** was carried out by bulb-to-bulb distillation (185–220 °C (bath temperature)/0.80 mmHg): colorless oil (70% yield); ¹H NMR (C₆D₆, δ) 0.69–0.85 (m, 6H, Si–CH₂–CH₃), 0.98 (t, 9H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 2.10 (s, 3H, *p*-CH₃ in mesityl group), 2.51 (s, 6H, *o*-CH₃ in mesityl group), 6.00 (s, 1H, ¹J_{SiH} = 204 Hz, Si–H), 6.73 (s, 2H, *m*-H in mesityl group); ¹³C NMR (C₆D₆, δ) 3.38, 8.01, 21.09, 24.44, 128.17, 129.30, 140.45, 144.42; ²⁹Si NMR (C₆D₆, δ) –14.74 (SiH), –6.35 (SiEt₃).

4.2.9. 2,2,2-Triethyl-1-mesityl-1-(*N*-phenylamino)disilane (**6c**)

The isolation of **6c** was carried out by bulb-to-bulb distillation (230–250 °C (bath temperature)/0.15 mmHg): colorless oil (53% yield); ¹H NMR (C₆D₆, δ) 0.72 (q, 6H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 0.98 (t, 9H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 2.12 (s, 3H, *p*-CH₃ in mesityl group), 2.53 (s, 6H, *o*-CH₃ in mesityl group), 3.45 (d(br), 1H, ³J_{HH} = 2.8 Hz, N–H), 5.92 (d, 1H, ³J_{HH} = 4.0 Hz, ¹J_{SiH} = 195 Hz, Si–H), 6.71–6.82 (m, 5H, *m*-H in mesityl group and phenyl protons), 7.05–7.12 (m, 2H, phenyl protons); ¹³C NMR (C₆D₆, δ) 4.15, 8.32, 21.26, 23.86, 116.24, 118.73, 128.73, 129.46, 129.58, 139.23, 144.26, 148.09; ²⁹Si NMR (C₆D₆, δ) –40.36 (SiH), –9.56 (SiEt₃); Anal. Calc. for C₂₁H₃₃NSi₂: C, 70.92; H, 9.35; N, 3.94. Found: C, 70.57; H, 9.42; N, 3.57%.

4.2.10. 2,2,2-Triethyl-1-mesityl-1-(phenylthio)disilane (**6d**)

The isolation of **6d** was carried out by bulb-to-bulb distillation (230–250 °C (bath temperature)/0.30 mmHg): colorless oil (48% yield); ¹H NMR (C₆D₆, δ) 0.73–0.91 (m, 6H, Si–CH₂–CH₃), 1.04 (t, 9H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 2.09 (s, 3H, *p*-CH₃ in mesityl group), 2.56 (s, 6H, *o*-CH₃ in mesityl group), 5.79 (s, 1H, ¹J_{SiH} = 198 Hz, Si–H), 6.75 (s, 2H, *m*-H in mesityl group), 6.86–6.95 (m, 3H, phenyl protons), 7.48–7.52 (m, 2H, phenyl protons); ¹³C NMR (C₆D₆, δ) 4.60, 8.24, 21.11, 24.75, 126.47, 128.99, 129.26, 133.66, 135.51, 139.69, 144.66; ²⁹Si NMR (C₆D₆, δ) –28.00 (SiH), –5.18 (SiEt₃);

Anal. Calc. for C₂₁H₃₂SSi₂: C, 67.67; H, 8.65. Found: C, 67.76; H, 8.60%.

4.2.11. 1,1,1-Triethyl-2-mesityl-3,3,3-trimethyltrisilane (**6e**) [14a]

The isolation of **6e** was carried out by recycling reverse-phase liquid chromatography using CH₃CN as eluent (*R_f* = 0.25): colorless oil (42% yield); ¹H NMR (C₆D₆, δ) 0.29 (s, 9H, SiMe₃), 0.77–0.83 (m, 6H, Si–CH₂–CH₃), 1.03 (t, 9H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 2.16 (s, 3H, *p*-CH₃ in mesityl group), 2.43 and 2.58 (brs, 6H, *o*-CH₃ in mesityl group), 4.35 (s, 1H, ¹J_{SiH} = 160 Hz, Si–H), 6.82 and 6.85 (brs, 2H, *m*-H in mesityl group); ¹³C NMR (C₆D₆, δ) 0.89, 5.65, 8.43, 21.08, 25.26, 26.29, 128.46, 128.64, 128.97, 129.20, 137.61; ²⁹Si NMR (C₆D₆, δ) –81.23 (SiH), –13.22 (SiMe₃), –1.98 (SiEt₃).

4.2.12. Photolysis of 7-silanorbornadiene derivatives **1** with a high-pressure mercury lamp: general procedure for trapping experiment of silylenes **5** with HSiEt₃

A mixture of silanorbornadiene **1** (0.10 mmol) and triethylsilane (1.0 mmol or 10 mmol) in benzene-*d*₆ (1.0 mL) in a Schlenk tube or a pressure-resistant glass container was degassed by the freeze-pump-thaw method three times. The mixture was irradiated with a high-pressure mercury lamp (λ = 313 nm) at room temperature. After the irradiation, the reaction mixture was concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation or recycling reverse-phase liquid chromatography using CH₃CN as eluent to give disilane **6**.

4.2.13. 1,1,1-Triethyl-2-mesityldisilane (**6a**)

The isolation of **6a** was carried out by recycling reverse-phase liquid chromatography using CH₃CN as eluent (*R_f* = 0.30): 46% yield.

4.2.14. Formation of **6b** and reaction with PhLi

(1) A mixture of **1b** (123 mg, 0.200 mmol) and triethylsilane (0.32 mL, 2.0 mmol) in benzene-*d*₆ (2.0 mL) was irradiated for 48 h to give a mixture of **6b** and **7**. (2) A solution of PhLi in cyclohexane–Et₂O (1.04 M, 0.23 mL, 0.24 mmol) was added to the mixture of **6b** and **7** in Et₂O (2.0 mL) over 1 min at 0 °C. The reaction mixture was stirred for 5 min at 0 °C and for another 5 h at room temperature. Then, methyl iodide (0.015 mL, 0.25 mmol) was added to the reaction mixture at 0 °C. The mixture was stirred for 5 min and was allowed to warm to room temperature. The reaction mixture was concentrated in vacuo and the residue was subjected to reverse-phase column chromatography (50 mL) using CH₃CN–THF (2/1) as eluent (*R_f* = 0.55) to give **8**.

1,1,1-Triethyl-2-mesityl-2-phenyldisilane (**8**) [14a]: colorless oil (43% yield); ¹H NMR (C₆D₆, δ) 0.87 (q, 6H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 1.03 (t, 9H, ³J_{HH} = 8.0 Hz, Si–CH₂–CH₃), 2.17 (s, 3H, *p*-CH₃ in mesityl group), 2.48 (s, 6H, *o*-CH₃ in mesityl group), 5.54 (s, 1H, ¹J_{SiH} = 177 Hz), 6.85 (s, 2H, *m*-H in mesityl group), 7.16–7.18 (m, 3H, phenyl protons), 7.68–7.70 (m, 2H, phenyl protons); ¹³C NMR (C₆D₆, δ) 5.20, 8.56, 21.30, 25.46, 128.24, 128.92, 128.99, 135.47, 135.86, 138.98, 144.80; ²⁹Si NMR (C₆D₆, δ) –48.64 (SiH), –6.98 (SiEt₃).

4.2.15. 2,2,2-Triethyl-1-mesityl-1-(phenylthio)disilane (**6d**)

The isolation of **6d** was carried out by bulb-to-bulb distillation (240–250 °C (bath temperature)/0.50 mmHg): 35% yield.

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