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Synthesis of Kinetically Stabilized 1-Silanaphthalenes and Their Properties

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The first kinetically stabilized 1-silanaphthalenes bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group or a 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group were synthesized from the corresponding overcrowded bromosilanes by dehydrobromination using LDA (lithium diisopropylamide) in THF at −40 °C, respectively. The structures of 1-silanaphthalenes were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR, UV–vis, Raman, and high-resolution mass spectroscopic analyses. These results and the NICS calculations indicated high aromaticity of the 1-silanaphthalenes. In spite of such high aromaticity, Tbt-substituted 1-silanaphthalene is thermally unstable and undergoes gradual dimerization in C_6D_6 solution to give the corresponding [4 + 2] dimer. By contrast, 1-silanaphthalene bearing a Bbt group on the Si atom was thermally stable even on heating in C_6D_6 at 120 °C. Tbt-substituted 1-silanaphthalene has high reactivity toward addition reactions at both 1,2- and 1,4-positions, giving the corresponding adducts in the reactions with H_2O, MeOH, mesitonitrile oxide, benzophenone, and elemental chalcogens. Tbt-substituted 1-silanaphthalene underwent 1,4-addition reaction with CCl_4 to give cis- and trans-adducts having a Cl atom on the Si atom and a CCl_3 group at the 4-position.

Heteroaromatic compounds containing a heavier main group element have attracted much interest from the standpoints of fundamental and applied chemistry. As for the elements of the third period, the chemistry of $[4n + 2]\pi$ electron systems containing a phosphorus atom has been extensively studied,[1] and the compounds are known to show highly aromatic characters in their structures, properties, and reactivities. By contrast, the chemistry of silaaromatic compounds has been less developed because of the extremely high reactivity and instability of low-coordinated silicon compounds.[2]

On the other hand, we have reported the synthesis of various low-coordinated compounds, such as heavy ketones[3] and heavy azo compounds,[4] by taking advantage of kinetic stabilization afforded by an effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt),[5] and revealed their structures and properties of such compounds. As an extension of this chemistry to the field of low-coordinated silicon compounds, we have succeeded in the synthesis of kinetically stabilized silaaromatic compounds, e.g., silabenzene, 2-silanaphthalene, and 9-silaanthracene, bearing a Tbt group on the central Si atom.[6] The aromatic character of these species was revealed and confirmed by NMR, UV–vis, and Raman spectral data, X-ray crystallographic analyses and theoretical calculations. In spite of having considerable aromatic character, these compounds were found to undergo ready 1,2- and/or 1,4-addition reactions due to the high reactivity of the Si–C double bond.[6,7]

Although there has been no example for the synthesis of 1-silanaphthalenes, we have already revealed by the NICS calculations that the aromaticity of 1- and 2-silanaphthalenes is comparable to each other and slightly less than that of naphthalene.[6a] On the other hand, Ashe et al. reported the synthesis of 1-boratanaphthalene and 1-arsanaphthalene, in which they used 1-bromo-2-(3-bromoallyl)benzene as a key precursor for 1-heteranaphthalenes.[8] These results prompted us to examine the synthesis of a 1-silanaphthalene using 1-bromo-2-(3-bromoallyl)benzene as a starting material.

In a preliminary communication, we have already described the synthesis of the first 1-silanaphthalene **1a** bearing a Tbt group and found that **1a** gradually dimerized at room temperature to afford the corresponding [4 + 2] dimer.[9] We now wish to delineate the synthesis, properties, and reactivities of kinetically stabilized 1-silanaphthalenes **1a** and **1b**, the latter of which bears a sterically bulkier ligand, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt)[10] (Chart 1).

Results and Discussion

At first, 1,4-dihydro-1-silanaphthalene **2a** was synthesized by the reaction of 1-bromo-2-(3-bromoallyl)benzene with *t*-butyllithium in Et_2O at −78 °C, followed by the subsequent addition of $TbtSiH_3$ at room temperature. Bromination of **2a** with NBS (1 molar amount) at room temperature in benzene resulted in the formation of the corresponding bromosilane **3a**,

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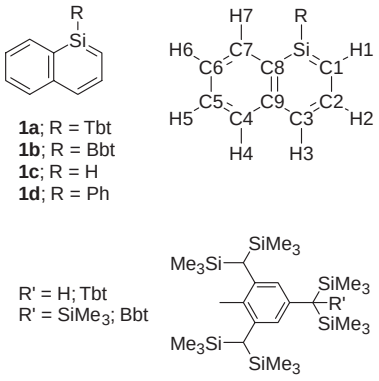
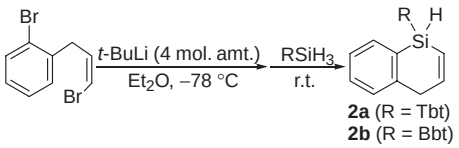
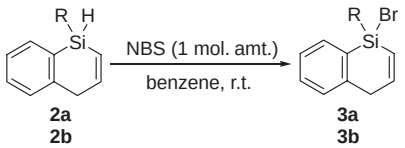
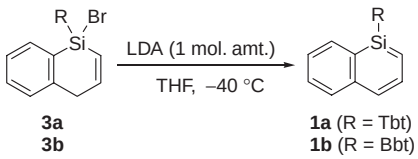


Chart 1.





Scheme 1.



Scheme 2.

which is a suitable precursor of 1-silanaphthalene **1a** (Scheme 1). Another precursor **3b** was prepared by the same procedure as that for **3a**, using $BbtSiH_3$[11] instead of $TbtSiH_3$.

1-Silanaphthalenes **1a** and **1b** were synthesized by the dehydrobromination of bromosilanes **3a** and **3b** using LDA in THF at −40 °C, respectively (Scheme 2). 1-Silanaphthalene **1a** is thermally unstable at room temperature to give the corresponding dimer **4**, while **1b** is thermally stable (the details of the dimerization reaction are described below). 1-Silanaphthalenes **1a** and **1b** are highly moisture-sensitive.

Properties of 1-Silanaphthalenes. The structures of 1-silanaphthalenes **1a** and **1b** were unambiguously confirmed by ^1H, ^{13}C, ^{29}Si NMR, Raman, UV–vis, and high-resolution mass spectroscopy, although good crystals suitable for X-ray structural analysis could not be obtained in either case. The ^1H and ^{13}C NMR signals of **1a** and **1b** were assigned by 2D NMR techniques. In the ^1H NMR spectra, characteristic down-field shifts were observed for the protons at 4-position (from 3.76–3.79 ppm for **2a** to 7.17 ppm for **1a** and from 3.75–3.85 ppm for **2b** to 7.14 ppm for **1b**), and all peaks assignable to those for the 1-silanaphthalene rings of **1a** and **1b** in the ^1H and ^{13}C NMR spectra were observed in aromatic regions (Table 1). The ^{29}Si NMR spectra of **1a** and **1b** showed signals at 91.7 (**1a**) and 90.9 (**1b**) ppm, respectively, which were assigned to those for the sp^2 silicon atoms. The ^{29}Si NMR chemical shift for **1a** (91.2 ppm) in the mixed solvent (THF:C_6D_6 = 5:1) was very similar to that in C_6D_6, suggesting the absence of the coordination of THF as a Lewis base to the silicon atom of the 1-silanaphthalene ring. Since it is well known that the coupling constant between adjacent two atoms can be a good index for the π-bond order,[12] measurement of the $^1J_{Si-C}$ values for the two Si–C bonds in the 1-silanaphthalene rings may give useful information about the properties of the 1-silanaphthalene rings. Although the $^1J_{Si-C}$ values in **1a** could not be measured due to the gradual dimerization of **1a** at 10 °C (vide infra), we could observe those in **1b** as 90 (Si–C1) and 77 Hz (Si–C8). The $^1J_{Si-C}$ values in **1b** are close to those (76–92 Hz) for the silaaromatic compounds previously synthesized,[6] and the bond order of the 1,2-bond is larger than that of the 1,9-bond in **1b** as well as naphthalene ($^1J_{C-C}$ = 60.3 and 55.9 Hz, respectively). The results of NMR studies on **1a** and **1b** strongly suggest the delocalized 10π-electron structure for the 1-silanaphthalene ring system, i.e., the aromatic character of 1-silanaphthalene. In order to confirm the conclusion deduced from the experimental NMR data, we carried out theoretical calculations for the model compounds, 1-silanaphthalene (**1c**) and 1-phenyl-1-silanaphthalene (**1d**) (Table 1). It seems that the results for **1c** disagree with the chemical shifts observed for **1a** and **1b**. However, it is likely that the calculated NMR chemical shifts of **1c** were influenced by the polar Si–H bond. The chemical shifts calculated for **1d** are in good agreement with those experimentally observed for **1a** and **1b**, indicating little perturbation by the bulky Tbt or Bbt group attached to the 1-silanaphthalene system.[13,14]

Table 1. Observed and Calculated ^{29}Si, ^1H, and ^{13}C NMR Chemical Shifts of 1-Silanaphthalenes

	Observed		Calculated[a)]	
	1a (R = Tbt)	**1b** (R = Bbt)	**1c** (R = H)	**1d** (R = Ph)
Si	91.74	90.89	75.66	95.03
H1	7.10	7.00	7.38	7.00
H2	8.07	8.03	8.02	8.05
H3	7.17	7.14	7.25	7.14
H4	7.73	7.72	7.82	7.80
H5	7.36	7.34	7.60	7.58
H6	7.15	7.12	7.24	7.22
H7	8.22	8.18	8.11	8.38
C1	116.74	115.68	126.63	115.85
C2	137.95	137.89	142.39	142.58
C3	116.89	116.71	123.49	121.17
C4	131.40	131.35	135.92	135.71
C5	128.76	128.77	132.98	132.59
C6	120.58	120.61	125.03	124.71
C7	133.19	133.19	136.01	135.66
C8	131.52	131.03	140.86	135.37
C9	145.33	145.36	150.22	150.64

a) Calculated by GIAO-B3LYP/6-311G(d)(6-311G(3d) for Si and 6-311G(d) for C, H)//B3LYP/6-31G(d) level.

The UV–vis spectra of **1a** and **1b** showed absorption maxima red-shifted over 300 nm [λ_{max} 249 (ε, 7×10^4), 255 (7×10^4), 261 (6×10^4), 304 (2×10^4), 354 (2×10^4), 367 (2×10^4), and 379 (1×10^4) nm for **1a** and λ_{max} 255 (ε,

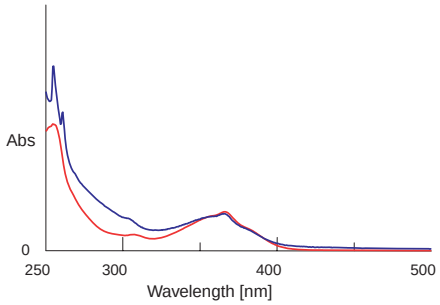


Fig. 1. UV–vis spectra of 1-silanaphthalenes **1a** (blue line) and **1b** (red line).

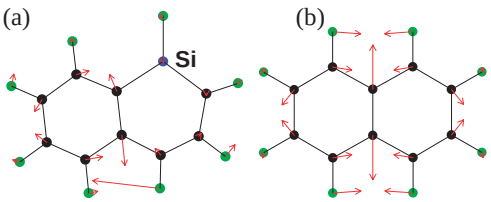
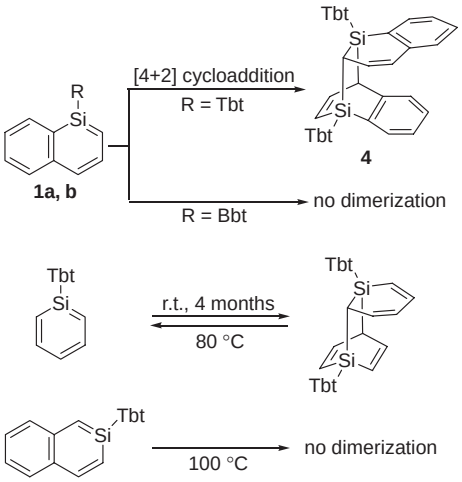


Fig. 2. Calculated vibration modes with maximum intensity: (a) 1-silanaphthalene **1c** (1328 cm^{-1}) (b) naphthalene (1360 cm^{-1}).

5×10^4), 307 (7×10^3), 356 (1×10^4), 367 (2×10^4), and 384 (9×10^3) nm for **1b**] (Fig. 1). Although these maxima are shifted to a longer wavelength region than those of naphthalene, the spectral patterns observed for **1a** and **1b** were similar to those reported for naphthalene [221 (ε, 1.33×10^5), 286 (9.3×10^3), and 312 (2.9×10^2) nm][15] and Tbt-substituted 2-silanaphthalene [267 (ε, 2×10^4), 327 (7×10^3), and 387 (2×10^3) nm].[6a,b] Two prominent bands of **1a** and **1b** in the regions around 250 nm and 300–400 nm are assignable to the ^1B band and the overlapped ^1L_a and ^1L_b bands, respectively. These results suggest that the 1-silanaphthalene ring system has an electronic structure similar to those of naphthalene and 2-silanaphthalene.

The Raman spectrum of **1a**, which is well reproduced in the calculations of vibrational frequencies for 1-silanaphthalene **1c**, showed some characteristic strong lines (Fig. 2). The strongest line of **1a** (1340 cm^{-1}) corresponding to the most intense lines of **1c** (1328 cm^{-1}) and **1d** (1326 cm^{-1})[16] was assigned to the skeletal vibration within the 1-silanaphthalene ring plane. It also resembles those assigned to the most intense line of naphthalene and the Tbt-substituted 2-silanaphthalene,[6a,b] indicating that **1a** has a ring skeleton similar to those of naphthalene and the Tbt-substituted 2-silanaphthalene.

In our previous report, we proposed that 1-silanaphthalene has as much aromaticity as naphthalene, judging from the results of theoretical calculations, i.e., the NICS(1) values and the energies for aromatic isodesmic isomerizations.[6,17–19] The NICS(1) values for 1-silanaphthalene (**1c**) were calculated as large negative values (−9.1 ppm for the C_5Si ring and −10.9 ppm for the C_6 ring), which were comparable to that for naphthalene (−11.5 ppm) [GIAO-B3LYP/6-311G(d) level]. If one takes into account all the results of spectroscopic studies and theoretical calculations, one can conclude that 1-silanaphthalenes **1a** and **1b** are as highly aromatic as the silaaromatic compounds previously reported.[6]



Scheme 3.

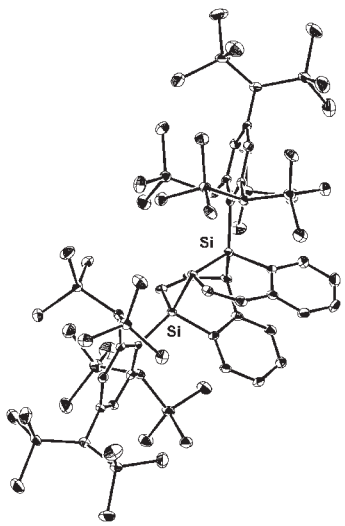


Fig. 3. Molecular structure of 1-silanaphthalene dimer **4** (50% probability). All hydrogen atoms and solvated CH_2Cl_2 molecules are omitted for clarity.

Reactivity of 1-Silanaphthalene. Despite the high aromaticity of 1-silanaphthalene **1a**, its Si–C double bond (Si–C1) and 1-silabuta-1,3-diene (Si–C1–C2–C3) moiety are quite reactive toward various reagents with the modes of 1,2- and/or 1,4-addition reactions.

In contrast to other stable silaaromatic compounds,[6] 1-silanaphthalene **1a** was found to undergo gradual dimerization in solution at room temperature to give the corresponding dimer **4** via a [4 + 2] cycloaddtion reaction (Scheme 3). The structure of dimer **4** was confirmed based on the ^1H, ^{13}C, and ^{29}Si NMR spectral data, and the stereochemistry in **4** was finally determined by an X-ray structural analysis (Fig. 3). The dimerization reaction of **1a** was completed in 1 month at room temperature, while heating of **1a** in C_6D_6 at 100 °C for 12 h afforded the dimer **4** in 49% yield with complete consumption of **1a**. This conversion of **1a** into **4** indicates that dimer **4** is thermodynamically more stable than **1a** under these conditions. A Tbt-substituted silabenzene also gives the corresponding [4 + 2] dimer when its C_6D_6 solution is left at room temperature for 4 months, and the dimer dissociates into the monomer quanti-

tatively by heating at 80 °C for 9 h.[11,20] By contrast, thermolysis of **4** at 120 °C in the presence of benzophenone gave no benzophenone adduct of **1a** (vide infra), indicating no dissociation of **4** into **1a** by heating at this temperature. A Tbt-substituted 2-silanaphtalene did not give any dimers on heating in C_6D_6 solution at 100 °C.[6a,b] The difference between 1-silanaphthalene **1a** and the Tbt-substituted 2-silanaphthalene in the dimerization can be explained using the results of theoretical calculations [B3LYP/6-31G(d)] on the dimerization energies (Table 2). Three types of structures (Type A, B, and C) are expected as dimerization products of silanaphthalenes (Chart 2), and each type of structure will have two endo- and exo-isomers and two combinations of (C, Si) and (Si, C), respectively. In this case, dimer **4** is the type A-endo (C, Si). One can see from Table 2 that the dimerized reactions of 1-silanaphthalene are more exothermic (Type A: $\Delta H = -174$–119 kJ/mol) than those of 2-silanaphthalene (Type B: $\Delta H = -28.0$–-11.7 kJ/mol and Type C: $\Delta H = -47.7$–38.5 kJ/mol) (Scheme 4). Type B dimers are presumably unstable due to the unfavorable structures with a weak Si–C double bond, and Type C dimers are also undesirable products because they lose the aromaticity of both silabenzene and benzene moieties.

Table 2. Calculated ΔH (kJ/mol) of Dimerization Reaction for Silanaphthalenes [B3LYP/6-31G(d)]

	(E, E′)			
	exo (C, Si)	endo (C, Si)	exo (Si, C)	endo (Si, C)
Type A	−174	−173	−120	−119
Type B	−13.8	−11.7	−28.0	−27.6
Type C	−47.7	−46.4	34.7	38.5

On the other hand, 1-silanaphthalene **1b** bearing a Bbt group on the Si atom did not dimerize, but kept the monomeric structure under the same conditions as those for **1a**. It should be noted that thermal stability of 1-silanaphthalene is dramatically changed by the slight modification of a protection group from Tbt to Bbt. These results suggested that Bbt group, which can avoid the dimerization of **1b**, is slightly bulkier than Tbt group. However, both 1-silanaphthalenes, **1a** and **1b**, have enough reaction space for small molecules around the reactive center. Indeed, the reaction of **1b** with H_2O afforded the corresponding 1,2- and 1,4-adducts, as in the case of **1a**.

Reactions of **1a** with H_2O and MeOH afforded the corresponding 1,2- and 1,4-adducts competitively in both cases. In the reaction with MeOH, the ratio of **6a** and **6b** was dependent upon the solvent used (Scheme 5, Table 3).[21]

When 1-silanaphthalene **1a** was allowed to react with mesitonitrile oxide and benzophenone, [2 + 3] and [4 + 2] cycloaddition reactions proceeded to afford the corresponding cycloadducts **7** and **8** in 49% and 60% yields, respectively (Fig. 4). These cycloaddition reactions of **1a** can be understood as typical reactions of the previously reported silenes and 1-silabuta-1,3-diene, respectively.

It is known that Si=C and Si=Si bonds react with elemental sulfur to afford the corresponding three-membered ring compounds, i.e., sulfurized products having an episulfide skeleton.[22] Meanwhile, we have synthesized a variety of cyclic polysulfides containing group 14 elements as stable compounds by taking advantage of a Tbt group,[23] and we have recently reported the sulfurization and selenation of germaaromatic compounds kinetically stabilized by a Tbt group, leading to the formation of the corresponding three- or five-membered cyclic chalcogenides.[18,24] Based on these situations, sulfurization of **1a** was examined in the hope of forming the corresponding

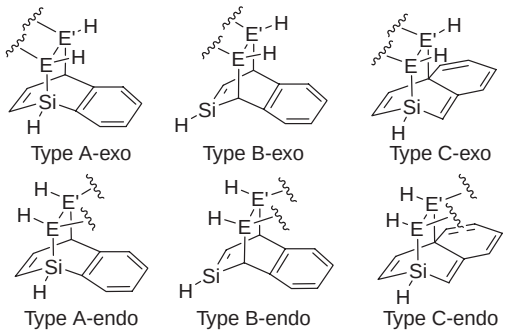
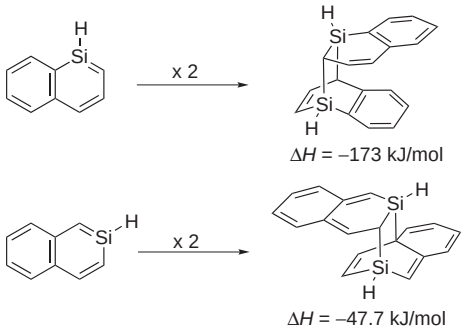
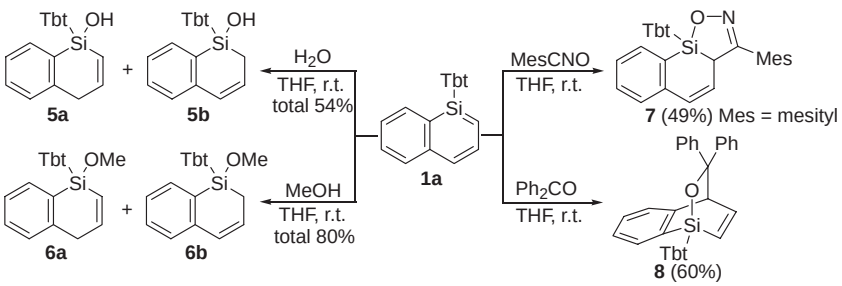


Chart 2.



Scheme 4.



Scheme 5.

Table 3. The Ratio of 1,2-Adduct to 1,4-Adduct in the Reaction of 1-Silanaphthalene **1a** with Methanol

Solvent	Ratio		Yield (%)
	1,4-Adduct	1,2-Adduct	
THF	3	5	80
Hexane	10	9	87

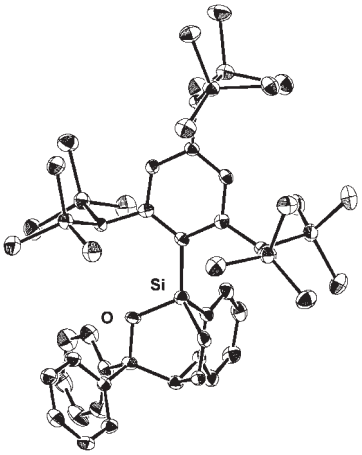
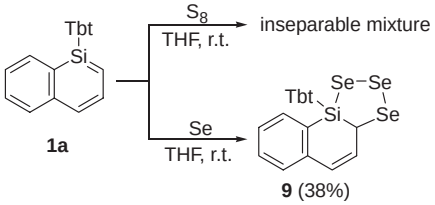


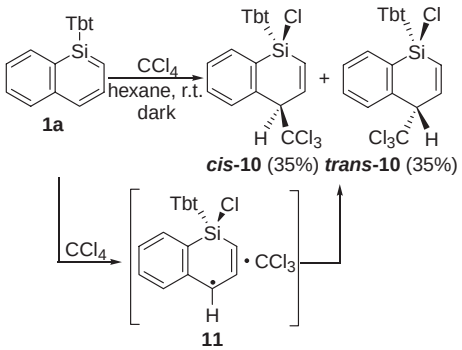
Fig. 4. Molecular structure of benzophenone adduct of 1-silanaphthalene **8** (50% probability). All hydrogen atoms are omitted for clarity.



Scheme 6.

polysulfides fused with the 1-silanaphthalene ring. In contrast to the case of Tbt-substituted 2-silanaphthalene, which gave the corresponding five-membered cyclic trisulfide in 20% yield selectively, the reaction of **1a** with elemental sulfur afforded an inseparable mixture. Although the mass spectrum of the mixture indicated the formation of three- and five-membered-ring products, further attempts of separation and characterization of these products were unsuccessful. On the other hand, the reaction of **1a** with elemental selenium afforded the corresponding five-membered-ring compound **9** in 38% yield (Scheme 6). The structure of **9** was determined by ^{1}H, ^{13}C, ^{29}Si, and ^{77}Se NMR spectrometry together with elemental analysis. In the ^{77}Se NMR spectrum, three signals assignable to those of the triselenasilolane ring were observed at 332.4, 567.1, and 743.3 ppm.

It has already been reported that the reaction of anthracene with CCl_4 under photo-irradiation gives a 9-chloro-10-trichloromethyl adduct of anthracene.[25] As for the reactions of low-coordinated silicon compounds with haloalkanes, Kira et al. have performed detailed kinetic studies on the reactions of disilenes with haloalkanes.[26] More recently, the reaction of di-



Scheme 7.

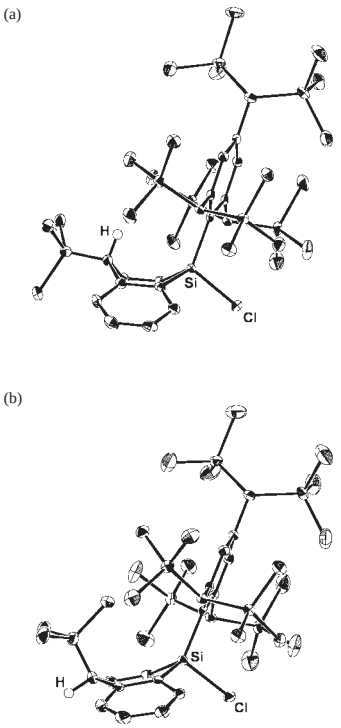


Fig. 5. Molecular structures of ***cis*-10** (a) and ***trans*-10** (b) (50% probability). Hydrogen atoms except for the hydrogen atom at the 4-position of the 1,4-dihydro-1-silanaphthalene ring are omitted for clarity.

metallenes with carbon tetrachloride was theoretically studied using DFT calculations.[27] However, the reactivity of silaaromatic compounds toward CCl_4 has been unknown so far. Interestingly, 1-silanaphthalene **1a** reacted with CCl_4 in hexane to give two types of products, ***cis*-10** and ***trans*-10**, each in 35% yield, as shown in Scheme 7. The regio- and stereochemistries of the products were confirmed by X-ray crystallographic analysis (Fig. 5, Table 4). The reaction of **1a** with CCl_4 using THF as a solvent instead of hexane resulted in the formation of a complex mixture. Although the mechanism of non-selective formation of ***cis*-10** and ***trans*-10** in hexane is not clear at present, one can postulate the initial formation of the corresponding reactive radical pairs **11**, followed by the radical coupling reactions giving the products (Scheme 7). In THF, the intermediate **11** might be generated as in the case of hexane, and it probably reacted with THF to afford a complex mixture.

Table 4. Crystallographic Data for Compounds **4**, **8**, ***cis*-10**, and ***trans*-10b**

	4·1.5CH_2Cl_2	**8**	***cis*-10**	***trans*-10b**
Formula	$C_{72}H_{132}Si_{14}\cdot 1.5CH_2Cl_2$	$C_{49}H_{76}OSi_7$	$C_{37}H_{66}Cl_4Si_7$	$C_{37}H_{66}Cl_4Si_7$
Formula weight	1518.43	877.73	849.33	849.33
Crystal size (mm^3)	0.30 × 0.25 × 0.25	0.10 × 0.10 × 0.10	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.20
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	13.1719(4)	11.1554(6)	9.649(2)	9.392(3)
b (Å)	18.4733(3)	13.6820(8)	13.051(3)	13.041(4)
c (Å)	20.1882(4)	17.8237(12)	20.681(5)	20.882(7)
α (deg)	74.8772(7)	78.780(2)	91.9360(19)	80.398(12)
β (deg)	79.6862(8)	79.610(3)	99.205(3)	80.142(13)
γ (deg)	78.213(2)	82.755(5)	111.9395(19)	70.886(8)
V ($Å^3$)	4600.96(18)	2613.0(3)	2372.1(9)	2363.9(14)
Z	2	2	2	2
D_{calc} ($g\cdot cm^{-3}$)	1.096	1.116	1.189	1.193
Independent reflections	15217	8617	8350	8306
No. of parameters	865	532	697	621
R_1 ($I > 2\sigma(I)$)	0.059	0.054	0.036	0.049
wR_2 (all data)	0.177	0.116	0.105	0.124
Goodness of fit	1.05	1.11	1.10	1.06

Conclusion

We succeeded in the synthesis of 1-silanaphthalenes **1a** and **1b**, the first examples of a stable 1-silanaphthalene. Detailed analyses of the spectral data (^1H, ^{13}C, ^{29}Si NMR, UV–vis, and Raman spectra) and theoretical calculations revealed that 1-silanaphthalenes **1a** and **1b** have a delocalized 10π-electron ring system and high aromaticity. Although 1-silanaphthalene **1a** bearing a Tbt group was thermally unstable to give the corresponding [4 + 2] dimer **4**, **1b** bearing a Bbt group, which is slightly bulkier than the Tbt group, was stable in solution even at 100 °C. In spite of its aromaticity, 1-silanaphthalene **1a** readily reacted with some reagents to give the corresponding adducts at the 1,2- and 1,4-positions of the 1-silanaphthalene ring. In addition, the reaction of **1a** with CCl_4 afforded the corresponding 1,4-adducts, ***cis*-10** and ***trans*-10**. The geometries of ***cis*-10** and ***trans*-10** were confirmed by X-ray crystallographic analysis to show that a Cl atom was introduced onto the Si atom and a CCl_3 group was on the 4-position in both compounds. We propose that this reaction proceeded via a radical mechanisim, i.e., the initial formation of a radical pair intermediate and the subsequent radical coupling reaction. Further experiments and theoretical calculations to confirm the reaction mechanism of silaaromatic compounds with CCl_4 are currently in progress.

Experimental

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and were freshly distilled prior to use. The ^1H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-400 or AL-300 spectrometer using $CHCl_3$ (7.25 ppm) or C_6D_5H (7.15 ppm) as an internal standard for ^1H NMR spectrometry, and using $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm) as the standard for ^{13}C NMR spectrometry. The ^{29}Si NMR (59 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL AL-300 spectrometer using tetramethylsilane as an external standard. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Wet column chromatography (WCC) was performed on Nacalai Tesque Silica Gel 60. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908, LC-918, or LC-908-C60 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (for LC-908 and LC-918) or JAIGEL 1H-40 and 2H-40 columns (for LC-908-C60) (eluent: chloroform or toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Electronic spectra were recorded on a JASCO Ubest V-570. Raman spectra were measured at room temperature on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG & G PARC 1421 intensified photodiode array detector. An NEC GLG 108 He–Ne laser (632.8 nm) was used for Raman excitation. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 1-Bromo-2-(3-bromoallyl)benzene,[8] {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane ($TbtSiH_3$),[28] and {2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}silane ($BbtSiH_3$)[11] were prepared according to the reported procedure.

Theoretical Calculations. The geometries of related reference molecules **1c** and **1d** were optimized by using the Gaussian 98 program[14] at the B3LYP/6-31G(d) level of density functional theory. The GIAO-B3LYP and NICS[17] calculations were carried out with the 6-311G(3d) basis set for Si and the 6-311G(d) basis set for C and H.

Preparation of 1-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene (2a). To a solution of 1-bromo-2-(3-bromoallyl)benzene (0.991 g, 3.62 mmol) in ether (10 mL) was added 2.32 mol/L pentane solution of *t*-butyllithium (6.24 mL, 14.5 mmol) at −78 °C. After the solution was stirred at −78 °C for 1.5 h and at room temperature for 1 h, a solution of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane (357 mg, 0.613 mmol) in ether (4 mL) was added at room temperature. After further stirring for 1 h, the reaction mixture was quenched with

an aqueous solution of NH_4Cl and extracted with ether. The organic layer was dried over Na_2SO_4, filtered, and then evaporated. The crude product was purified by FCC (hexane) and GPLC ($CHCl_3$) to give 1,4-dihydro-1-silanaphthalene, **2a** (152 mg, 43%). **2a**: colorless powder. mp. 168–171 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.19 (s, 9H), −0.16 (s, 9H), 0.04 (s, 18H), 0.06 (s, 18H), 1.32 (s, 1H), 2.30 (br s, 1H), 2.33 (br s, 1H), 3.76–3.79 (m, 2H), 5.58–5.60 (m, 1H), 6.14 (ddd, C*H*Si, ^3J = 14 Hz, ^4J = 2 Hz, ^4J = 2 Hz, 1H), 6.29 (br s, 1H), 6.38 (br s, 1H), 6.94 (ddd, SiCHC*H*, ^3J = 14 Hz, ^3J = 4 Hz, ^3J = 4 Hz, 1H), 7.11–7.19 (m, 2H), 7.26–7.32 (m, 1H), 7.44 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.52 (q), 0.72 (q), 0.76 (q), 0.98 (q), 1.27 (q), 28.17 (d), 28.48 (d), 30.53 (d), 36.08 (t), 121.93 (d), 123.72 (s), 124.95 (d), 125.56 (d), 126.91 (d), 128.99 (d), 129.17 (d), 131.33 (s), 136.09 (d), 144.25 (s), 144.97 (s), 146.07 (d), 152.69 (s), 152.87 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −54.4, 1.8, 1.9. Anal. Calcd for $C_{36}H_{68}Si_7$: C, 61.99; H, 9.83%. Found: C, 61.93; H, 10.06%.

Preparation of 1-{2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene (2b). Compound **2b** was synthesized from 1-bromo-2-(3-bromoallyl)benzene (750 mg, 2.74 mmol) and {2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}silane (1.79 g, 2.74 mmol) in 26% yield (552 mg) by the same procedure as that used for **2a**. **2b**: colorless powder. mp. 223–225 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.16 (s, 18H), 0.09 (s, 18H), 0.25 (s, 27H), 2.48 (s, 2H), 3.75–3.85 (m, 2H), 5.62–5.64 (m, 1H), 6.17 (ddd, C*H*Si, ^3J = 14 Hz, ^4J = 2 Hz, ^4J = 2 Hz, 1H), 6.71 (s, 2H), 6.95 (ddd, SiCHC*H*, ^3J = 14 Hz, ^3J = 4 Hz, ^3J = 4 Hz, 1H), 7.12–7.20 (m, 2H), 7.28–7.33 (m, 1H), 7.44 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 1.21 (q), 1.74 (q), 5.43 (q), 22.11 (s), 29.41 (d), 36.14 (t), 124.85 (d), 125.60 (d), 126.41 (s), 126.64 (d), 129.10 (d), 129.34 (d), 131.05 (s), 136.04 (d), 144.15 (s), 146.08 (d), 146.75 (s), 152.69 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −53.90, 0.70, 1.53, 1.61. Anal. Calcd for $C_{39}H_{76}Si_8$: C, 60.86; H, 9.95%. Found: C, 60.74; H, 10.05%.

Preparation of 1-Bromo-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene (3a). A solution of **2a** (47.2 mg, 0.0678 mmol) and NBS (12.1 mg, 0.0678 mmol) in benzene (3 mL) was stirred in the air. After 12 h, the solvent was evaporated. Separation of the mixture by GPC ($CHCl_3$) afforded bromosilane **3a** (49.2 mg, 94%). **3a**: colorless powder. mp. 208–210 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.17 (s, 9H), 0.14 (s, 9H), 0.03 (s, 9H), 0.04 (s, 18H), 0.06 (s, 9H), 1.30 (s, 1H), 2.50 (br s, 1H), 2.56 (br s, 1H), 3.49–3.64 (m, 2H), 6.26 (br s, 1H), 6.49 (dd, ^3J = 14 Hz, ^4J = 2 Hz, 1H), 6.79 (br s, 1H), 6.98 (ddd, ^3J = 14 Hz, ^3J = 5 Hz, ^3J = 4 Hz, 1H), 7.14–7.17 (m, 1H), 7.28–7.39 (m, 2H), 8.02 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.76 (q), 0.80 (q), 1.06 (q), 1.25 (q), 1.40 (q), 28.22 (d), 28.64 (d), 30.65 (d), 36.28 (t), 122.59 (d), 122.90 (s), 126.58 (d), 127.68 (d), 128.57 (d), 129.39 (d), 130.59 (d), 136.44 (s), 137.99 (d), 144.50 (s), 146.16 (s), 146.19 (d), 152.78 (s), 153.29 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −23.4, −0.7, 2.6, 2.8. Anal. Calcd for $C_{36}H_{67}Si_7Br$: C, 55.69; H, 8.70%. Found: C, 55.67; H, 8.74%.

Preparation of 1-Bromo-1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene (3b). Compound **3b** was synthesized from **2b** (135.3 mg, 0.160 mmol) by the same procedure as that used for **3a**. **3b** (136.4 mg, 91%): colorless powder. mp. 220–222 °C (dec). ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.06 (s, 18H), 0.09 (s, 18H), 0.28 (s, 27H), 2.77 (s, 2H), 3.46–3.61 (m, 2H), 6.54 (d, ^3J = 13 Hz, 1H), 6.69 (s, 2H), 6.99 (dd, ^3J = 13 Hz, ^3J = 4 Hz, 1H) 7.15 (d, ^3J = 7 Hz, 1H), 7.26–7.37 (m, 2H), 8.02 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 1.64 (q), 1.94 (q), 5.55 (q), 22.39 (s), 29.14 (d), 36.32 (t), 125.93 (s), 126.72 (d), 127.57 (d), 128.53 (d), 129.34 (d), 131.18 (d), 136.83 (s), 138.15 (d), 144.99 (s), 146.38 (d), 148.16 (s), 152.88 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −22.88, 1.15, 2.08, 2.23. Anal. Calcd for $C_{39}H_{75}Si_8Br$: C, 55.20; H, 8.91%. Found: C, 55.15; H, 8.89%.

Synthesis of 1-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1-silanaphthalene (1a). In a glovebox filled with argon, **3a** (40.2 mg, 0.0519 mmol) was dissolved in THF (2 mL). To this solution was added lithium diisopropylamide (a 2.0 mol/L solution in heptane/THF/ethylbenzene, 0.026 mL, 0.052 mmol, Aldrich Chemicals Co.) at −40 °C. After the removal of solvents under reduced pressure, cold hexane was added to the residue and the resulting suspension was filtered through Celite®. Evaporation of the filtrate afforded **1a** (34.8 mg, 97%). **1a**: pale yellow crystals. mp. 127–132 °C (dec). ^{1}H NMR (400 MHz, 10 °C, C_6D_6) δ 0.04 (s, 9H), 0.08 (s, 9H), 0.15 (s, 18H), 0.18 (s, 18H), 1.55 (s, 1H), 2.49 (br s, 1H), 2.57 (br s, 1H), 6.64 (br s, 1H), 6.77 (br s, 1H), 7.10 (d, ^3J = 12 Hz, 1H), 7.15 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 7.17 (d, ^3J = 9 Hz, 1H), 7.36 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.73 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 8.07 (dd, ^3J = 12 Hz, ^3J = 9 Hz, 1H), 8.22 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (100 MHz, 10 °C, C_6D_6) δ 0.94 (q), 1.20 (q), 1.26 (q), 1.54 (q), 31.68 (d), 36.52 (d), 36.95 (d), 116.74 (d), 116.89 (d), 120.58 (d), 121.77 (d), 123.64 (s), 126.29 (d), 128.76 (d), 131.40 (d), 131.52 (s), 133.19 (d), 137.95 (d), 145.33 (s), 148.16 (s), 153.05 (s), 153.16 (s). ^{29}Si NMR (59 MHz, 10 °C, C_6D_6) δ 2.2, 2.5, 2.6, 3.3, 91.7. UV–vis (hexane) λ_{max} 244 ($\varepsilon = 6 \times 10^4$), 249 ($7 \times 10^4$), 255 ($7 \times 10^4$), 261 ($6 \times 10^4$), 304 ($2 \times 10^4$), 354 ($2 \times 10^4$), 367 ($2 \times 10^4$), and 379 ($1 \times 10^4$) nm. Anal. Calcd for $C_{36}H_{66}Si_7$: C, 62.17; H, 9.56%. Found: C, 60.41; H, 9.31% [analyzed as a hydrolysis product of **1a** (calcd for $C_{36}H_{68}OSi_7$: C, 60.60; H, 9.61%.) due to its high sensitivity to moisture]. High resolution FAB-MS m/z calcd for $C_{36}H_{66}Si_7$ ($[M]^+$): 694.3549, found: 694.3556 ($[M]^+$).

Synthesis of 1-{2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1-silanaphthalene (1b). 1-Silanaphthalene **1b** was synthesized from **3b** (26.9 mg, 0.0318 mmol) by the same procedure as that used for **1a**. **1b** (24.3 mg, 99%): pale yellow crystals. mp. 177–178 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.07 (s, 18H), 0.15 (s, 18H), 0.37 (s, 27H), 2.73 (s, 2H), 7.00 (d, ^3J = 12 Hz, 1H), 7.07 (s, 2H), 7.12 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 7.14 (d, ^3J = 9 Hz, 1H), 7.34 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.72 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 8.03 (dd, ^3J = 12 Hz, ^3J = 9 Hz, 1H), 8.18 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ 1.35 (q), 1.52 (q), 5.45 (q), 23.19 (s), 38.56 (d), 115.68 (d), 116.71 (d), 120.61 (d), 126.31 (d), 126.77 (s), 128.77 (d), 131.03 (s), 131.35 (d), 133.19 (d), 137.89 (d), 145.36 (s), 149.77 (s), 152.87 (s). ^{29}Si NMR (60 MHz, C_6D_6) δ 1.14, 1.57, 2.93, 90.89. UV–vis (hexane) λ_{max} 255 ($\varepsilon = 5 \times 10^4$), 307 ($7 \times 10^3$), 356 ($1 \times 10^4$), 367 ($2 \times 10^4$), and 384 ($9 \times 10^3$) nm. Anal. Calcd for $C_{39}H_{74}Si_8$: C, 61.02; H, 9.72%. Found: C, 59.65; H, 9.81% [analyzed as a hydrolysis product of **1b** (calcd for $C_{39}H_{76}OSi_8$: C, 59.62; H, 9.75%) due to its high sensitivity to moisture]. High resolution FAB-MS m/z calcd for $C_{39}H_{74}Si_8$ ($[M]^+$): 766.3945, found: 766.3947 ($[M]^+$).

Dimerization of 1a. In a glovebox filled with argon, **1a** (32.4 mg, 0.0466 mmol) was dissolved in C_6D_6 (0.6 mL). The solution was degassed and sealed in a 5 ϕ NMR tube. After heating at 100 °C for 12 h, the tube was opened. The solvent was evaporated and hexane was added to the residue. Filtration of the reaction mixture through Celite®, followed by separation with GPLC ($CHCl_3$) and PTLC (hexane), afforded **4** (15.9 mg, 49%). **4**: colorless powder. mp. 144–148 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.25 (s, 9H), −0.22 (s, 9H), −0.18 (s, 18H), 0.04 (s, 27H), 0.08 (s, 9H), 0.09 (s, 18H), 0.18 (s, 9H), 0.21 (s, 9H), 1.26 (d, ^3J = 10 Hz, 1H), 1.28 (s, 1H), 1.35 (s, 1H), 2.10–2.16 (m, 4H), 4.02 (d, ^3J = 7 Hz, 1H), 5.89 (d, ^3J = 11 Hz, 1H), 6.10 (d, ^3J = 8 Hz, 1H), 6.26–6.48 (m, 6H), 6.57–6.59 (m, 1H), 6.77–6.79 (m, 1H), 6.81–6.84 (m, 2H), 6.95–6.98 (m, 1H), 7.57–7.64 (m, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.81 (q), 0.91 (q), 0.98 (q), 0.99 (q), 1.14 (q), 1.27 (q), 1.37 (q), 1.49 (q), 1.69 (q), 1.75 (q), 2.06 (q), 2.12 (q), 15.36 (d), 27.11 (d), 27.21 (d), 28.48 (d × 2), 30.30 (d), 30.46 (d), 42.28 (d), 122.89 (d), 122.93 (d), 123.18 (d), 123.23 (s), 125.82 (d), 125.85 (d), 127.60 (d), 127.84 (d), 127.86 (d), 127.95 (d), 128.32 (s), 128.59 (d), 128.66 (d), 129.53 (d), 131.21 (d), 133.40 (d), 133.81 (d), 134.81 (s), 135.40 (s), 140.57 (s), 143.87 (s), 144.46 (s), 144.88 (s), 148.91 (d), 152.39 (s), 152.54 (s), 152.83 (s), 152.99 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −33.2, −24.6, 1.67, 1.71, 1.9, 1.98, 2.04, 2.1, 2.2, 2.3, 2.7. Anal. Calcd for $C_{72}H_{132}Si_{14}$: C, 62.17; H, 9.56%. Found: C, 61.85; H, 9.53%.

Reaction of 1a with H_2O. To a THF solution (2 mL) of **1a** (30.0 mg, 0.0432 mmol) was added H_2O (0.5 mL) at room temperature, and the solution was stirred for 1.5 h. After the solvent was removed, the reaction mixture was subjected to GPLC and PTLC (hexane:THF = 10:1) to afford a mixture of 1-{2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene-1-ol (**5a**) and 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-1-silanaphthalene-1-ol (**5b**) (21.6 mg, total 54%). The ratio of **5a** and **5b** was 5:6, as judged by ^{1}H NMR. Careful purification by PTLC (hexane:THF = 10:1) resulted in the separation into 3 portions: pure **5a** (the top; 5.4 mg), a mixture of **5a** and **5b** (the middle; 13.4 mg), and pure **5b** (the bottom; 2.8 mg). **5a**: colorless powder. mp. 181–183 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.14 (s, 18H), 0.00 (s, 18H), 0.037 (s, 9H), 0.041 (s, 9H), 1.30 (s, 1H), 1.83 (s, Si–O*H*, 1H), 2.51 (br s, 1H), 2.54 (br s, 1H), 3.62–3.78 (m, 2H), 6.26 (br s, 1H), 6.29 (ddd, ^3J = 15 Hz, ^4J = 2 Hz, ^4J = 2 Hz, 1H), 6.36 (br s, 1H), 6.92 (ddd, ^3J = 15 Hz, ^3J = 5 Hz, ^3J = 4 Hz, 1H), 7.21 (m, 2H), 7.31 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.63 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.75 (q), 0.76 (q), 0.90 (q), 1.05 (q), 1.25 (q), 27.11 (d), 27.38 (d), 30.39 (d), 36.12 (t), 122.35 (d), 124.05 (s), 125.99 (d), 127.51 (d), 128.76 (d), 129.25 (d), 129.94 (d), 135.00 (d), 137.04 (s), 144.02 (s), 144.81 (s), 145.33 (d), 152.71 (s), 152.98 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −27.88, 0.60, 0.64, 0.72, 0.83. Anal. Calcd for $C_{36}H_{68}OSi_7$: C, 60.60; H, 9.61%. Found: C, 60.40; H, 9.62%. **5b**: colorless powder. mp. 199–200 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.13 (s, 18H), −0.007 (s, 9H), 0.010 (s, 9H), 0.04 (s, 9H), 0.05 (s, 9H), 1.30 (s, 1H), 1.77–1.85 (m, 1H), 1.88 (s, Si–O*H*, 1H), 2.02 (ddd, ^2J = 19 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 2.30 (s, 2H), 6.01–6.08 (m, 1H), 6.25 (br s, 1H), 6.36 (br s, 1H), 6.42 (dd, ^3J = 11 Hz, ^4J = 1 Hz, 1H), 7.09 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.19 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1H), 7.34 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.59 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.76 (q), 0.77 (q), 0.81 (q), 0.90 (q), 1.14 (q), 1.27 (q), 18.53 (t), 27.34 (d), 27.66 (d), 30.39 (d), 122.25 (d), 125.39 (s), 127.03 (d), 127.35 (d), 127.68 (d), 128.59 (d), 130.32 (d), 130.61 (d), 134.39 (d), 135.67 (s), 142.15 (s), 144.86 (s), 152.21 (s), 152.50 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −11.66, 1.65, 1.78, 1.84, 1.94. Anal. Calcd for $C_{36}H_{68}OSi_7$: C, 60.60; H, 9.61%. Found: C, 60.31; H, 9.75%.

Reaction of 1a with Methanol. To a solution of **1a** (26.7 mg, 0.0384 mmol) in THF (2 mL), was added MeOH (0.5 mL) at room temperature, and the solution was stirred for 30 min. After the solvent was removed, the mixture was subjected to GPLC and PTLC (hexane) to afford a mixture of 1-methoxy-1-{2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl}-1,4-dihydro-1-silanaphthalene (**6a**) and 1-methoxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-1-silanaphthalene (**6b**) (22.3 mg, total 80%), and the ratio of **6a** and **6b** was 3:5 as judged by ^{1}H NMR. The mixture was separated into 3 portion by careful purification with PTLC (hexane): pure **6b** (the top; 6.3 mg), a mixture of **6a** and **6b** (the middle; 12.6 mg), and pure **6a** (the bottom; 3.4 mg). **6a**: colorless powder. mp. 172–174 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.17 (s, 18H), −0.01 (s, 9H), 0.01 (s, 9H), 0.03 (s, 18H), 1.28 (s, 1H), 2.61 (s, 1H), 2.62 (s, 1H), 3.09 (s, 3H), 3.62–3.81 (m, 2H), 6.14 (ddd, ^3J = 15 Hz, ^4J = 3 Hz, ^4J = 1 Hz, 1H), 6.23 (br s, 1H), 6.34 (br s, 1H), 7.00 (ddd, ^3J = 15 Hz, ^3J = 5 Hz, ^3J = 3 Hz, 1H), 7.16–7.21 (m, 2H), 7.30 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1.5 Hz, 1H), 7.53 (dd, ^3J = 8 Hz, ^4J = 3 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.67 (q), 0.74 (q), 0.77 (q), 0.90 (q), 0.99 (q), 1.27 (q), 26.76 (d), 26.96 (d), 30.32 (d), 36.14 (t), 49.56 (q), 122.38 (d), 123.49 (s), 125.74 (d), 127.48 (d), 127.72 (d), 128.66 (d), 129.10 (d), 133.93 (s), 135.04 (d), 144.66 (s), 144.84 (s), 146.75 (d), 152.89 (s), 153.20 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −24.62, 1.51, 1.55, 1.71, 1.78. Anal. Calcd for $C_{37}H_{70}OSi_7$: C, 61.08; H, 9.70%. Found: C, 60.84; H, 9.73%. **6b**: colorless powder. mp. 192–194 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.16 (s, 18H), −0.01 (s, 9H), 0.02 (s, 9H), 0.028 (s, 9H), 0.030 (s, 9H), 1.28 (s, 1H), 1.84–1.86 (m, 2H), 2.38 (s, 1H), 2.41 (s, 1H), 3.21 (s, 3H), 6.03–6.10 (m, 1H), 6.23 (br s, 1H), 6.34 (br s, 1H), 6.42 (dd, ^3J = 11 Hz, ^4J = 2 Hz, 1H), 7.10 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.17 (ddd, ^3J = 9 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 7.33 (ddd, ^3J = 9 Hz, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 7.50 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.75 (q), 0.76 (q), 0.96 (q), 1.09 (q), 1.33 (q), 14.67 (t), 26.91 (d), 27.19 (d), 30.33 (d), 49.89 (q), 122.29 (d), 124.90 (s), 126.75 (d), 127.34 (d), 128.00 (d), 128.74 (d), 130.17 (d), 130.80 (d), 132.23 (s), 134.93 (d), 143.00 (s), 144.73 (s), 152.49 (s), 152.78 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −9.62, 1.61, 1.73, 1.94. Anal. Calcd for $C_{37}H_{70}OSi_7$: C, 61.08; H, 9.70%. Found: C, 60.90; H, 9.71%.

Reaction of 1a with Mesitonitrile Oxide. In a glovebox filled with argon, **1a** (42.7 mg, 0.0614 mmol) and mesitonitrile oxide (30.3 mg, 0.188 mmol) were dissolved in THF (2 mL). After stirring for a few minutes, the solvent was evaporated and hexane was added to the residue. Filtration of the mixture through Celite®, followed by separation with GPLC ($CHCl_3$) and PTLC ($CHCl_3$/hexane = 1/1), afforded **7** (23.5 mg, 45%). **7**: colorless powder. mp. 206–209 °C. ^{1}H NMR (300 MHz, 50 °C, $CDCl_3$) δ −0.17 (br s, 18H), 0.05 (s, 9H), 0.06 (s, 9H), 0.14 (s, 9H), 0.16 (s, 9H), 1.39 (s, 1H), 1.99 (s, 3H), 2.20 (s, 3H), 2.22 (br s, 1H), 2.27 (s, 4H), 3.45 (d, ^3J = 8 Hz, 1H), 5.85 (dd, ^3J = 11 Hz, ^3J = 8 Hz, 1H), 6.40 (br s, 1H), 6.49 (br s, 1H), 6.51 (d, ^3J = 11 Hz, 1H), 6.84 (br s, 2H), 7.13–7.39 (m, 3H), 7.69 (d, ^3J = 7 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.20 (q), 0.52 (q), 0.63 (q), 0.78 (q), 1.55 (q), 1.86 (q), 19.89 (q), 20.07 (q), 21.06 (q), 28.89 (d), 29.34 (d),

30.78 (d), 36.89 (d), 121.92 (d), 122.72 (d), 123.61 (s), 126.78 (d), 127.70 (d), 128.40 (d), 128.60 (d), 129.37 (s), 129.70 (d), 130.24 (s), 131.04 (d), 133.53 (d), 135.35 (d), 135.46 (s), 137.64 (s), 138.19 (s), 140.29 (s), 146.44 (s), 152.50 (s), 152.73 (s), 164.86 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ 1.88, 1.96, 2.06, 2.31, 6.38. Anal. Calcd for $C_{49}H_{76}OSi_7$: C, 64.49; H, 9.06%. Found: C, 64.15; H, 9.22%.

Reaction of 1a with Benzophenone. In a glovebox filled with argon, **1a** (39.5 mg, 0.0570 mmol) and benzophenone (33.0 mg, 0.182 mmol) were dissolved in THF (2 mL). After stirring for 12 h, the solvent was evaporated and hexane was added to the residue. Filtration of the mixture through Celite®, followed by separation with GPLC (toluene) and PTLC ($CHCl_3$/hexane = 1/10), afforded **8** (30.0 mg, 60%). **8**: colorless powder. mp. 209–210 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ 0.04 (br s, 36H), 0.11 (s, 9H), 0.12 (s, 9H), 1.43 (s, 1H), 2.61 (br s, 1H), 2.96 (br s, 1H), 4.87 (dd, ^3J = 7 Hz, ^4J = 1 Hz, 1H), 6.44 (br s, 1H), 6.53 (br s, 1H), 6.58 (dd, ^3J = 13 Hz, ^4J = 1 Hz, 1H), 6.83–7.35 (m, 13H), 7.63–7.66 (m, 2H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.81 (q), 0.98 (q), 1.20 (q), 1.32 (q), 1.78 (q), 27.45 (d), 27.90 (d), 30.80 (d), 53.14 (d), 84.40 (s), 118.3 (s), 122.69 (d), 124.62 (d), 125.82 (d), 126.21 (d), 126.25 (d), 127.17 (d), 127.19 (d), 127.43 (d), 127.62 (d), 127.90 (d), 128.12 (d), 131.39 (d), 136.20 (d), 138.75 (s), 145.80 (s), 146.16 (s), 146.25 (s), 146.69 (s), 148.98 (d), 153.38 (s), 153.57 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −23.6, 2.0, 2.1, 2.39, 2.44, 2.5. Anal. Calcd for $C_{53}H_{78}OSi_7$: C, 67.05; H, 8.73%. Found: C, 66.83; H, 9.00%.

Reaction of 1a with Elemental Selenium. To a solution of **1a** (54.7 mg, 0.0787 mmol) in THF (2 mL) was added elemental selenium (51.8 mg, 0.648 mmol) at room temperature. The solution was stirred for 48 h. After the solvent was removed in vacuo, purification of the residue by GPLC (toluene) and FCC (hexane) afforded 9b-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3a,9b-dihydro-1,2,3-triselena-9b-silacyclopenta[α]naphthalene (**9**) (28.0 mg, 38%) as orange brown powder. **9**: mp. 153–155 °C. ^{1}H NMR (300 MHz, rt, C_6D_6) δ 0.14 (s, 9H), 0.15 (s, 18H), 0.16 (s, 9H), 0.20 (s, 18H), 1.46 (s, 1H), 2.57 (s, 1H), 2.59 (s, 1H), 4.67 (d, ^3J = 6 Hz, 1 H), 6.21–6.34 (m, 2H), 6.57 (br s, 1H), 6.66 (br s, 1H), 6.79 (dd, ^3J = 7 Hz, ^4J = 4 Hz, 1H), 7.00–7.03 (m, 2H), 8.03 (dd, ^3J = 5 Hz, ^4J = 3 Hz, 1H). ^{13}C NMR (75 MHz, rt, C_6D_6) δ 0.99 (q), 1.39 (q), 1.46 (q), 1.74 (q), 1.87 (q), 29.93 (d), 30.22 (d), 31.20 (d), 37.23 (d), 122.61 (s), 123.45 (d), 128.53 (d), 128.66 (d), 128.71 (d), 130.12 (d), 130.59 (d), 131.67 (d), 135.17 (s), 137.96 (d), 141.60 (s), 146.57 (s), 153.94 (s), 154.32 (s). ^{29}Si NMR (59 MHz, rt, C_6D_6) δ 2.13, 2.52, 3.00, 21.56. ^{77}Se NMR (57 MHz, rt, C_6D_6) δ 332.4, 567.1, 743.3. Anal. Calcd for $C_{36}H_{66}Se_3Si_7$: C, 46.37; H, 7.13%. Found: C, 46.37; H, 7.20%.

Reaction of 1a with CCl_4. To a 2 mL of hexane solution of **1a** (37.6 mg, 0.0542 mmol) was added CCl_4 (0.1 mL). The solution was stirred for 12 h in the dark. The solvent was evaporated and filtration of the mixture through Celite®, followed by separation with GPLC ($CHCl_3$) and PTLC (hexane), afforded *cis*- and *trans*-1-chloro-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4-trichloromethyl-1,4-dihydro-1-silanaphthalene, ***cis*-10** (16.2 mg, 35%) and ***trans*-10** (15.9 mg, 35%).

***cis*-10:** colorless powder. mp. 222–224 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.08 (s, 9H), −0.05 (s, 9H), 0.05 (s, 36H), 1.33 (s, 1H), 2.38 (br s, 1H), 2.43 (br s, 1H), 4.52 (dd, ^3J = 4 Hz, ^4J = 2 Hz, 1H), 6.28 (br s, 1H), 6.40 (br s, 1H), 6.58 (dd, ^3J = 13 Hz, ^4J = 2 Hz, 1H), 7.21 (dd, ^3J = 13 Hz, ^3J = 4 Hz, 1H), 7.37–7.41 (m, 2H), 7.92 (dd, ^3J = 5 Hz, ^4J = 4 Hz, 1H), 8.04 (dd, ^3J = 5 Hz, ^4J = 3 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.71 (q), 0.86 (q), 0.95 (q), 1.15 (q), 1.23 (q), 28.82 (d), 29.12 (d), 30.85 (d), 62.77 (d), 100.00 (s), 122.01 (s), 122.62 (d), 126.86 (d), 127.14 (d), 127.58 (d), 128.57 (d), 135.12 (d), 137.26 (d), 139.91 (s), 142.62 (s), 146.92 (s), 147.00 (d), 153.52 (s), 153.83 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −16.3, 2.0, 2.1, 2.3. Anal. Calcd for $C_{37}H_{66}Cl_4Si_7$: C, 52.32; H, 7.83%. Found: C, 52.04; H, 7.74%.

***trans*-10:** colorless powder. mp. 225–226 °C. ^{1}H NMR (300 MHz, rt, $CDCl_3$) δ −0.14 (s, 9H), −0.02 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.14 (s, 9H), 0.16 (s, 9H), 1.31 (s, 1H), 2.58 (s, 1H), 2.63 (s, 1H), 4.65 (d, ^3J = 7 Hz, 1H), 6.12 (br s, 1H), 6.35 (br s, 1H), 6.83 (d, ^3J = 14 Hz, 1H), 7.15 (dd, ^3J = 14 Hz, ^3J = 7 Hz, 1H), 7.38–7.53 (m, 3H), 8.17 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H). ^{13}C NMR (75 MHz, rt, $CDCl_3$) δ 0.87 (q), 1.00 (q), 1.16 (q), 1.63 (q), 1.88 (q), 28.06 (d), 28.65 (d), 30.52 (d), 63.06 (d), 102.04 (s), 122.87 (d), 124.10 (s), 127.67 (d), 128.62 (d), 128.93 (d), 133.40 (d), 138.06 (d), 138.83 (d), 139.37 (s), 140.87 (s), 143.44 (d), 145.95 (s), 152.09 (s), 152.72 (s). ^{29}Si NMR (59 MHz, rt, $CDCl_3$) δ −22.4, 2.0, 2.3. Anal. Calcd for $C_{37}H_{66}Cl_4Si_7$: C, 52.32; H, 7.83%. Found: C, 51.92; H, 7.83%.

X-ray Structural Determination. Crystallographic data for [**4**·1.5CH_2Cl_2], **8**, ***cis*-10**, and ***trans*-10** are collected in Table 4. Single crystals were grown at room temperature by the slow evaporation of the corresponding saturated solution in CH_2Cl_2/CH_3CN for [**4**·1.5CH_2Cl_2], and $CHCl_3$/CH_3CN for **8**, ***cis*-10**, and ***trans*-10**, respectively. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 7.1071 Å) to $2\theta_{max}$ = 50 at 93 K. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[29] The structures of the disordered CH_2Cl_2 molecules in [**4**·1.5CH_2Cl_2] were restrained using the SADI and ISOR instructions. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in [**4**·1.5CH_2Cl_2] and **8** were placed using AFIX instructions. All hydrogen atoms in ***cis*-10** were refined isotropically. Some hydrogen atoms of ***trans*-10** were refined isotropically, while the other hydrogen atoms were placed using AFIX instructions. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (Nos. CCDC 257052 for [**4**·1.5CH_2Cl_2], CCDC 257053 for **8**, CCDC 257054 for ***cis*-10**, and CCDC 257055 for ***trans*-10**). Copies of the data can be obtained free of charge 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).

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