Synthesis and Properties of a Kinetically Stabilized 9-Silaphenanthrene[#]

Norihiro Tokitoh,*,[§] Akihiro Shinohara,[§] Takeshi Matsumoto,[§] Takahiro Sasamori,[§]
Nobuhiro Takeda,[§,1] and Yukio Furukawa[†]

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan, and Department of Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Reaction of 9-bromo-9,10-dihydro-9-silaphenanthrene (**6**) with lithium diisopropylamide (LDA) in THF at room temperature afforded kinetically stabilized 9-silaphenanthrene **1a** bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). 9-Silaphenanthrene **1a** was isolated as pale yellow crystals, and the structure of **1a** was completely determined by spectroscopic and X-ray crystallographic analyses. The ^{1}H and ^{13}C NMR chemical shifts corresponding to the 9-silaphenanthrene ring of **1a** were observed in a typical aromatic region, while the central silicon atom showed the characteristic signal at 86.9 ppm in the ^{29}Si NMR in C_6D_6. The 9-silaphenanthrene ring of **1a** showed completely planar geometry, indicating that 9-silaphenanthrene has a delocalized 14π-electron system as an aromatic compound. In spite of its high thermal stability, **1a** still has high reactivity at the 9,10-position toward small reagents such as H_2O.

Introduction

Aromatic compounds have an important role in organic chemistry, and a lot of studies have been reported about the concept of *aromaticity*.[2] Despite many theoretical studies on silaaromatic compounds, which contain one or more silicon atoms in the ring system, silaaromatic compounds were still elusive and difficult to isolate under ambient conditions. In the past decade, we have made many efforts to establish the chemistry of neutral metallaaromatic systems and succeeded in the synthesis of a variety of sila- and germaaromatic compounds as stable compounds by taking advantage of efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl (denoted as Bbt).[3−5] These studies demonstrated that the kinetically stabilized neutral metallaaromatic compounds containing a heavier group 14 element possess considerable aromaticity as well as the corresponding all-carbon systems. Very recently, we have reported the synthesis, properties, and reactivities of the first stable neutral stannaaromatic compound, 2-Tbt-3-*tert*-butyl-2-stannanaphthalene.[6]

Meanwhile, polynuclear aromatic systems are classified into two categories: one is the acene series, i.e., linearly fused type such as anthracene, and the other is the phene series, i.e., zigzag type such as phenanthrene. It should be of great importance to elucidate the similarities and differences between the two types of polynuclear aromatic systems containing a heavier group 14 element such as metallaanthracene and metallaphenanthrene (Scheme 1). Very recently, we have preliminarily reported the comparison of structures and properties between the kinetically stabilized 14π-electron germaaromatic systems, 9-Bbt-9-germaanthracene and 9-Tbt-9-germaphenanthrene.[5] In the case of silaaromatic compounds, theoretical calculations reported by Sastry and co-workers showed that 9-silaphenanthrene should be more stable than 9-silaanthracene by 1.9 kcal/mol at the B3LYP/6-31G(d) level.[7] Although we have succeeded in the synthesis of a kinetically stabilized 9-silaanthracene, 9-Tbt-9-silaanthracene,[3f,q] there has been no stable example of 9-silaphenanthrene except for the trapping experiments of transient 9-silaphenanthrene derivatives reported by Nishiyama and co-workers in 2001.[8] On the other hand, we have reported that 9-Tbt-9-stannaphenanthrene can be generated as a metastable

[#] Dedicated to the late Prof. Yoshihiko Itoh.

* Corresponding author. Tel: +81-774-38-3200. Fax: +81-774-38-3209. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

[§] Kyoto University.

[†] Waseda University.

(1) Present address: Department of Applied Chemistry, Faculty of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515, Japan.

(2) (a) Minkin, V. J.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.

(3) (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (c) Wakita, K.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2157. (d) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 634. (e) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648. (f) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256. (g) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024. (h) Shinohara, A.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 977. (i) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6914. (j) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Organomet. Chem.* **2003**, *672*, 66. (k) Nakata, N.; Takeda, N.; Tokitoh, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 115. (l) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2001**, *20*, 5507. (m) Nakata, N.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2002**, *31*, 818. (n) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2003**, *22*, 481. (o) Shinohara, A.; Takeda, N.; Sasamori, T.; Matsumoto, T.; Tokitoh, N. *Organometallics* **2005**, *24*, 6141. (p) Nakata, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6915. (q) Shinohara, A.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2003**, *125*, 10805.

(4) For recent reviews on sila- and germaaromatic compounds kinetically stabilized with a Tbt group, see: (a) Tokitoh, N. *Acc. Chem. Res.* **2004**, *37*, 86. (b) Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 429.

(5) Sasamori, T.; Inamura, K.; Hoshino, W.; Nakata, N.; Mizuhata, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Organometallics* **2006**, *25*, 3533.

(6) Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1050.
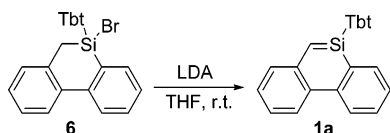
(7) Dhevi, D. M.; Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2003**, *68*, 1168.

(8) Oba, M.; Iida, M.; Nishiyama, K. *Organometallics* **2001**, *20*, 4287.

Scheme 1. Synthesis of the Precursor of 9-Silaphenanthrene[a]
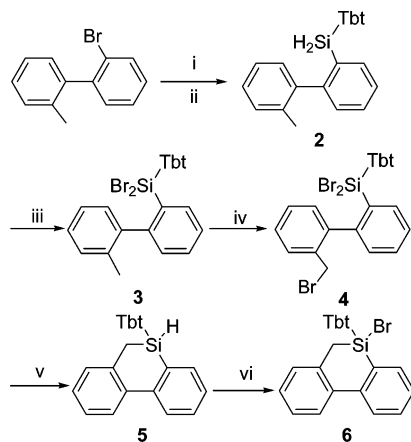
[a] Key: (i) *n*-BuLi/Et$_2$O, rt; (ii) TbtSiH$_3$; (iii) NBS/benzene, reflux; (iv) NBS and AIBN/benzene, reflux; (v) LiC$_{10}$H$_8$/THF, −78 °C; (vi) NBS/CCl$_4$, 4 °C.
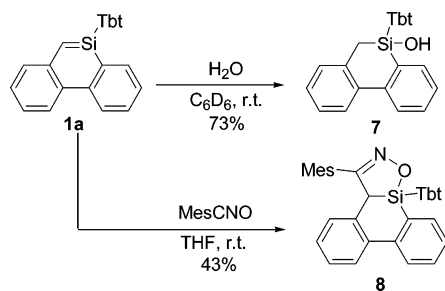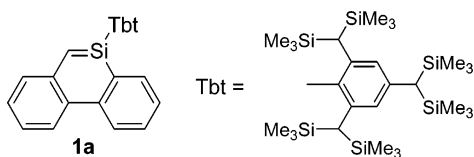
Scheme 2

Scheme 3

Chart 1

compound at −78 °C and undergoes ready dimerization to afford the corresponding [2+2] dimer stereoselectively at room temperature.[9]

In order to make progress in the chemistry of aromatic compounds containing a heavier group 14 element, the synthesis of a stable 9-silaphenanthrene derivative should be very meaningful as a new member of the 14π-electron phene systems. We report here the synthesis, structure, and reactivity of stable 9-silaphenanthrene **1a**, bearing a 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) group.

Results and Discussion

Synthesis of a Precursor for a 9-Silaphenanthrene. At the first stage of the construction of the 9-silaphenanthrene skeleton, compound **2** was prepared by the treatment of an Et$_2$O solution

(9) Mizuhata, Y.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 1088.

Table 1. Comparisons of δ_{Si} (ppm), Longest Absorption Maxima λ_{max} (nm), and Si−C Bond Lengths (Å) of Tbt-Substituted Silaaromatic Compounds

	δ_{Si}	λ_{max}	Si−C	ref
silabenzene	91.3	331	1.765(4), 1.770(4)	2d,e
1-silanaphthalene	91.6	378		2h
9-silaanthracene	91.7	503	1.784(3), 1.787(3)	2f
2-silanaphthalene	87.2	387	1.728(3), 1.800(3)	2a,b,c
9-silaphenanthrene	86.9	404	1.712(4), 1.804(4)	this work
			1.717(4), 1.798(4)	

of 2-bromo-2′-(methyl)biphenyl[10] with dropwise addition of *n*-BuLi followed by the addition of TbtSiH$_3$[11] at ambient temperature (Scheme 1). The reaction of **2** with 2 equiv of NBS in refluxing benzene afforded dibromosilane **3**. Further bromination of **3** was achieved by treatment with an additional equivalent amount of NBS and a catalytic amount of AIBN in benzene for 1 h under reflux. Treatment of **4** with lithium naphthalenide (1.0 M in THF, 5 equiv) in THF at −78 °C gave the corresponding 9,10-dihydro-10-silaphenanthrene **5** in 66% yield.[12] The bromination of **5** with an equimolar amount of NBS at 4 °C afforded bromosilane **6**, the precursor of 9-silaphenanthrene, in 83% yield.

Synthesis and Characterization of 9-Silaphenanthrene. Taking into account our previous reports on the synthesis of the kinetically stabilized silaaromatic systems,[4] lithium diisopropylamide (LDA) should be a suitable base for the dehydrohalogenation reaction of bromosilane **6** for the synthesis of the corresponding 9-silaphenanthrene. As expected, 9-silaphenanthrene **1a** was obtained as a stable crystalline compound by the reaction of **6** with LDA in THF at ambient temperature. Recrystallization at −40 °C from hexane afforded pure **1a** as pale yellow crystals in 63% yield.

9-Silaphenanthrene **1a** was thermally stable even on heating at 100 °C in benzene-*d$_6$* in a sealed tube, though it underwent ready hydrolysis and/or decomposition on exposure to the air. No dimerization reaction was observed for **1a** even on heating for a long time, in contrast to the case of 9-Tbt-9-silaanthracene, which is known to undergo thermal dimerization at 110 °C for 15 days.[3q]

All the ^{1}H and ^{13}C NMR chemical shifts corresponding to the 9-silaphenanthrene ring of **1a** were found to be in the aromatic region. In the ^{1}H and ^{13}C NMR spectra, the signals for the H and C atoms at the 10-position of **1a** were observed at a definitely downfield region due to the ring current effect (δ_H = 7.27 and δ_C = 115.16 ppm) compared with those of 9,-10-dihydro-9-silaphenanthrene **5** (δ_H = 2.46 and 2.63 and δ_C = 20.23). The ^{29}Si NMR spectrum of **1a** in C$_6$D$_6$ showed a characteristic signal assignable to the central silicon atom at 86.9 ppm similarly to the case of the silaaromatic compounds previously reported (Table 1).[3,4]

The UV/vis spectrum of **1a** in hexane [λ_{max} = 230 (ϵ 1 × 10^5), 262 (6 × 10^4), 288 (4 × 10^4), 304 (2 × 10^4), 366 (2 ×

(10) Wolfe, J. P.; Singer, R. A.; Yang, B. H., Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

(11) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016.

(12) When a 2.2 equiv molar amount of lithium naphthalenide was added to a THF solution of **4** at −78 °C, the mixture of **4** and bromosilane **6** was obtained. The use of a 4.2 equiv molar amount of lithium naphthalenide resulted in the formation of compounds **5** and **6**. We postulated the mechanism where the silylene was generated by the reduction of the dibromosilane moiety inserted intramolecularly into the C−Br bond, and then hydrosilane **5** was formed by the further reduction of the Si−Br bond of **6** by lithium naphthalenide.
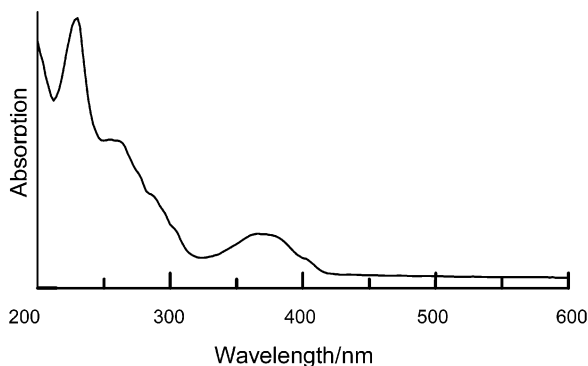
**Figure 1.** UV/vis spectrum of 9-silaphenanthrene **1a** in hexane.

10^4), 376 (2×10^4), 404 nm (1×10^4)] is shown in Figure 1.[13] While the longest absorption maxima ($\lambda_{max} = 404$ nm) of **1a** was longer than those of Tbt-substituted 1- and 2-silanaphthalenes ($\lambda_{max} = 378$ and 387 nm, respectively), it was more blue-shifted compared with that ($\lambda_{max} = 503$ nm) of 9-Tbt-9-silaanthracene, the structural isomer of **1a**. This unique feature of the longest absorption maxima, which should be assignable to the HOMO−LUMO electron transitions, indicated that the 14π-electron conjugated systems of silaaromatic compounds could be extensively conjugated in the acene series but not so effectively in the phene series, which is also the case for carbon and germanium analogues.[5] The Raman spectrum of **1a** exhibited the most intense line at 1323 cm^{-1}, which could be assigned as a characteristic in-plane vibrational mode of the 9-silaphenanthrene skeleton on the basis of the simulated spectra for the model compound, 9-phenyl-9-silaphenanthrene (**1b**) (Figure 2), indicating that the skeletal features of **1a** are similar to those of the theoretically optimized structure of **1b**. In addition, the simulated Raman spectra for **1b** suggested that the relatively intense Raman shifts observed at 1298, 1467, 1552, and 1575 cm^{-1} should also correspond to the in-plane vibrational modes (see Supporting Information).[14,15] The similarity of the spectra observed for **1a** and simulated for the less hindered model compound (**1b**) indicates that the Tbt group should afford little electronic perturbation to the central 9-silaphenanthrene ring skeleton.

The X-ray crystallographic analysis revealed the structure of 9-silaphenanthrene **1a**. Two independent molecules were found in the unit cell, and their structures were similar to each other. The 9-silanaphthalene rings are completely planar, and the silicon atoms at the 9-position have trigonal-planar geometries (Figure 3). In both independent molecules, the 9-silaphenanthrene ring is perpendicularly oriented to the benzene ring of
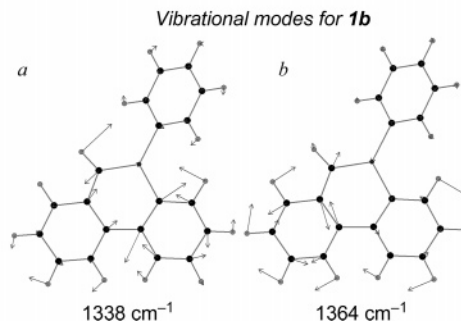
(13) The photophysical and photochemical processes of 9-silaphenanthrene derivatives at 77 K have been reported, and the fluorescence spectrum of 9-Tbt-9-silaphenanthrene is shown there. The lifetimes of the fluorescence of Tbt-9-silaphenanthrene were 6.9 ns (94%) and 2.4 ns (6%). Hiratsuka, H.; Horiuchi, H.; Furukawa, Y.; Watanabe, H.; Ishihara, A.; Okutsu, T.; Tobita, S.; Yoshinaga, T.; Shinohara, A.; Tokitoh, N.; Oba, M.; Nishiyama K. *J. Phys. Chem. A* **2006**, *110*, 3868.

(14) Calculated at the B3LYP/6−31G(d) level. Results of the theoretical calculations for **1b** are shown in the Supporting Information.

(15) The $\nu_{C=C}$ Raman lines for the cyclic diaminometallylenes, which possess the cyclic 6π-electon system containing a silicon or germanium atom, have been observed in the range ca. 1550−1570 cm^{-1}; see: Leites, L. A.; Bukalov, S. S.; Zabula, A. V.; Garbuzova, I. A.; Moser, D. F.; West, R. *J. Am. Chem. Soc.* **2004**, *126*, 4114.
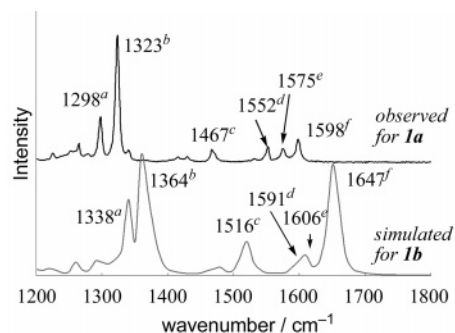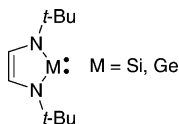
Figure 2. Observed (**1a**) and simulated (**1b**, B3LYP/6-31G(d), uncorrected) Raman spectra. The vibrational modes calculated for **1b** (1338 and 1364 cm^{-1}) are shown.[14]
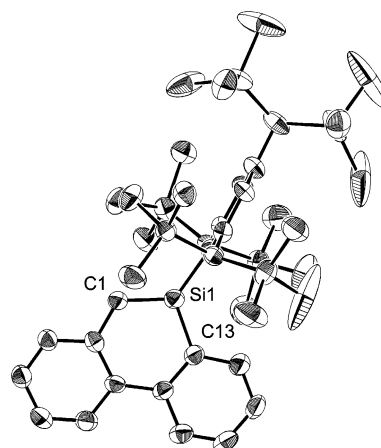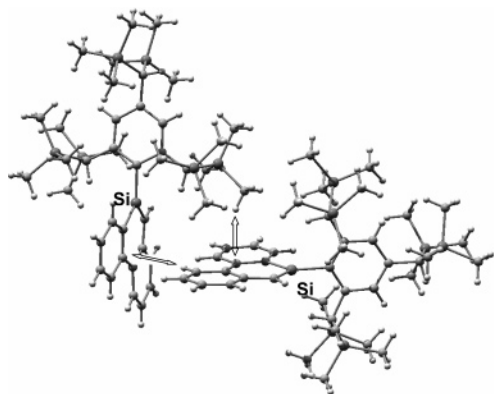

Figure 3. ORTEP drawing of 9-silaphenanthrene **1a** (50% probability). One of the two independent molecules found in the unit cell is shown here. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C1 1.712(4), Si1−C13 1.804(4), C1−Si1−C13 108.1(2).

the Tbt moiety. The two Si−C bond lengths in the 9-silaphenanthrene rings [molecule A, 1.712(4) and 1.804(4) Å; molecule B, 1.717(4) and 1.798(4) Å] lie between the typical Si−C double and single bond lengths (ca. 1.70[16] and 1.89 Å,[17] respectively). It should be noted that the Si−C bond length of the 9,10-position was the shortest among those of other silaaromatic compounds,[3,4] suggesting its higher Si−C double-bond character. As for the C−C bond lengths of the 9-silaphenanthrene ring, considerable bond alternation (1.36−

(16) (a) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (b) Gutowsky, H. S.; Chen, J.; Hajduk, P. J.; Keen, J. D.; Chuang, C.; Emilsson, T. *J. Am. Chem. Soc.* **1991**, *113*, 4747.

(17) Sheldrick, W. M. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 246.
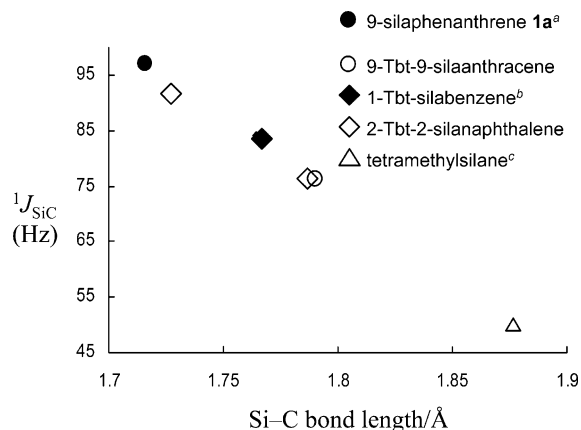
Figure 4. Intermolecular CH−π interactions in the crystalline state of 9-silaphenanthrene **1a**.

1.47 Å) was observed, as in the parent phenanthrene.[18] As shown in the crystal packing of 9-silaphenanthrene **1a** (Figure 4), the intermolecular CH−π interactions were observed in the crystalline state, as in the case of 9-Tbt-9-germaphenenthrene.[5] One is between the two 9-silaphenanthrene rings (the distance between the edge carbon atom and the aromatic ring is ca. 3.65 Å), and the other is between the methyl group and the 9-silaphenanthrene ring (the distance between the closest methyl carbon and the aromatic ring is ca. 3.43 Å).[19]

It is well-established that the coupling constant between two adjacent nuclei should be a good index for the bond order.[20] Coupling constants of typical Si−C single bonds are known to be $J_{SiC} \approx 50$ Hz, whereas those of Si=C double bonds have been reported as $J_{SiC} \approx 73-85$ Hz.[21] Since stable examples of Si−C double-bond compounds (silenes) are still limited, the measurement of $^{1}J_{SiC}$ values in the 9-silaphenanthrene ring should give useful information for the Si−C bond order. Although the $^{1}J_{SiC}$ coupling constant between the central Si atom and the C atom at the 8a-position could not be identified due to the overlap with other signals, the $^{1}J_{SiC}$ value for Si−C (10-position) of **1a** was observed as a satellite signal of 97 Hz, which is the largest value among those of other stable silaaromatic compounds bearing a Tbt group (76−92 Hz).[3,4] One can see good correlation between the Si−C bond lengths and $^{1}J_{SiC}$ values, as shown in Figure 5.

These spectral data (NMR, UV/vis, and Raman) and X-ray crystallographic analysis of **1a** strongly suggest the aromatic character of 9-silaphenanthene **1a**, as in the case of other silaaromatic compounds,[3,4] although the Si−C bond (9,10-

(18) The C−C bond lengths of phenanthrene are 1.372−1.457 Å. See: Trotter, J. *Acta Crystallogr.* **1963**, *16*, 605.

(19) Although the degree of T-shaped CH−π interaction should be discussed on the basis of the distance between the center of the aromatic ring and the aromatic plane, it is somewhat difficult to define the center of the 9-silaphenanthrene ring due to the slight deformation of the skeleton. It was reported that the T-shaped CH−π interaction in a benzene dimer should be highly effective when the distance between the center of the aromatic ring and the aromatic plane is ca. 5.0 Å; that is, that between the C atom at the edge and the aromatic plane is ca. 3.6 Å. The C−C distance (ca. 3.7 Å) due to the CH−π interaction observed for **1a** should be similar to those observed for phenanthrene. See: (a) Mason, R. *Mol. Phys.* **1961**, *4*, 413. (b) Trotter, J. *Acta Crystallogr.* **1963**, *16*, 605. (c) Pawliszyn, J.; Szczesniak, M. M.; Scheiner, S. *J. Phys. Chem.* **1984**, *88*, 1726. (d) Felker, P. M.; Maxton, P. M.; Schaeffer, M. W. *Chem. Rev.* **1994**, *94*, 1787. (e) Sinnokrot, M. O.; Sherrill, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 7690. (f) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200. (g) Sato, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2005**, *123*, 104307. (h) Nishio, M. *CrystEngComm* **2004**, *6*, 130.

(20) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; translated by Becconsall, J. K.; Wiley: New York, 1986.

(21) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Vol. 1, p 511.

Figure 5. Plot of the Si−C bond lengths with the Si−C coupling constants. [a]Mean value for the two nonidentical molecules of 9-silaphenanthrene **1a**. [b]Mean value of the two Si−C bonds of 1-Tbt-silabenzene. [c]See ref 22.
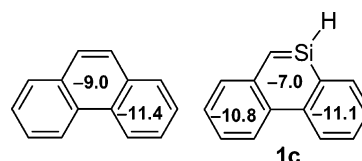
Figure 6. NICS(1) values for phenanthrene and parent 9-silaphenanthrene **1c** at the GIAO B3LYP/6-311(d) level.

position) of **1a** has a considerable double-bond character. From the standpoint of theoretical calculations, the aromatic character of the parent 9-silaphenanthrene **1c** is reasonably supported by the large negative NICS (nucleus-independent chemical shift) values[23] calculated at the B3LYP/6-311G(d) level for the 9-silaphenanthrene ring systems, which are comparable to those for phenanthrene (Figure 6). Taking into account the experimental and calculated results, it can be concluded that 9-silaphenanthrene **1a** should be highly aromatic.

While 9-silaphenanthrene **1a** shows considerable aromaticity, it still has high reactivity toward small molecules. The reaction of **1a** with water at ambient temperature afforded the corresponding 9,10-adduct hydroxysilane **7** in 73% yield. Mesitonitrile oxide (MesCNO, Mes = mesityl) reacted with **1a** smoothly as a 1,3-dipolarophile at room temperature to give the [2+3] cycloadduct **8** in 45% yield. Since the less-hindered transient 9-silaphenanthrene derivatives generated in the gas phase are known to show a reactivity similar to that of **1a**,[8] 9-silaphenanthrene **1a** still keeps enough reaction space around the central Si atom to react with a small reagent such as H$_2$O and MesCNO although the Tbt group seems to effectively suppress the self-oligomerization of **1a**, leading to its outstanding kinetic stability.

In summary, 9-silaphenanthrene **1a** was synthesized as a stable crystalline compound and was fully characterized by spectroscopic and X-ray crystallographic analyses. Taking all experimental and theoretical investigations into consideration, it can be concluded that 9-silaphenanthrene **1a** is highly aromatic. It was found that 9-silaphenanthrene **1a** still keeps

(22) (a) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401. (b) Campanelli, A. R.; Ramondo, F.; Domenicano, A.; Hargittai, I. *Struct. Chem.* **2000**, *11*, 155.

(23) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

its inherent reactivity similar to those of less hindered 9-si-laphenanthrenes previously reported. The synthesis and isolation of **1a** should be noted as not only the first example of a stable 9-silaphenanthrene but also a stable phene silaaromatic compound.

Experimental Section

General Procedures. All experiments were performed under an argon atmosphere using standard Schlenk and glovebox techniques unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. The ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in CDCl$_3$ or C$_6$D$_6$ with a JEOL AL-400 or AL-300 spectrometer. The ^{29}Si NMR (59 MHz) spectra were measured in CDCl$_3$ or C$_6$D$_6$ 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 Wakogel C-200. 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). Electronic spectra were recorded on a JASCO Ubest-50 UV/vis spectrometer. 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. 2-Bromo-2′-methylbiphenyl[10] and TbtSiH$_3$[11] were prepared according to the reported procedures.

Preparation of 2-Methyl-2′-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}silylbiphenyl (2). To a solution of 2-bromo-2′-(methyl)biphenyl (525 mg, 2.13 mmol) in ether (10 mL) was added *n*-BuLi (1.5 mol/L solution in hexane, 1.4 mL, 2.1 mmol) at 0 °C. After the solution was stirred at room temperature for 1 h, a solution of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane (1.24 g, 2.13 mmol) in ether (13 mL) was added at room temperature. After further stirring for 12 h, the reaction mixture was quenched with an aqueous solution of NH$_4$Cl and extracted with ether. The organic layer was dried over MgSO$_4$, then filtrated and evaporated. The crude product was purified by WCC (hexane) to give **2** (1.31 g, 1.75 mmol, 82%). **2**: colorless powder; mp 196–197 °C; ^{1}H NMR (300 MHz, rt, CDCl$_3$) δ −0.06 (s, 18H), −0.05 (s, 18H), 0.05 (s, 18H), 1.34 (s, 1H), 1.95 (br s, 2H), 2.15 (s, 3H), 4.47 (d, J = 3.0 Hz, 1H), 4.55 (d, J = 3.0 Hz, 1H), 6.30 (br s, 1H), 6.42 (br s, 1H), 7.18–7.24 (m, 4H), 7.27–7.30 (m, 2H), 7.37–7.45 (m, 2H); ^{13}C NMR (75 MHz, rt, CDCl$_3$) δ 0.72 (q), 0.84 (q), 1.07 (q), 20.42 (q), 29.19 (d), 29.55 (d), 30.56 (d), 121.64 (d), 122.93 (s), 125.33 (d), 126.10 (d), 126.44 (d), 127.47 (d), 128.92 (d), 129.33 (d), 129.38 (d), 129.79 (d), 131.38 (s), 135.62 (s), 137.40 (d), 142.52 (s), 145.05 (s), 148.65 (s), 152.39 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ −53.92, 1.75, 2.25; high-resolution MS (FAB) *m/z* calcd for C$_{40}$H$_{72}$Si$_7$ 748.4019 ([M]$^+$), found 748.4021 ([M]$^+$). Anal. Calcd for C$_{40}$H$_{72}$Si$_7$: C, 64.09; H, 9.68. Found: C, 63.87; H, 9.81.

Preparation of 2-{(Dibromo)-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}silyl}-2-methylbiphenyl (3). A solution of **2** (473 mg, 0.632 mmol) and NBS (248 mg, 1.39 mmol) in benzene (40 mL) was refluxed for 1 h. After the solvent was evaporated, the mixture was purified by GPLC (CHCl$_3$) to afford **3** (534 mg, 0.589 mmol, 93%). **3**: colorless powder; mp 186–189 °C (dec); ^{1}H NMR (300 MHz, rt, CDCl$_3$) δ −0.06 (s, 9H), −0.03 (s, 9H), 0.00 (s, 9H), 0.02 (s, 9H), 0.07 (s, 9H), 0.08 (s, 9H), 1.37 (s, 1H), 2.19 (s, 3H), 2.69 (br s, 1H), 2.89 (br s, 1H), 6.29 (br s, 1H), 6.44 (br s, 1H), 7.00–7.10 (m, 1H), 7.17–7.24 (m, 4H), 7.31–7.36 (m, 1H), 7.41–7.45 (m, 1H) 7.73 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz,

rt, CDCl$_3$) δ 1.24 (q), 1.28 (q), 1.79 (q), 1.98 (q), 2.09 (q), 2.26 (q), 21.31 (d), 28.80 (d), 31.22 (q), 121.39 (s), 123.81 (d), 125.29 (d), 127.42 (d), 128.05 (d), 129.18 (d), 130.39 (d), 130.45 (d), 130.48 (d), 132.02 (d), 136.39 (d), 136.80 (s), 136.86 (s), 141.80 (s), 146.12 (s), 147.34 (s), 153.19 (s), 154.02 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ −13.83, 2.52, 3.30. High-resolution MS (FAB) *m/z* calcd for C$_{40}$H$_{70}$^{79}Br^{81}BrSi$_7$ 906.2209 ([M]$^+$), found 906.2210 ([M]$^+$). Anal. Calcd for C$_{40}$H$_{70}$Br$_2$Si$_7$: C, 52.95; H, 7.78. Found: C, 52.93; H, 7.83.

Preparation of 2-Bromomethyl-2′-{(dibromo){2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}silyl}biphenyl (4). A solution of **3** (534 mg, 0.591 mmol), NBS (115 mg, 0.649 mmol), and AIBN (19 mg, 20 mol %) in benzene (50 mL) was refluxed under air for 1 h. The solvent was evaporated, and the separation of the mixture by GPLC (CHCl$_3$) afforded **4** (459 mg, 0.465 mmol, 79%). **4**: colorless powder; mp 211–213 °C (dec); ^{1}H NMR (300 MHz, rt, CDCl$_3$) δ −0.08 (s, 9H), −0.05 (s, 9H), 0.03 (s, 9H), 0.07 (s, 9H), 0.08 (s, 18H), 1.37 (s, 1H), 2.69 (br s, 1H), 2.84 (br s, 1H), 4.24 (d, J = 10.2 Hz, 1H), 4.48 (d, J = 10.2 Hz, 1H), 6.29 (br s, 1H), 6.44 (br s, 1H), 7.20–7.22 (m, 1H), 7.33–7.54 (m, 5H), 7.67–7.70 (m, 2H); ^{13}C NMR (75 MHz, rt, CDCl$_3$) δ 0.93 (q), 0.95 (q), 1.48 (q), 1.64 (q), 1.79 (q), 1.95 (q), 28.51 (d), 28.57 (d), 31.00 (d), 32.97 (t), 120.33 (s), 123.54 (d), 127.81 (d), 127.86 (d), 128.63 (d), 128.82 (d), 130.27 (d), 130.83 (d), 130.91 (d), 131.66 (d), 135.72 (d), 136.32 (s), 136.46 (s), 141.06 (s), 143.55 (s), 147.31 (s), 152.96 (s), 153.72 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ −14.67, 2.21, 2.85, 3.05; high-resolution MS (FAB) *m/z* calcd for C$_{40}$H$_{69}$^{79}Br^{81}Br$_2$Si$_7$ 986.1293 ([M]$^+$), found 986.1285 ([M]$^+$). Anal. Calcd for C$_{40}$H$_{69}$Br$_3$Si$_7$: C, 48.71; H, 7.05. Found: C, 48.09; H, 7.05.

Preparation of 9-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-9,10-dihydro-9-silaphenanthrene (5). To a solution of **4** (459 mg, 0.466 mmol) in THF (50 mL) was added lithium naphthalenide (1 M solution in THF, 2.3 mL, 2.3 mmol) at −78 °C. After stirring for 1 h, the solvent was evaporated. The separation of the mixture by GPLC (CHCl$_3$) and WCC (hexane) afforded **5** (230 mg, 0.308 mmol, 66%). **5**: colorless powder; mp 227–229 °C; ^{1}H NMR (300 MHz, CDCl$_3$, rt) δ −0.23 (s, 9H), −0.16 (s, 9H), −0.11 (s, 9H), −0.01 (s, 9H), 0.02 (s, 18H), 1.28 (s, 1H), 1.87 (br s, 1H), 1.97 (br s, 1H), 2.46 (d, J = 15 Hz, 1H), 2.63 (dd, J = 15, 3 Hz, 1H), 5.06 (d, J = 3 Hz, 1H), 6.20 (br s, 1H), 6.33 (br s, 1H), 7.11–7.27 (m, 4H), 7.45–7.51 (m, 1H), 7.61–7.75 (m, 3H); ^{13}C NMR (CDCl$_3$, rt) δ 0.32 (q), 0.69 (q), 0.73 (q), 1.07 (q), 20.23 (t), 28.63 (d), 29.03 (d), 30.47 (d), 121.63 (d), 123.01 (s), 126.46 (d), 126.52 (d), 126.56 (d), 126.87 (d), 127.96 (d), 128.19 (d), 130.64 (d), 132.16 (d), 133.53 (s), 135.70 (s), 136.82 (d), 137.68 (d), 144.89 (s), 145.15 (s), 152.35 (s), 152.45 (s); ^{29}Si NMR (59 MHz, CDCl$_3$, rt) δ −38.69, 1.69, 1.73, 1.78, 1.84; high-resolution MS (FAB) *m/z* calcd for C$_{40}$H$_{70}$Si$_7$ 746.3862 ([M]$^+$), found 746.3860 ([M]$^+$). Anal. Calcd for C$_{40}$H$_{70}$Si$_7$: C, 64.26; H, 9.44. Found: C, 63.98; H, 9.52.

Preparation of 9-Bromo-9-{2,4,6-tris[bis(trimethylsilyl)m-ethyl]phenyl}-9,10-dihydro-9-silaphenanthrene (6). Compound **5** (188 mg, 0.251 mmol) and NBS (45 mg, 0.25 mmol) were dissolved in CCl$_4$ (20 mL) under dry air, and the solution was stirred at 4 °C. After the disappearance of **5** over 4 days, the solution was evaporated. A 50 mL amount of hexane was added to the residue, and the mixture was filtered. Removal of the solvent afforded bromosilane **6** (174 mg, 0.211 mmol, 83%). **6**: colorless powder; mp 239–241 °C; ^{1}H NMR (300 MHz, rt, CDCl$_3$) δ −0.12 (s, 9H), −0.16 (s, 9H), −0.001 (s, 9H), 0.002 (s, 9H), 0.02 (s, 9H), 0.07 (s, 9H), 1.26 (s, 1H), 2.33 (s, 1H), 2.44 (s, 1H), 2.95 (br s, 2H), 6.19 (br s, 1H), 6.32 (br s, 1H), 7.10–7.12 (m, 2H), 7.18–7.25 (m, 1H), 7.40 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.53 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 7.58–7.65 (m, 2H), 8.12 (dd, J = 7.2, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, rt, CDCl$_3$) δ 0.62 (q), 0.74 (q), 0.84 (q), 1.18 (q), 1.23 (q), 1.61 (q), 27.73 (t), 28.77 (d), 29.19 (d), 30.75 (d), 121.37 (s), 122.45 (d), 127.04 (d), 127.07 (d), 127.51 (d), 127.66 (d), 128.00 (d), 128.03 (d), 130.95 (d), 131.94 (d), 133.48 (s), 136.55 (s), 137.71

Table 2. Crystallographic Data for 1a

formula	$C_{40}H_{68}Si_7$
fw	745.57
cryst size (mm)	$0.20 \times 0.20 \times 0.10$
cryst syst	monoclinic
space group	*C2/c* (#15)
a (Å)	45.186(5)
b (Å)	9.3647(6)
c (Å)	43.241(4)
β (deg)	90.875(4)
V (Å³)	18295(3)
Z	16
D_{calc} (g cm^{-3})	1.083
F(000)	6496
R_1 ($I > 2\sigma(I)$)	0.0601
wR_2 (all data)	0.1556
goodness of fit	1.051

(s), 137.77 (d), 143.10 (s), 146.46 (s), 153.20 (s), 153.62 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ -7.39, 1.69, 1.78, 1.98, 2.04, 2.19; high-resolution MS (FAB) m/z calcd for $C_{40}H_{69}{}^{79}BrSi_7$ 824.2968 ([M]$^+$), found 824.2968 ([M]$^+$). Anal. Calcd for $C_{40}H_{69}BrSi_7$: C, 58.13; H, 8.41. Found: C, 58.07; H, 8.42.

Synthesis of 9-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-9-silaphenanthrene (1a). In a glovebox, lithium diisopropylamide (2.0 N in heptane/THF/ethylbenzene, 0.11 mL, 0.21 mmol, Aldrich Chemicals Co.) was added to the THF solution (3 mL) of **6** (174 mg, 0.211 mmol). After stirring for 1 h, all the volatiles were pumped off and hexane was added to the residue. The resulting suspension was filtered to remove the insoluble inorganic salts. Recrystallization of the filtrate by standing overnight at $-40\ ^{\circ}$C afforded **1a** (99 mg, 0.13 mmol, 63%). **1a**: pale yellow crystals; mp 173–176 $^{\circ}$C (dec); ^{1}H NMR (400 MHz, rt, C$_6$D$_6$) δ 0.05 (s, 18H), 0.16 (s, 18H), 0.19 (s, 18H), 1.57 (s, 1H), 2.52 (br s, 1H), 2.56 (br s, 1H), 6.67 (br s, 1H), 6.80 (br s, 1H), 7.14 (ddd, $J = 8.4$, 6.8 Hz, 1.2 Hz, 1H), 7.27 (s, 1H), 7.32 (ddd, $J = 8.0$, 6.8, 0.6 Hz, 1H), 7.33 (ddd, $J = 7.6$, 7.0, 0.8 Hz, 1H), 7.50 (ddd, $J = 8.7$, 7.0, 1.5 Hz, 1H), 7.72 (dd, $J = 8.0$, 1.2 Hz, 1H), 8.23 (dd, $J = 7.6$, 1.2 Hz, 1H), 8.55 (dd, $J = 8.4$, 0.6 Hz, 1H), 8.68 (dd, $J = 8.7$, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, rt, C$_6$D$_6$) δ 0.62 (q), 0.75 (q), 0.90 (q), 1.15 (q), 31.62 (d), 36.44 (d) 36.79 (d), 115.16 (d), 121.51 (d), 121.89 (d), 123.05 (s), 123.29 (d), 126.24 (d × 2), 126.48 (d), 126.63 (s), 127.07 (d), 129.80 (d), 129.96 (d), 130.43 (s), 134.07 (d), 143.67 (s), 144.43 (s), 148.45 (s), 153.49 (s × 2); ^{29}Si NMR (59 MHz, rt, C$_6$D$_6$) δ 1.85, 2.35, 3.51, 86.93; UV/vis (hexane) λ_{max} 230 (ϵ, 1×10^5), 262 (6×10^4), 288 (4×10^4), 304 (2×10^4), 366 (2×10^4), 376 (2×10^4), and 404 (1×10^4) nm; high-resolution FAB-MS m/z calcd for $C_{40}H_{68}Si_7$ ([M]$^+$): 744.3706, found m/z 744.3699 ([M]$^+$). It was difficult to obtain a satisfactory result for the elemental analysis of **1a** due to the extremely high air- and moisture-sensitivity even after several trials. The result of combustion analysis of **1a** indicated the formation of the hydrolyzed product of **1a**. (Anal. Calcd for [**1a**+H$_2$O]: C, 62.92; H, 9.24. Found: C, 62.71; H, 9.13.) The purity of **1a** was confirmed by the ^{1}H NMR spectrum as shown in the Supporting Information.

X-ray Data Collection of 9-Silaphenanthrene 1a. Colorless and prismatic single crystals of **1a** were grown by the slow evaporation of its hexane and benzene solution in a glovebox filled with Ar. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50^{\circ}$ at 103 K. The structure of **1a** was solved by direct methods (SHELXS-97)[24] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[24] One of the trimethylsilyl groups was disordered. All hydrogen atoms were placed using AFIX instructions. All the non-hydrogen atoms were refined anisotropically. Crystallographic data for **1a** are given in Table 2.

Reaction of 1a with Water. To a THF solution (2 mL) of **1a** (25.2 mg, 33.9 μmol) was added water (0.5 mL) at ambient temperature, and the solution was stirred for 30 min. After the solvent was removed, the mixture was subjected to GPLC (CHCl$_3$) and the fraction was separated by PTLC (CHCl$_3$/hexane, 1:1) to afford 9-hydroxy-9-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-9,10-dihydro-9-silaphenanthrene (**7**) (19.1 mg, 25.0 μmol, 74%). **7**: colorless powder; mp 229–231 $^{\circ}$C; ^{1}H NMR (300 MHz, rt, CDCl$_3$) δ -0.28 (s, 9H), -0.18 (s, 9H), -0.04 (s, 9H), 0.01 (s, 27H), 1.26 (s, 1H), 1.92 (Si–OH, s, 1H), 2.09 (br s, 1H), 2.22 (br s, 1H), 2.56 (d, $J = 15$ Hz, 1H), 2.61 (d, $J = 15$ Hz, 1H), 6.19 (br s, 1H), 6.32 (br s, 1H), 7.10–7.11 (m, 2H), 7.17–7.24 (m, 1H), 7.35 (ddd, $J = 7.8$, 7.4, 1.0 Hz, 1H), 7.59 (ddd, $J = 7.8$, 7.4, 1.5 Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.80 (dd, $J = 7.4$, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, rt, CDCl$_3$) δ 0.31 (q), 0.39 (q), 0.71 (q), 0.76 (q), 0.94 (q), 1.30 (q), 25.84 (t), 28.54 (d), 28.89 (d), 30.44 (d), 121.93 (d), 124.87 (s), 126.45 (d), 126.91 (d), 126.95 (d), 127.33 (d), 127.89 (d), 127.93 (d), 130.66 (d), 132.08 (d), 134.11 (d), 134.74 (s), 137.58 (s) 138.56 (s), 144.27 (s), 145.12 (s), 152.17 (s), 152.53 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ -14.88, 1.67, 1.82, 2.13, 2.21, 3.92; high-resolution MS (FAB) m/z calcd for $C_{40}H_{70}OSi_7$ ([M]$^+$) 768.3812, found 768.3807 ([M]$^+$). Anal. Calcd for $C_{40}H_{70}OSi_7$: C, 62.92; H, 9.24. Found: C, 62.72; H, 9.40.

Reaction of 1a with Mesitonitrile Oxide. In a glovebox, **1a** (42.0 mg, 56.5 μmol) and mesitonitrile oxide (46.3 mg, 0.288 mmol) were dissolved in THF (2 mL). After stirring for 12 h, the solvent was evaporated and hexane was added to the residue. The filtration of the mixture through Celite followed by separation with GPLC (CHCl$_3$) and PTLC (CHCl$_3$/hexane, 1:1) afforded 3-(2,4,6-trimethylphenyl)-11*b*-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3a,-11*b*-dihydro-1-oxa-2-aza-11*b*-silacyclopenta[*l*]phenanthrene (**8**) (23.5 mg, 25.9 μmol, 45%). **8**: colorless powder; mp 217–219 $^{\circ}$C; ^{1}H NMR (300 MHz, 40 $^{\circ}$C, CDCl$_3$) δ -0.23 (s, 9H), -0.18 (s, 9H), -0.02 (s, 18H), 0.05 (s, 9H), 0.06 (s, 9H), 1.357 (s, 1H), 1.364 (s, 3H), 2.17 (br s, 1H), 2.18 (s, 3H), 2.316 (br s, 1H), 2.324 (s, 3H), 3.907–3.914 (m, 1H), 6.37 (br s, 1H), 6.48 (br s, 1H), 6.52 (s, H), 6.62 (ddd, $J = 9.2$, 2.6, 2.6, 1H), 6.80 (s, 1H), 6.93–6.99 (m, 1H), 7.22–7.35 (m, 2H), 7.46–7.53 (m, 1H), 7.70–7.84 (m, 3H); ^{13}C NMR (75 MHz, 40 $^{\circ}$C, CDCl$_3$) δ 0.52 (q), 0.73 (q), 0.81 (q), 1.26 (q), 18.91 (q), 20.08 (q), 20.98 (q), 28.94 (d), 29.23 (d), 30.98 (d), 41.50 (d), 120.81 (s), 122.53 (d), 126.30 (d), 127.46 (d), 127.49 (d), 127.80 (d), 127.83 (d), 128.00 (d), 128.03 (d), 128.17 (d), 128.82 (s), 130.88 (s), 131.43 (d), 131.83 (s), 135.10 (d and s) 135.18 (d), 137.03 (s), 133.77 (s), 137.89 (s), 143.25 (s), 146.71 (s), 153.48 (s), 153.89 (s), 166.43 (s); ^{29}Si NMR (59 MHz, rt, CDCl$_3$) δ 2.23, 2.57, 3.92; high-resolution MS (FAB) m/z calcd for $C_{50}H_{80}ONSi_7$ ([M + H]$^+$) 906.4625, found 906.4622 ([M + H]$^+$). Anal. Calcd for $C_{50}H_{79}NOSi_7$: C, 66.23; H, 8.78. Found: C, 66.07; H, 8.79.

Supporting Information Available: X-ray crystallographic of **1a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700347Z

(24) Sheldrick, G. M. *SHELX-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.