

Synthesis of Stable 2-Silanaphthalenes and Their Aromaticity

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Abstract: Stable neutral silaaromatic compounds, 2-silanaphthalenes (**1a**; R = Tbt, **1b**; R = Bbt), were synthesized by taking advantage of extremely bulky and efficient steric protection groups, 2,4,6-tris(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt). 2-Silanaphthalenes **1a,b** were isolated as colorless crystalline compounds, and the structure of Tbt-substituted **1a** was determined by X-ray crystallographic analysis. All ¹H, ¹³C, and ²⁹Si NMR signals of the silanaphthalene ring of **1** were in good agreement with those calculated; downfield-shifted ¹H signals indicating aromatization were observed. Refined NICS (nucleus-independent chemical shift) calculations which separate the σ and π contributions revealed the presence of comparably large ring current effects in the two rings of 2-silanaphthalene. The aromatic stabilization energies (ASEs) of 1-, 2-, and 9-silanaphthalenes, computed by a novel isomerization method, are almost the same as naphthalene. UV-vis and Raman spectra, and the computed (B3LYP/6-311+G(d,p)) structure of 2-silanaphthalene were similar to those of naphthalene, although characteristic changes resulting from the replacement of carbon to silicon were observed. 2-Silanaphthalene **1a** is still highly reactive due to its polarized Si=C moiety, but was relatively stable toward air in the solid state and showed no complex formation with THF in solution. Considering all experimental and theoretical results, the 2-silanaphthalenes were concluded to have considerable aromatic character, closely approaching that of naphthalene itself.

Introduction

Much attention in recent decades has been focused on silaaromatic compounds,¹ namely, Si-containing $[4n + 2]\pi$ ring systems, since these represent the heavier congeners of the carbocyclic aromatic compounds² which play such important roles in organic chemistry. Although the aromatic character of silole anions and dianions,³ as well as those of cyclic diaminosilylenes,⁴ were recently revealed from experimental and

theoretical results, simple silaaromatic compounds such as silabenzene and disilabenzene are highly reactive and have only been characterized spectroscopically in low-temperature matrices or in the gas phase.⁵ Märkl et al. reported the synthesis of a “stable” silabenzene, 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene, but this survives only in solution (THF/Et₂O/petroleum ether, 4:1:1) below -100 °C. The stabilization is, however, apparently due to coordination of the solvent Lewis base, judging from the ²⁹Si NMR chemical shift ($\delta_{\text{Si}} = 26.8$) observed at a relatively high field (vide infra).^{1d,e,6,7}

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Many theoretical calculations have been reported for sila- and disilabenzenes,^{1c,e} and they indicate that silabenzenes have a delocalized structure and considerable aromaticity (e.g., ~80% of benzene from energetic criteria⁸). This implies that silaarenes might exist as stable molecules if their high reactivity could be suppressed.

In view of the increasing number of stable unconjugated doubly bonded organosilicon compounds which were synthesized successfully by taking advantage of steric protection,^{9,10} stable silaaromatic compounds with appropriately bulky substituents are expected to be synthesizable.

We have already developed an extremely bulky and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter),¹¹ and many novel reactive species have been prepared as stable compounds by taking advantage of this Tbt group. For example, a stable silanethione¹² and its heavier element group 14 analogues^{13,14} (we call these compounds "heavy ketones") were successfully synthesized utilizing a single Tbt group in combination with another considerably bulky substituent (bulky substituents can only be introduced onto one terminal of the double bond). Moreover, the first stable distibene¹⁵ and dibismuthene¹⁶ were also synthesized by introducing the Tbt group on each group 15 element where only one substituent can be introduced.

In a preliminary contribution,¹⁷ we reported that the successful application of the Tbt group to the kinetic stabilization of silaaromatic compounds led to the first isolation of a stable 2-silanaphthalene. In this paper, we describe the details of the synthesis, structure, and reactivity of the kinetically stabilized 2-silanaphthalenes bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt)¹¹ and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt groups).^{18,19} These results, as well as those of theoretical calculations focus on the aromaticity of these new silaaromatics in particular.

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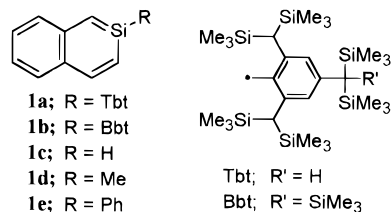
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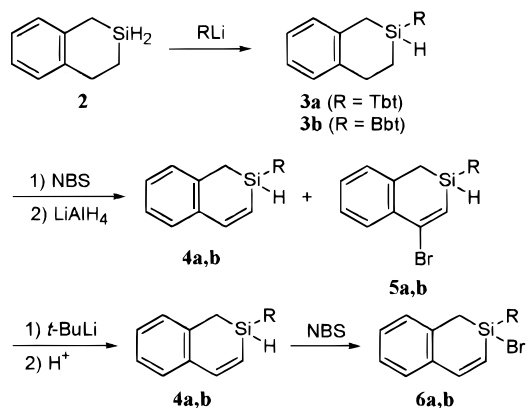


Results and Discussion

Synthesis of 2-Silanaphthalenes. Although many synthetic routes to silabenzenes have been developed,^{1a,b} the flow pyrolysis of 2-allyl-2-methyl-1,2-dihydro-2-silanaphthalene was the only example reported for the preparation of a transient 2-silanaphthalene derivative.²⁰ To synthesize 2-silanaphthalenes in a preparative scale, we selected a method based on treatment of the corresponding halosilanes with a base.

Bromosilanes **6a,b**, the precursors of 2-silanaphthalenes **1a,b**, were synthesized from 1,2,3,4-tetrahydro-2-silanaphthalene **2**,^{21,22} following the route shown in Scheme 1. Thus, treatment

Scheme 1



of **2** with TbtLi or BbtLi resulted in moderate yields of hydrosilanes **3a,b** bearing these bulky substituents. The bromination of **3** with excess NBS gave a complex mixture containing products with a 3,4-double bond; this mixture was further reduced with LiAlH₄ to give an inseparable mixture of **4** and **5**.²³ Lithiation of the mixture of **4** and **5** with *t*-BuLi followed by quenching with aqueous solution of NH₄Cl afforded hydrosilanes **4** as pure compounds. Finally, bromosilanes **6a,b**, the precursors of 2-silanaphthalenes, were prepared as pure, stable compounds by careful bromination of **4** with equimolar amounts of NBS at 0 °C.

Treatment of the bromosilanes **6a,b** thus obtained with 1 equiv of *t*-BuLi in hexane resulted in the formation of the expected 2-silanaphthalenes **1a,b** (~80% conversion based on NMR), which were confirmed by their characteristic low-field ²⁹Si NMR signals (**1a**, 87.3 ppm; **1b**, 86.7 ppm; in C₆D₆) (Scheme 2).²⁴ 2-Silanaphthalenes **1a,b** were isolated as colorless

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Table 1. Observed and Calculated ^{13}C and ^{29}Si NMR Chemical Shifts (ppm) for 2-Silanaphthalenes

compound	C1	Si2	C3	C4	C5	C6	C7	C8	C9	C10
1a (R = Tbt, obsd)	116.0	87.3	122.6	149.0	133.3	120.6	126.7	128.8	146.5	128.3
1b (R = Bbt, obsd)	115.0	86.8	122.0	149.0	133.3	120.6	126.8	128.7	146.5	128.6
1c (R = H, calcd) ^a	128.5	67.8	125.1	153.4	137.3	125.4	130.5	131.8	151.7	134.5
1d (R = Me, calcd) ^a	120.4	101.0	122.7	153.3	137.2	124.0	130.4	131.7	152.0	133.7
1e (R = Ph, calcd) ^{a,b}	121.6	94.3	123.6	152.5	137.1	124.5	130.4	132.3	151.6	133.7

^a Calculated by GIAO-B3LYP/6-311G(d)(6-311G(3d) for Si)//B3LYP/6-31G(d) level. ^b The phenyl group is fixed in such a way that it is perpendicular to the 2-silanaphthalene ring.

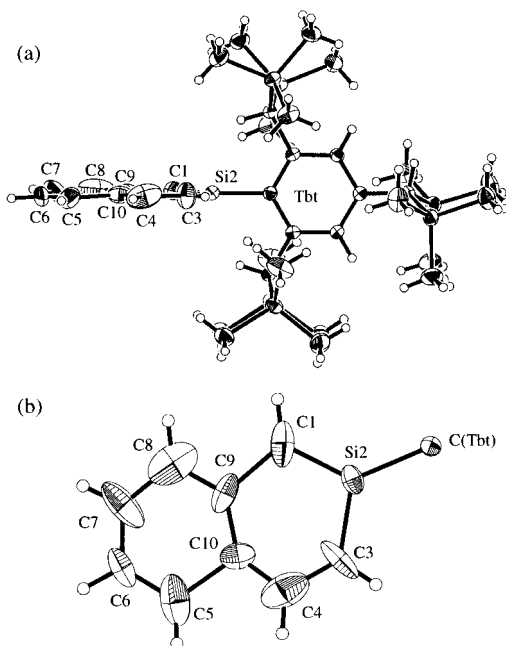
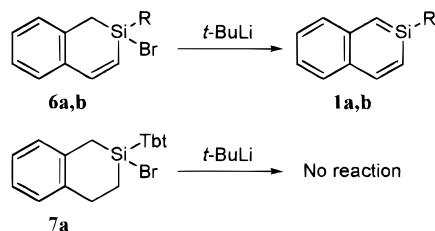


Figure 1. X-ray crystallographic analysis of **1a** (ORTEP, 30% probability). (a) Full view of the molecule. (b) Top view of the 2-silanaphthalene ring. Data collection was performed at $-80\text{ }^{\circ}\text{C}$.

crystals by recrystallization from hexane in a glovebox filled with argon. Interestingly, bromosilane **7a**, prepared by NBS bromination of **3a**, did not react with *t*-BuLi under the same conditions as those for **6a**.

Scheme 2



Although 2-silanaphthalene **1a** was moisture-sensitive, it was thermally very stable under an inert atmosphere in the solid state at room temperature or in solution at $100\text{ }^{\circ}\text{C}$; no dimerization product was detected. The high stability of **1a** demonstrates the excellent steric protection afforded by the Tbt group. In contrast, the *tert*-butyl group in 1,4-di-*tert*-butyl-1-silabenzene, which reportedly undergoes facile dimerization even at $0\text{ }^{\circ}\text{C}$, is ineffective.²⁵

The structure of **1a** was finally determined by X-ray crystallographic analysis, which revealed the planar geometry of the 2-silanaphthalene ring and the central silicon atom (Figure 1). Despite a number of trials using different single crystals even

with low-temperature data collection, we could not obtain refined data free from severe disorder around the 2-silanaphthalene ring. This prevented accurate experimental determination of bond lengths and angles in the 2-silanaphthalene ring. We will discuss, therefore, the structure of 2-silanaphthalene based on the available spectroscopic data and theoretical calculations.

NMR Spectra, NICS, and Energetic Evaluation of Aromaticity. As mentioned above, 2-silanaphthalene **1** showed ^{29}Si NMR signals of the central Si atoms around 87 ppm. Unconjugated silenes are also known to have low-field shifted δ_{Si} values, but they are widely scattered depending on the difference of substituents (41–144 ppm).^{1d} Although no simple silene with carbon substituents has been reported yet, the δ_{Si} values of **1** are reasonably compared with that of Couret's $\text{Mes}_2\text{Si}=\text{C}(\text{H})-\text{CH}_2(t\text{-Bu})$ ($\delta_{\text{Si}} = 77.6$)²⁶ and clearly different from that of Märkl's 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butyl-1-silabenzene ($\delta_{\text{Si}} = 26.8$).⁶ At present, however, we cannot judge the aromaticity from the ^{29}Si chemical shifts because of the scarcity of examples for both silenes and sila-aromatic compounds.

The ^1H and ^{13}C signals of **1** were assigned by 2D NMR techniques together with differential NOE and decoupling experiments. The ^{13}C NMR assignments are listed in Table 1 along with the calculated values for some other 2-silanaphthalenes. The agreement between experimental and theoretical values is excellent, especially for **1e** (R = Ph).

It is well-established that the coupling constant of adjacent two atoms can be a good index for the bond order.²⁷ Values around 50 Hz are known for typical Si–C single bonds,²⁷ whereas 83–85 Hz values are reported for Si–C double bonds (although the number of examples is still limited).²⁸ For **1a**, $J_{\text{Si}-\text{C}1}$ and $J_{\text{Si}-\text{C}3}$ were measured to be 92 and 76 Hz, respectively; both values exceeded those of Si–C single bonds considerably, and suggest double bond character for these Si–C bonds as in naphthalene (see below).

The assignments of ^1H signals of 2-silanaphthalenes **1a,b** are shown in Table 2, including calculated values for **1c–e** and those observed for the dihydro derivatives **4a,b**. H3 and H4 protons in **1a,b** resonate at approximately 1 ppm lower field than those in **4a,b** consistent with the predicted aromatization effect of the Si-containing rings in **1c–e**. A similar change also occurs between naphthalene (H3, 7.46; H4 7.81 ppm) and 1,2-dihydronaphthalene (H3, 5.82; H4, 6.33 ppm).

We have recently proposed the nucleus-independent chemical shifts (NICSS) as convenient criteria of aromaticity,²⁹ and NICSSs of silanaphthalenes were reported in the preliminary communication.¹⁷ We have refined this method further to separate the π and σ contributions.³⁰ The refined NICSSs are shown in

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Table 2. Observed and Calculated ^1H NMR Chemical Shifts (ppm) for 2-Silanaphthalenes and Their Dihydro Derivatives

compound	H1	H2	H3	H4	H5	H6	H7	H8
1a (R = Tbt, obsd)	7.40		7.24	8.48	7.60	6.99	7.20	7.64
1b (R = Bbt, obsd)	7.33		7.19	8.49	7.60	7.00	7.20	7.64
1c (R = H, calcd) ^a	7.74	6.37	7.27	8.64	7.69	7.23	7.40	7.62
1d (R = Me, calcd) ^a	7.26		7.03	8.50	7.60	7.11	7.32	7.54
1e (R = Ph, calcd) ^{a,b}	7.32		7.08	8.55	7.67	7.17	7.36	7.59
4a (R = Tbt, obsd)	2.45 ^c		6.27	7.30	~7.1 ^d	~7.1 ^d	~7.1 ^d	~7.1 ^d
4b (R = Bbt, obsd)	2.46 ^c		6.30	7.29	~7.1 ^d	~7.1 ^d	~7.1 ^d	~7.1 ^d

^a Calculated by GIAO-B3LYP/6-311G(d)(6-311G(3d) for Si)//B3LYP/6-31G(d) level. ^b The phenyl group is fixed in such a way that it is perpendicular to the 2-silanaphthalene ring. ^c These values are the average of the chemical shifts of two geminal protons. ^d These signals are observed in the range between 7.09 and 7.15 ppm but cannot be exactly assigned due to the overlap of the signals.

Table 3. Calculated NICSs of 2-Silanaphthalene **1c** (IGLO pw91/III)^a

	NICS(0)total	NICS(1)total	NICS(0) π	NICS(1) π
Si-ring	-8.0	-9.4	-17.7 [-0.3]	-9.5 [-0.1]
C-ring	-8.4	-10.3	-20.7 [-0.4]	-10.5 [-0.3]
naphthalene	-8.9	-10.8	-20.3 [0.0]	-10.1 [0.0]

^a Distances from ring centers to the calculated points (\AA) are described in parentheses, and contribution of the opposite rings are in square brackets (see the text for details). Data for naphthalene are provided for comparison.

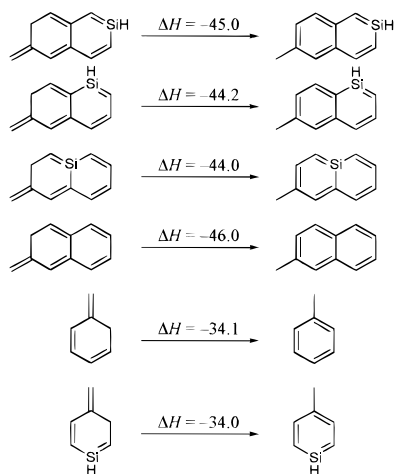
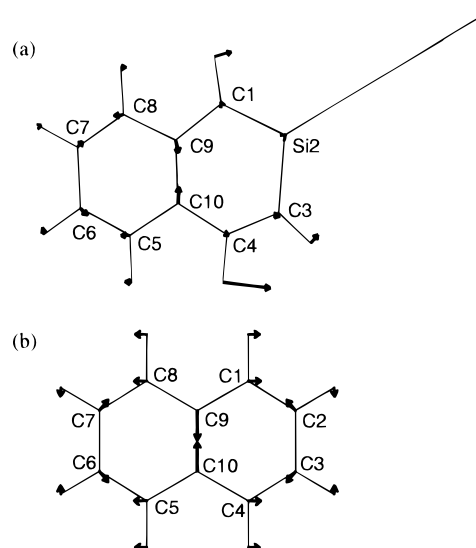
**Figure 2.** Calculated isodesmic isomerization energies (kcal/mol, B3LYP/6-311+G(d,p)/Fopt).

Table 3. Although quite different methods and levels are employed (here IGLO PW91/III), the NICS(0) values here are not very different from those we obtained earlier (-8.9 for Si-ring, -9.5 for C-ring, GIAO-SCF/6-31G(d) level).¹⁷ All the data show the Si-ring to be only slightly less aromatic than the C-ring. The other (C-C and C-H σ bonds etc.) contributions are paratropic, explaining why the NICS(0) π values are larger in magnitude than the NICS(0)total values. Fortunately, the other contributions decrease and largely cancel at points 1 \AA above the rings; hence, the NICS(1)total and NICS(1) π values are nearly the same. This supports our suggestion that NICS-(1)total values may serve as a good indicator of ring current effects (aromaticity).

The two rings do not influence each other significantly. This is shown by the small values in square brackets, which summarize the π contributions from the two remote double bonds in the opposite rings.

We have also carried out the quantitative energetic evaluation of 1- (**1c**), 2-, and 9-silanaphthalene isomers along with those for naphthalene, benzene, and silabenzene for comparison, the results of which are summarized in Figure 2. The novel method employed is based on the DFT-computed isodesmic isomerization energies of nonaromatic polyenes into the corresponding

**Figure 3.** Calculated vibration modes with maximum intensity. (a) 2-Phenyl-2-silanaphthalene. (b) Naphthalene.

methyl-substituted aromatic isomers. The evaluations are self-consistent, and methyl groups have little effect on arene aromaticity. We argue that such isomerization reactions, involving highly similar structures, provide better aromaticity estimates than more conventional equations based on small reference molecules. These do not balance the strain and other energetic effects as effectively.

The data demonstrate that incorporation of silicon into the arene frameworks not only has very little effect on the aromatic stabilization but also shows that there is no significant position dependence in naphthalene.

UV-Vis Spectra. 2-Silanaphthalene **1a** shows three absorption maxima at 267 ($\epsilon \times 10^4$), 327 (7×10^3), and 387 (2×10^3) nm in hexane. Despite the shift to longer wavelengths, they clearly correspond to the *E1*, *E2*, and *B* bands of naphthalene [221 ($\epsilon \times 1.33 \times 10^5$), 286 (9.3×10^3), and 312 (2.9×10^2) nm]. This documents the structural resemblance between 2-silanaphthalene and naphthalene. Similar UV-vis spectra relationships are also observed for the benzene-silabenzene-1,4-disilabenzene series in low-temperature matrix spectra.^{5f}

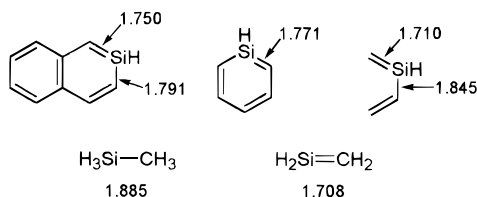
Raman Spectra. The Raman spectrum of **1a** showed the most intense Raman line at 1368 cm^{-1} , while the most intense line for naphthalene was observed at 1382 cm^{-1} . The strongest Raman shifts observed for **1a** and naphthalene are in good agreement with the theoretically calculated vibrational frequencies (1377 and 1389 cm^{-1} for **1e** and naphthalene, respectively, computed at the B3LYP/6-31G(d) level and scaled by 0.98^{31}). Furthermore, the calculated vibration modes of **1e** showed a

(31) For the scaling factor of 0.98, see: Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

Table 4. Observed and Calculated Bond Lengths (Å) of 2-Silanaphthalenes, Their Isomers, and Parent Naphthalene (Si–C Lengths Are Described in Bold Type)

compound	1–2	2–3	3–4	4–10	10–5	5–6	6–7	7–8	8–9	9–1	9–10
1a (R = Tbt, obsd) ^a	1.704	1.765	1.36	1.27	1.66	1.36	1.37	1.40	1.30	1.64	1.39
1c (R = H, calcd) ^b	1.750	1.791	1.379	1.432	1.422	1.376	1.414	1.375	1.428	1.426	1.445
1-silanaphthalene (calcd) ^b	1.750	1.417	1.382	1.429	1.424	1.374	1.412	1.376	1.419	1.803	1.418
9-silanaphthalene (calcd) ^b	1.386	1.424	1.383	1.418	1.418	1.383	1.424	1.386	1.786	1.786	1.792
naphthalene (obsd) ^c	1.378	1.421	1.378	1.425	1.425	1.378	1.421	1.378	1.425	1.425	1.426
naphthalene (calcd) ^b	1.375	1.415	1.374	1.420	1.420	1.374	1.415	1.374	1.420	1.420	1.431

^a These values are not exact as mentioned in the text. ^b B3LYP/6-311+G(d,p) ^c From ref 32.

**Figure 4.** Calculated Si–C bond lengths (Å) of 2-silanaphthalene **1c** and related compounds (B3LYP/6-311+G(d,p)).**Table 5.** Relative Energies of Silanaphthalene Isomers (B3LYP/6-311+G(d,p), kcal/mol)

compound	relative energy
1-silanaphthalene	0.2
2-silanaphthalene	0
9-silanaphthalene	2.9

close resemblance to those of naphthalene (Figure 3), suggesting the structural similarity between 2-silanaphthalene and naphthalene.

Theoretically Optimized Structures. Table 4 summarizes the observed and calculated bond lengths of silanaphthalenes and naphthalene. Some computed Si–C bond lengths are also shown in Figure 4. The two different types of Si–C bond lengths (1.750 and 1.791 Å) in 2-silanaphthalene **1c** are between those of Si–C single (1.885 Å) and double bonds (1.708 Å), have the same average length as the 1.771 Å Si–C bond of silabenzene, and are clearly different from the Si–C lengths computed for the nonaromatic 2-silabutadiene.

In some fused aromatic systems, it is known that the aromaticity of one ring can be influenced by that of another ring.³³ If one ring is more aromatic, the aromaticity of a second ring may be reduced. However, the similar bond length patterns in 2-sila- vs naphthalene, as well as the similar ASEs (Figure 2) indicated that the degree of electron delocalization of the ring containing Si-atom is not appreciably reduced. This is consistent with the conclusion obtained by NMR spectra and NICS calculations.

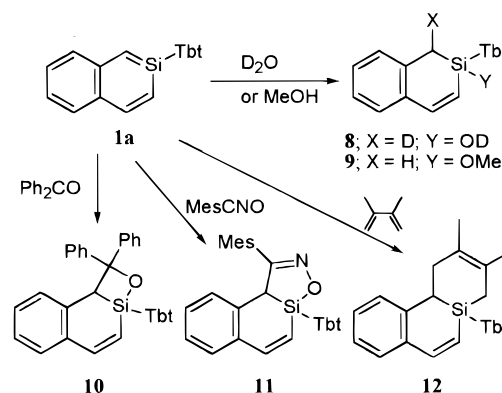
Comparison between Silanaphthalene Isomers. To obtain information about possibilities to synthesize other silanaphthalene isomers, 1- and 9-silanaphthalenes, theoretical calculations were performed on these isomers, the calculated bond lengths and relative energies of which are shown in Tables 4 and 5, respectively.

As shown in Table 4, all Si–C bond lengths of silanaphthalenes are between those of typical Si–C single (1.89 Å) and double bonds (1.71 Å), and the C–C bond lengths of silanaphthalenes have a close resemblance to those of naphthalene. Differences in relative energies between the silanaphthalene

isomers are small, 1- and 2-silanaphthalenes having almost the same energy. These results indicate that three silanaphthalene isomers have similar delocalized structure and stability. Thus, 1- and 9-silanaphthalenes can be synthetic targets if an effective steric protection group is introduced and an adequate synthetic route is developed.

Reactivity of 2-Silanaphthalene. Aromatic compounds are generally stable and have low reactivity despite the presence of unsaturated bonds. Silicon-containing doubly bonded compounds are highly reactive, more so than their carbon counterparts. Hence, sila-aromatic compounds can be expected to behave not only as heteroaromatic compounds but as conjugated double-bond organosilicon compounds. Judging from the reactions reported for transient silabenzenes and 1,4-disilabenzenes,^{1a,b} sila-aromatic species are still highly reactive, serving as Si-containing ethylene or 1,3-butadiene. The considerable aromatic stabilization predicted theoretically is not sufficient to overcome the inherent reactivity conferred by the presence of the silicon.

Indeed, despite the high thermal stability of 2-silanaphthalene **1a**, its Si=C bond is quite reactive toward various reagents as shown in Scheme 3. D₂O and MeOH reacted smoothly with **1a**

Scheme 3

to give the corresponding adducts **8** (72%) and **9** (59%), respectively. Reactions of **1a** with benzophenone, mesitronitrile oxide, and 2,3-dimethyl-1,3-butadiene afforded the corresponding [2 + 2], [2 + 3], and [2 + 4] cycloadducts **10**, **11**, and **12** in good yields. All of these reactions are similar to those of silenes whose reactivity has been much explored.^{1a,d} Attempted reactions of **1a** with dienophiles such as phenylacetylene, maleic anhydride, or tetracyanoethylene gave none of the expected cycloadducts, but rather complex mixtures.

The structure of **12** was established by X-ray crystallographic analysis, the results of which are shown in Figure 5 and Table 6. The high reactivity of 2-silanaphthalene **1a** and the inspection of the molecular structure of **12** indicate that Tbt group affords enough reaction space around the central Si atom despite its strong steric protection.

It is known that Si=C and Si=Si bonds react with elemental sulfur to afford the corresponding three-membered rings.³⁴

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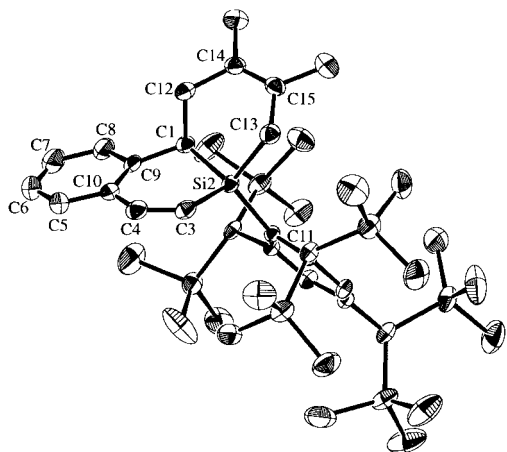


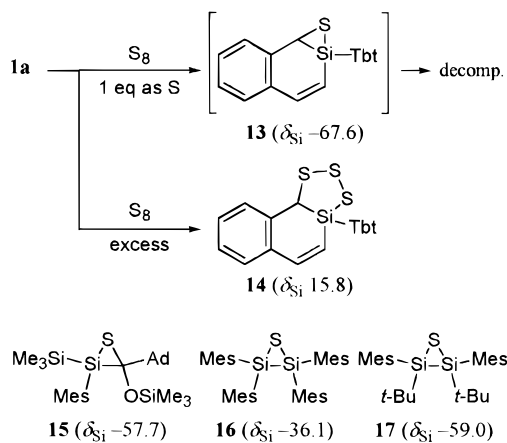
Figure 5. ORTEP drawing of **12** (30% probability) with nonhydrogen atoms.

Table 6. Selected Bond Lengths of **12** (Å)

C1–Si2	1.900(4)	C8–C9	1.385(5)
Si2–C3	1.853(4)	C9–C1	1.515(3)
C3–C4	1.326(5)	C9–C10	1.395(6)
C4–C10	1.467(7)	Si2–C11	1.914(3)
C10–C5	1.400(6)	C1–C12	1.565(2)
C5–C6	1.377(7)	Si2–C13	1.896(4)
C6–C7	1.386(6)	C14–C15	1.326(5)

Moreover, a variety of cyclic polysulfides containing group 14 elements were synthesized as stable compounds by utilizing the steric protection due to the Tbt group.³⁵ Sulfurization of **1a** was examined in the hope of obtaining some polysulfides fused with a 2-silanaphthalene ring. The reaction mixture of 2-silanaphthalene **1a** with 1 equiv (as S atom) of elemental sulfur showed a ²⁹Si NMR signal at -67.6 ppm, assignable to thiasililane **13** by comparison with the values reported for thiasililane and thiadisililane rings **15–17**. However, **13** decomposed during attempted separation, and its exact structure was not determined. Reaction of excess sulfur with **1a** afforded a new cyclic trisulfide **14** (Scheme 4). The formation of the five-membered ring in

Scheme 4



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this reaction may be due to steric effects. Indeed, most cyclic polysulfides containing Tbt-substituted group 14 elements have five-membered rings.^{12–14}

Stability of 2-Silanaphthalene. 2-Silanaphthalene **1a** was moisture-sensitive as mentioned above, but about one-third of **1a** was recovered after exposure to air in the solid state for 30 min. This remarkable stability toward air is noticeable when compared with that of unconjugated $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{Ad})\text{OSiMe}_3$ which reportedly decomposes in air immediately even in the solid state.³⁶

It is known that the silicon center of silenes has a strong Lewis acid character and is stabilized by complexation with Lewis bases such as THF, Me_3N , F^- , etc.³⁷ Such complex formation results in an upfield shift in the ²⁹Si NMR spectrum.^{1d,7} The ²⁹Si chemical shift of 2-silanaphthalene **1a** ($\delta_{\text{Si}} = 87.3$) in THF/ C_6D_6 (6:1), however, did not differ from that measured in C_6D_6 , indicating that **1a** does not form a complex with THF. In contrast, as mentioned earlier, the Si chemical shift of Märkl's silabenzene measured in THF/Et₂O/petroleum ether (4:1:1)⁶ is at a much higher field ($\delta_{\text{Si}} = 26.8$) than that of **1a**, indicating that it is coordinated with the solvent molecule, most likely THF, and hence stabilized in such a mixed solvent. The absence of complex formation of **1a** suggests the remarkable effectiveness of Tbt as a steric protecting group.

Conclusion and Outlook

Is the 2-silanaphthalene aromatic? Finally, we must answer this simple, yet important question from the results obtained experimentally and theoretically in this study. Although the definitive structural parameters were not determined experimentally by X-ray analysis, theoretical calculations revealed the structure of 2-silanaphthalene. Furthermore, important features theoretically predicted for the 2-silanaphthalene, namely, the delocalization of the Si=C double bond and structural similarity between 2-silanaphthalene and naphthalene, are also supported by the experimental NMR coupling constants and UV–vis and Raman spectra. Large negative NICS values and theoretical energetic evaluations (Figure 2) also indicate the ring current effects and energetic stabilization of the 2-silanaphthalene. Thus, all the results obtained theoretically and experimentally point to the aromatic character of the 2-silanaphthalene.

Despite its aromatic character, 2-silanaphthalene **1a**, unlike naphthalene, is highly reactive and similar to unsaturated silicon compounds. Molecules with an isolated Si=C double bond are inherently much more reactive than those with a C=C double bond. For example, addition of water to a Si=C double bond is more exothermic than addition to a C=C double bond by 60 kcal/mol.³⁸ Since the data in Figure 2 indicate that the six-membered ring containing silicon in the 2-silanaphthalene has essentially the same aromatic stabilization effect toward reactions which result in a single benzene moiety as that of naphthalene (around 11–12 kcal/mol³⁹), the energy of addition of water to 2-silanaphthalene is greater. Thus, the high reactivity

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(39) In typical reactions of naphthalene involving one of the rings, the total aromatic stabilization energy (ASE) of naphthalene must be reduced by the ASE of benzene since one benzene moiety remains after the reaction. The ASEs depend on the method of evaluation as described in ref 2. For a recent paper, see: Wiberg, K. B. *J. Org. Chem.* **1997**, *62*, 5720.

of the 2-silanaphthalene is not inconsistent with its aromaticity, which is insufficient to suppress an addition reaction across the Si=C bond.

Considering all of the results, we can conclude with confidence that the 2-silanaphthalene is highly aromatic.

Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ^1H (500 MHz), ^{13}C (125 MHz), and ^{29}Si (99 or 54 MHz) NMR spectra were recorded on a JEOL JNM-A500, Bruker AM-500, or JEOL JNM-EX270 spectrometer at room temperature. Chemical shifts were measured with tetramethylsilane as an external standard. High-resolution mass spectral data were obtained on a JEOL JMS-SX102 mass spectrometer. SCC (short column chromatography) and WCC (wet column chromatography) were performed on Wakogel C-200. PTL and DCC (dry column chromatography) were carried out on Merck Kieselgel 60 PF254 Art. 7743 and ICN Silica DCC 60A, respectively. Preparative HPLC was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAI-gel 1H and 2H columns (eluent: chloroform). 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 Department of Chemistry, Faculty of Science, The University of Tokyo. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr),¹¹ 1-bromo-2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]benzene (BbtBr),¹⁸ and 2,2-dichloro-1,2,3,4-tetrahydrosilanaphthalene⁴⁰ were prepared according to the reported procedures.

Computational Methods. The geometries of various silanaphthalenes and related reference molecules were optimized by using the Gaussian 98 program at B3LYP/6-311+G(d,p) levels of density functional theory.⁴¹ We have also carried out NICS calculations at the SOS-DFPT-IGLO⁴² level using the Perdew-Wang-91 exchange-correlation functional and the IGLO III TZ2P basis set as implemented in the deMon NMR program using the Pipek-Mezey localization procedure for analyzing the σ and π contributions.⁴³

Preparation of 1,2,3,4-Tetrahydro-2-silanaphthalene (2). To the suspension of LiAlH_4 (1.5 g, 40 mmol) in ether (30 mL) was added 1,2,3,4-tetrahydro-2,2-dichloro-2-silanaphthalene (5.95 g, 27.4 mmol) dropwise at room temperature. After the reaction mixture was stirred for 30 min, AcOEt (5 mL) was added to it, and the solvent was evaporated. Removal of inorganic salts by SCC ($\text{SiO}_2/\text{hexane}$) gave almost pure **2** (4.09 g, 100%) as a colorless liquid. **2**: bp 88 °C/23 mmHg; ^1H NMR (CDCl_3) δ 0.99–1.03 (m, 2H), 2.17 (t, $J = 3.2$ Hz, 2H), 2.78 (t, $J = 6.9$ Hz, 2H), 3.83 (quint, $J = 3.5$ Hz, 2H), 7.10–7.17 (m, 4H); ^{13}C NMR (CDCl_3) δ 3.51 (t), 12.94 (t), 29.07 (t), 125.38 (d), 126.73 (d), 128.22 (d), 129.52 (d), 136.97 (s), 141.40 (s); HRMS (EI, 70 eV): found m/z 148.0699, calcd for $\text{C}_9\text{H}_{12}\text{Si}$ ($[\text{M}]^+$) 148.0709. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{Si}$: C, 72.90; H, 8.15. Found: C, 73.08; H, 8.01.

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Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1,2,3,4-tetrahydro-2-silanaphthalene (3a). To a solution of TbtBr (4.08 g, 34%) in THF (100 mL) was added *t*-BuLi (1.75 M in pentane, 5.11 mmol) at -78 °C. After the mixture was stirred for 30 min, a solution of **2** (2.57 g, 17.3 mmol) in THF (20 mL) was added dropwise at -78 °C to it. The reaction mixture was warmed to room temperature within 10 h. After removal of the solvent the residue was dissolved in hexane (50 mL) and filtered. Purification by WCC ($\text{SiO}_2/\text{hexane}$) followed by reprecipitation from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ afforded **3a** (4.08 g, 34%) as a white powder. **3a**: mp 211–215 °C; ^1H NMR (CDCl_3) δ 0.01 (s, 18H), 0.04 (s, 18H), 0.04 (s, 18H), 1.09–1.13 (m, 2H), 1.32 (s, 1H), 2.04 (s, 2H), 2.29–2.38 (m, 2H), 2.86 (dt, $J = 14$, 8 Hz, 1H), 2.94 (d, $J = 8$, 5 Hz, 1H), 4.49 (quint, $J = 4$ Hz, 1H), 6.28 (br s, 1H), 6.40 (br s, 1H), 7.09–7.17 (m, 4H); ^{13}C NMR (CDCl_3) δ 0.72 (q), 0.75 (q), 1.04 (q), 6.77 (t), 20.52 (t), 28.64 (d), 29.06 (t), 29.92 (t), 30.42 (d), 121.78 (d), 124.95 (s), 125.38 (s), 126.64 (d), 126.84 (d), 128.13 (d), 129.64 (d), 138.25 (d), 141.10 (s), 144.65 (s), 151.48 (s), 151.82 (s); ^{29}Si NMR (CDCl_3) δ -26.59, 1.75, 1.89; HRMS (EI, 70 eV): found m/z 698.3868, calcd for $\text{C}_{36}\text{H}_{70}\text{Si}_7$ ($[\text{M}]^+$) 698.3863. Anal. Calcd for $\text{C}_{36}\text{H}_{70}\text{Si}_7$: C, 61.81; H, 10.09. Found: C, 61.52; H, 10.36.

Preparation of 2-{2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,2,3,4-tetrahydro-2-silanaphthalene (3b). Compound **3b** was synthesized by the same procedure as that for **3a**. The use of BbtBr (9.67 g, 13.7 mmol), *t*-BuLi (1.75 M, 26.8 mmol), and **2** (3.15 g, 23.1 mmol) gave **3b** as a white powder. **3b**: mp 276–280 °C dec; ^1H NMR (CDCl_3) δ 0.05 (s, 18H), 0.07 (s, 18H), 0.26 (s, 27H), 1.08–1.15 (m, 1H), 1.17–1.21 (m, 1H), 2.17 (s, 2H), 2.36 (dd, $J = 14.3$, 6.9 Hz, 1H), 2.37 (dd, $J = 14.3$, 2.5 Hz, 1H), 2.86 (td, $J = 13.8$, 5.0 Hz, 1H), 2.97 (dt, $J = 13.8$, 5.0, 1H), 4.44–4.47 (br m, 1H), 6.72 (s, 2H), 7.10–7.18 (m, 4H); ^{13}C NMR (CDCl_3) δ 1.43 (q), 1.45 (q), 5.47 (q), 9.16 (t), 21.04 (t), 22.23 (s), 29.85 (d), 29.97 (t), 125.43 (d), 126.50 (d), 126.69 (d), 127.94 (s), 128.12 (d), 129.56 (d), 138.15 (s), 140.92 (s), 146.49 (s), 151.52 (s); ^{29}Si NMR (CDCl_3) δ -25.77, 0.72, 1.51, 1.58; HRMS (EI, 70 eV): found m/z 770.4288, calcd for $\text{C}_{39}\text{H}_{78}\text{Si}_8$ ($[\text{M}]^+$) 770.4258. Anal. Calcd for $\text{C}_{39}\text{H}_{78}\text{Si}_8$: C, 60.69; H, 10.18. Found: C, 60.66; H, 9.96.

Preparation of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-silanaphthalene (4a). A mixture of **4a** (2.90 mg, 4.15 mmol), NBS (4.43 g, 24.9 mmol), and a catalytic amount of benzoyl peroxide was dissolved in benzene (300 mL) and refluxed for 2 h. After removal of the solvent, addition of THF (200 mL), and cooling to 0 °C, LiAlH_4 (1.5 g, 40 mmol) was added to the mixture, which was stirred for 2 h. AcOEt (20 mL) was added, the solvent evaporated, and the residue dissolved in chloroform (300 mL) and filtered. Purification by WCC ($\text{SiO}_2/\text{hexane}$) gave an inseparable mixture of **4a** and **5a** (~3:2 ratio determined by NMR).

This mixture was dissolved in THF (80 mL) and cooled to -78 °C; to this mixture was added *t*-BuLi (0.56 M in pentane, 3.6 mmol). After the solution was stirred for 1 min, excess amount of aqueous NH_4Cl was added. The solvent was evaporated, and inorganic salts were removed by SCC ($\text{SiO}_2/\text{hexane}$). Reprecipitation from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ gave pure **4a** (2.22 g, 77% from **3a**) as a white powder. **4a**: mp 135–138 °C; ^1H NMR (CDCl_3) δ -0.09 (s), -0.08 (s), -0.00 (s), -0.03 (s), -0.03 (s), 1.30 (s, 1H), 2.16 (br s, 1H), 2.22 (br s, 1H), 2.39 (dd, $J = 17$, 4 Hz, 1H), 2.50 (dd, $J = 17$, 5 Hz, 1H), 5.00 (t, $J = 4$ Hz, 1H), 6.24 (br s, 1H), 6.36 (br s, 1H), 6.27 (d, $J = 14$ Hz, 1H), 7.09–7.15 (m, 4H), 7.30 (d, $J = 14$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 0.39 (s), 0.67 (s), 0.70 (s), 1.01 (s), 17.37 (t), 28.66 (d), 28.98 (d), 30.46 (d), 121.71 (d), 124.52 (s), 125.89 (d), 126.29 (d), 126.65 (d), 127.75 (d), 130.75 (d), 132.29 (d), 135.14 (s), 135.40 (s), 144.90 (s), 147.00 (d), 151.83 (s), 152.10 (s); ^{29}Si NMR (CDCl_3) δ -43.91, 1.72, 1.81. HRMS (EI, 70 eV): found m/z 696.3702, calcd for $\text{C}_{36}\text{H}_{68}\text{Si}_7$ ($[\text{M}]^+$) 696.3706. Anal. Calcd for $\text{C}_{36}\text{H}_{68}\text{Si}_7$: C, 61.98; H, 9.82. Found: C, 61.70; H, 9.69.

Preparation of 2-{2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-silanaphthalene (4b). Compound **4b** was synthesized by the same procedure as that for **4a**. The use of **3b** (1.90 g, 2.46 mmol), NBS (2.67 mg, 1.50 mmol), and LiAlH_4 (0.7 g, 18 mmol) gave an inseparable mixture of **4b** and **5b** (~5:4 ratio determined by NMR), which was treated with *t*-BuLi (1.81 M in

pentane, 4.9 mmol) to afford **4b** as a white powder. **4b**: mp 208–212 °C; ¹H NMR (CDCl₃) δ -0.06 (s, 18H), 0.10 (s, 18H), 0.25 (s, 27H), 2.38 (s, 2H), 2.42 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.50 (dd, *J* = 16.8, 4.4 Hz, 1H), 5.03 (br m, 1H), 6.30 (d, *J* = 14.0 Hz, 1H), 6.70 (s, 2H), 7.10–7.14 (m, 4H), 7.29 (d, *J* = 14.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 1.11 (q), 1.46 (q), 5.40 (q), 17.36 (t), 22.23 (s), 22.91 (d), 125.96 (d), 126.39 (d), 126.55 (d), 127.09 (s), 127.76 (d), 130.74 (d), 132.19 (d), 135.07 (s), 135.33 (s), 146.68 (s), 146.77 (d), 151.78 (s); ²⁹Si NMR (CDCl₃) δ -42.82, 0.69, 1.44, 1.54. HRMS (EI, 70 eV): found *m/z* 768.4097, calcd for C₃₉H₇₆Si₈ ([M]⁺) 768.4101. Anal. Calcd for C₃₉H₇₆Si₈: C, 60.85; H, 9.95. Found: C, 60.69; H, 9.73.

Bromination of 4a. **4a** (50 mg, 0.072 mmol) and NBS (13 mg, 0.073 mmol) were dissolved in CCl₄ (10 mL) under dry air, and the solution was stirred at 0 °C. After disappearance of **4a** (~5 days) the solvent was evaporated, hexane (10 mL) was added, and the mixture was filtered. Removal of the solvent afforded almost pure 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-bromo-1,2-dihydro-2-silanaphthalene (**6a**) (48.5 mg, 87%) as white powder. As **6a** gradually decomposed in air to give TbtH, further purification was not performed. **6a**: mp 168–176 °C dec; ¹H NMR (C₆D₆, 500 MHz) δ 0.12 (s, 18H), 0.15 (s, 9H), 0.19 (s, 9H), 0.20 (s, 9H), 0.26 (s, 9H), 1.44 (s, 1H), 2.67 (br s, 1H), 2.70 (br s, 1H), 3.07 (d, *J* = 16.2 Hz, 1H), 3.19 (d, *J* = 16.2 Hz, 1H), 6.47 (br s, 1H), 6.60 (br s, 1H), 6.61 (d, *J* = 13.5 Hz, 1H), 6.87–7.06 (m, 5H); ¹³C NMR (C₆D₆, 126 MHz) δ 0.91 (q), 0.94 (q), 1.01 (q), 1.14 (q), 1.54 (q), 1.65 (q), 27.91 (t), 29.18 (d), 29.56 (d), 31.11 (d), 122.86 (d), 123.55 (s), 126.62 (d), 128.29 (d), 128.42 (d), 129.40 (d), 130.68 (d), 132.00 (d), 134.79 (s), 135.04 (s), 144.85 (d), 146.82 (s), 152.84 (s), 153.46 (s); ²⁹Si NMR (C₆D₆, 54 MHz) δ -7.51, 1.68, 2.16, 2.30, 2.78. HRMS (FAB): found *m/z* 776.2819, calcd for C₃₆H₆₇⁸¹BrSi₇ ([M]⁺) 776.2790. Anal. Calcd for C₃₆H₆₇BrSi₇: C, 55.69; H, 8.69; Br, 10.29. Found: C, 56.43; H, 9.01; Br, 7.71.

Bromination of 4b. Bromination of **4b** was performed by the same procedure as that for **4a**. The use of **4b** (200 mg, 0.260 mmol), NBS (46.7 mg, 0.262 mmol) gave almost pure 2-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-2-bromo-1,2-dihydro-2-silanaphthalene (**6b**) (216 mg, 98%) as a white powder. **6b** was also unstable in air. **6b**: mp 192–198 °C dec; ¹H NMR (C₆D₆) δ 0.19 (s, 18H), 0.28 (s, 18H), 0.32 (s, 27H), 2.84 (s, 2H), 3.02 (d, *J* = 16.5 Hz, 1H), 3.18 (d, *J* = 16.5 Hz, 1H), 6.63 (d, *J* = 13.7 Hz, 1H), 6.88 (s, 2H), 6.88–6.97 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 1H); ¹³C NMR (C₆D₆) δ 1.87 (q), 2.01 (q), 5.67 (q), 22.67 (s), 27.74 (d), 30.04 (d), 126.32 (s), 126.64 (d), 127.71 (d), 128.29 (d), 128.44 (d), 129.60 (d), 130.61 (d), 131.92 (d), 134.70 (s), 134.89 (s), 144.41 (d), 148.73 (s), 152.81 (s); ²⁹Si NMR (C₆D₆) δ -8.12, 1.06, 1.96, 2.48. HRMS (FAB): found *m/z* 846.3199, calcd for C₃₉H₇₅⁷⁹BrSi₈ ([M]⁺) 846.3207. Anal. Calcd for C₃₉H₇₅BrSi₈: C, 55.19; H, 8.90; Br, 9.41. Found: C, 56.06; H, 8.83; Br, 8.74.

Bromination of 3a. Bromination of **3a** was performed by the same procedure as that for **4a**. The use of **3a** (50 mg, 0.071 mmol) and NBS (14.0 mg, 0.079 mmol) gave almost pure 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-bromo-1,2,3,4-tetrahydro-2-silanaphthalene (**7a**) (56.7 mg, 100%) as a white powder. **7a** was also unstable in air. **7a**: ¹H NMR (CDCl₃) δ 0.02 (s, 9H), 0.05 (s, 9H), 0.06 (s, 18H), 0.10 (s, 9H), 0.11 (s, 9H), 1.36 (s, 1H), 1.50 (ddd, *J* = 15.6, 10.8, 5.5 Hz, 1H), 1.72 (dt, *J* = 14.8, 5.2 Hz, 1H), 2.05 (br s, 1H), 2.11 (br s, 1H), 2.77 (ddd, *J* = 14.8, 10.8, 5.0 Hz, 1H), 2.83 (d, *J* = 14.5 Hz, 1H), 2.92 (d, *J* = 14.5 Hz, 1H), 2.97 (dt, *J* = 14.3, 5.6 Hz, 1H), 6.31 (br s, 1H), 6.44 (br s, 1H), 7.14–7.20 (m, 4H); ¹³C NMR (CDCl₃) δ 0.39 (q), 0.80 (q), 0.98 (q), 1.03 (q), 1.53 (q), 20.42 (t), 28.64 (d), 29.14 (d), 29.53 (t), 30.50 (t), 30.72 (d), 122.38 (d), 124.53 (s), 125.99 (d), 126.67 (d), 127.44 (d), 127.68 (d), 130.54 (d), 135.98 (s), 139.89 (s), 146.29 (s), 151.85 (s), 152.77 (s).

Synthesis of 1a. To a solution of **6a** (334 mg, 0.43 mmol) in hexane (10 mL) was added *t*-BuLi (0.59 M in hexane, 0.045 mmol) with stirring. The solution was transferred into a Pyrex tube and degassed and sealed. After opening the tube in the glovebox filled with argon, the solvent was slowly removed. Generation of 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-silanaphthalene (**1a**) was confirmed by NMR spectra (~80%), although only small amount of pure **1a** was obtained by careful recrystallization from hexane. This crude mixture was used for further reactions without purification, and yields

were calculated, assuming that **1a** was pure. **1a**: mp 151–155 °C (dec); ¹H NMR (C₆D₆) δ 0.14 (s, 36H), 0.16 (s, 18H), 1.53 (s, 1H), 2.61 (br s, 1H), 2.72 (br s, 1H), 6.61 (br s, 1H), 6.73 (br s, 1H), 6.99 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.24 (dd, *J* = 13.0, 2.2 Hz, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 8.48 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (C₆D₆, 126 MHz) δ 0.62 (q), 0.82 (q), 31.51 (d), 36.87 (d), 37.50 (d), 116.01 (d), 120.58 (d), 121.53 (d), 122.56 (d), 125.69 (s), 126.08 (d), 126.70 (d), 128.26 (s), 128.77 (d), 133.27 (d), 146.53 (s), 148.01 (s), 148.95 (d), 152.33 (s), 152.38 (s); ²⁹Si NMR (C₆D₆, 54 MHz) δ 2.2, 2.5, 87.3; UV-vis (hexane) λ_{max} 267 nm (ε 2 × 10⁴), 327 nm (ε 7 × 10³), 387 nm (ε 2 × 10³). HRMS (EI, 70 eV): found *m/z* 694.3554 ([M]⁺), calcd for C₃₆H₆₆Si₇ 694.3549. Anal. Calcd for C₃₆H₆₆Si₇: C, 62.17; H, 9.56. Found: C, 60.97; H, 9.44.

Synthesis of 1b. Compound **1b** was synthesized by the same procedure as that for **1a**. The use of **6b** (216 mg, 0.254 mmol) and *t*-BuLi (0.45 M in hexane, 3.0 mmol) gave 2-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-2-silanaphthalene (**1b**) (~50% yield estimated by NMR spectra). Recrystallization from hexane gave small amount of **1b** as a white powder. **1b**: ¹H NMR (C₆D₆) δ 0.15 (s, 36H), 0.36 (s, 27H), 2.85 (s, 2H), 7.00 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.06 (s, 2H), 7.19 (dd, *J* = 13.1, 2.2 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 13.1 Hz, 1H); ¹³C NMR (C₆D₆) δ 1.19 (q), 5.46 (q), 23.29 (s), 39.25 (s), 114.97 (d), 120.55 (d), 121.96 (d), 125.99 (d), 126.77 (d), 128.59 (s), 128.72 (s), 133.30 (d), 146.49 (s), 148.99 (d), 149.59 (s), 151.94 (s); ²⁹Si NMR (C₆D₆) δ 1.15, 2.18, 86.68.

Crystal Data of 1a. Formula C₃₆H₆₆Si₇, *M* = 695.52, monoclinic, space group *P*2₁/*c*, *a* = 12.762(6) Å, *b* = 9.91(1) Å, *c* = 34.67(1) Å, β = 96.58(3)°, *V* = 4356(4) Å³, *Z* = 4, *D*_c = 1.060 g cm⁻³, *R* = 0.071 (*R*_w = 0.047). Colorless and prismatic single crystals of **1a** were grown by the slow evaporation of its hexane solution. The intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 193 K. The structure was solved by direct method with SHELXS-86, and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located by calculation. The final cycles of the least-squares refinements were based on 6018 observed reflections (*I* > 5.00σ(*I*)) and 388 variable parameters.

Reaction of 1a with Deuterium Oxide. To **1a** (30 mg, 0.043 mmol if pure) was added deuterium oxide (0.5 mL) and THF (2 mL). After the solution was stirred for 10 min, the solvent was removed. Purification by PTLC (hexane/chloroform = 2:1) afforded 1-deuterio-2-hydroxy-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-silanaphthalene (**8**) as a white powder (25.8 mg, 84%). As the *D* content of the white powder was 70% (from ¹H NMR), the net yield of **8** was 59%. The following data were obtained for the sample which was prepared by the reaction of **1a** with H₂O: **8**: mp 169–171 °C dec; ¹H NMR (CDCl₃, 500 MHz) δ -0.07 (s, 9H), -0.05 (s, 9H), 0.04 (s, 18H), 0.05 (s, 9H), 0.09 (s, 9H), 1.31 (s, 1H), 1.67 (s, 1H), 2.42 (br s, 1H), 2.46 (br s, 1H), 2.48 (d, *J* = 16.8 Hz, 1H), 2.55 (d, *J* = 16.8 Hz, 1H), 6.25 (br s, 1H), 6.36 (d, *J* = 14.0 Hz, 1H), 6.37 (br s, 1H), 7.08–7.14 (m, 4H), 7.27 (d, *J* = 14.0 Hz, 1H); ¹³C NMR (CDCl₃, 126 MHz) δ 0.54 (q), 0.73 (q), 0.77 (q), 0.89 (q), 1.14 (q), 24.77 (t), 28.27 (d), 28.54 (d), 30.42 (d), 122.08 (d), 125.78 (d), 125.99 (s), 127.06 (d), 127.51 (d), 130.48 (d), 130.55 (d), 131.23 (d), 135.10 (s), 136.00 (s), 144.99 (s), 146.03 (d), 151.51 (s), 151.97 (s); ²⁹Si NMR (CDCl₃, 54 MHz) δ -11.70, 1.61, 1.78, 2.13. HRMS (FAB): found *m/z* 712.3628 ([M]⁺), calcd for C₃₆H₆₈OSi₇ 712.3655. Anal. Calcd for C₃₆H₆₈OSi₇: C, 60.59; H, 9.60. Found: C, 60.29; H, 9.65.

Reaction of 1a with Methanol. To **1a** (30 mg, 0.043 mmol if pure) was added methanol (0.5 mL) and THF (2 mL). After the solution was stirred for 10 min, the solvent was removed. Purification by PTLC (hexane/chloroform = 2:1) afforded 2-methoxy-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2-dihydro-2-silanaphthalene (**9**) as a white powder (22.6 mg, 72%). **9**: mp 162–164 °C; ¹H NMR (CDCl₃, 500 MHz) δ -0.10 (s, 9H), -0.07 (s, 9H), 0.03 (s, 18H), 0.05 (s, 9H), 0.08 (s, 9H), 1.29 (s, 1H), 2.34 (d, *J* = 17.2 Hz, 1H), 2.47 (br s, 1H), 2.50 (br s, 1H), 2.55 (d, *J* = 17.2 Hz, 1H), 3.32 (s, 3H), 6.22 (br s, 1H), 6.29 (d, *J* = 14.0 Hz, 1H), 6.35 (br s, 1H), 7.08–7.14 (m, 4H),

7.38 (d, $J = 14.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 0.50 (q), 0.72 (q), 0.73 (q), 0.77 (q), 0.86 (q), 1.17 (q), 21.63 (t), 28.09 (d), 28.33 (d), 30.34 (d), 50.21 (q), 122.02 (d), 125.64 (d), 125.65 (s), 126.97 (d), 127.45 (d), 128.20 (d), 130.72 (d), 132.17 (d), 135.12 (s), 136.48 (s), 144.73 (s), 147.30 (d), 151.66 (s), 152.14 (s); ^{29}Si NMR (CDCl_3 , 54 MHz) δ -11.12, 1.44, 1.75, 2.23. HRMS (FAB): found m/z 726.3784 ($[\text{M}]^+$), calcd for $\text{C}_{37}\text{H}_{70}\text{OSi}_7$ 726.3811. Anal. Calcd for $\text{C}_{37}\text{H}_{70}\text{OSi}_7 \cdot 0.5\text{H}_2\text{O}$: C, 60.33; H, 9.71. Found C, 60.29; H, 9.65.

Reaction of 1a with Benzophenone. **1a** (30 mg, 0.043 mmol if pure) and benzophenone (30 mg, 0.16 mmol) were dissolved in C_6D_6 (0.8 mL). **1a** disappeared immediately, and removal of the solvent followed by purification by PTLC (hexane/chloroform = 1:1) afforded 3,9b-dihydro-1,1-diphenyl-3-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-1H-[2]benzosilino[2,1-*b*][1,2]oxasilole (**10**) as a white powder (23.4 mg, 62%). **10**: mp 230–235 °C dec; ^1H NMR (CDCl_3) δ -0.19 (s, 9H), -0.15 (s, 9H), 0.013 (s, 18H), 0.017 (s, 9H), 0.05 (s, 9H), 1.32 (s, 1H), 1.90 (br s, 1H), 1.93 (br s, 1H), 4.49 (s, 1H), 6.09 (d, $J = 14.7$ Hz, 1H), 6.25 (br s, 1H), 6.36 (br s, 1H), 6.79 (d, $J = 7.0$ Hz, 1H), 6.88–6.91 (m, 4H), 7.05–7.14 (m, 4H), 7.19–7.27 (m, 3H), 7.43 (d, $J = 7.3$ Hz, 1H), 7.62 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 0.44 (q), 0.61 (q), 0.67 (q), 0.77 (q), 1.11 (q), 28.45 (d), 29.26 (d), 30.72 (d), 48.72 (q), 92.42 (s), 121.40 (d), 125.39 (d), 125.64 (d), 126.01 (d), 126.17 (s), 126.19 (d), 126.39 (d), 126.72 (d), 126.86 (d), 126.91 (d), 127.69 (d), 127.73 (d), 131.94 (d), 132.61 (d), 135.71 (s), 136.32 (s), 143.69 (s), 146.24 (s), 150.13 (d), 150.53 (s), 150.87 (s), 151.01 (s); ^{29}Si NMR (CDCl_3 , 54 MHz) δ 1.82, 2.40, 5.11. HRMS (FAB): observed m/z 877.4375 ($[\text{M} + \text{H}]^+$); calcd for $\text{C}_{49}\text{H}_{76}\text{OSi}_7$ 877.4375. Anal. Calcd for $\text{C}_{49}\text{H}_{76}\text{OSi}_7$: C, 67.05; H, 8.72. Found C, 67.32; H, 8.84.

Reaction of 1a with Mesitronitrile Oxide. By the same procedure as that for **9**, **1a** (30 mg, 0.043 mmol if pure) and mesitronitrile oxide (30 mg, 0.19 mmol) afforded 4,10b-dihydro-1-mesityl-4-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-[2]benzosilino-[1,2-*d*][1,2,5]oxazasilole (**11**) as a white powder (28.5 mg, 77%). **11**: mp 224–232 °C; ^1H NMR (CDCl_3) δ -0.12 (s, 9H), -0.08 (s, 9H), 0.01 (s, 18H), 0.03 (s, 9H), 0.05 (s, 9H), 1.36 (s, 1H), 1.38 (s, 3H), 1.88 (br s, 1H), 1.97 (br s, 1H), 2.20 (s, 3H), 2.25 (s, 3H), 3.85 (s, 1H), 6.25 (d, $J = 14.4$ Hz, 1H), 6.35 (br s, 1H), 6.46 (br s, 1H), 6.48 (d, $J = 7.6$ Hz, 1H), 6.55 (s, 1H), 6.83 (s, 1H), 6.90 (t, $J = 7.7$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.37 (d, $J = 14.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 0.34 (q), 0.68 (q), 0.71 (q), 0.91 (q), 1.23 (q), 18.60 (q), 19.68 (q), 21.03 (q), 29.37 (d), 29.83 (d), 30.79 (d), 41.65 (d), 121.85 (d), 123.71 (s), 125.56 (d), 126.80 (d), 127.45 (d), 127.83 (d), 127.86 (d), 127.98 (d), 128.63 (s), 130.22 (s), 131.84 (d), 134.74 (d), 135.20 (s), 135.30 (s), 137.89 (s), 138.03 (s), 146.27 (s), 148.48 (d), 151.87 (s), 152.26 (s), 166.04 (s). ^{29}Si NMR (CDCl_3 , 54 MHz) δ 1.61, 1.85, 2.68, 6.86. HRMS (FAB): observed m/z 856.4485 ($[\text{M} + \text{H}]^+$); calcd for $\text{C}_{46}\text{H}_{79}\text{ONSi}_7$ 856.4469. Anal. Calcd for $\text{C}_{46}\text{H}_{79}\text{ONSi}_7 \cdot \text{H}_2\text{O}$: C, 63.16; H, 9.10; N, 1.60. Found C, 63.47; H, 9.18; N, 1.35.

Reaction of 1a with 2,3-Dimethyl-1,3-butadiene. To a solution **6a** (87.8 mg, 0.113 mmol) in hexane (2 mL) was added *t*-BuLi (0.56 M in hexane, 0.134 mmol) and 2,3-dimethyl-1,3-butadiene (1 mL). The solution was transferred into a Pyrex tube and degassed and sealed. After heating at 100 °C for 20 h, the tube was opened. Purification by DCC (hexane) afforded 4b,5,8,8a-tetrahydro-6,7-dimethyl-8a-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-8a-silaphenanthrene (**12**) as a white powder (62.9 mg, 72%). **12**: mp 153–159 °C; ^1H NMR (CDCl_3) δ -0.07 (s, 9H), -0.06 (s, 9H), -0.04 (s, 9H), 0.009 (s, 9H), 0.011 (s, 9H), 0.04 (s, 9H), 1.26 (s, 1H), 1.49 (s, 3H), 1.66 (s, 3H), 1.70 (d, $J = 15.6$ Hz, 1H), 1.79 (t, $J = 6.7$ Hz, 1H), 2.10 (br s, 1H), 2.15 (br s, 1H), 2.36 (d, $J = 6.7$ Hz, 1H), 2.53 (t, $J = 6.7$ Hz, 1H), 6.06 (d, $J = 14.0$ Hz, 1H), 6.22 (br s, 1H), 6.34 (br s, 1H), 7.01–7.17 (m, 5H); ^{13}C NMR (CDCl_3) δ 0.62 (q), 0.72 (q), 0.82 (q), 0.86 (q), 1.06 (q), 1.40 (q), 20.80 (q), 22.45 (q), 23.04 (t), 28.01 (d), 28.40 (d), 28.60 (d), 30.26

(d), 41.84 (t), 122.18 (d), 125.86 (d), 126.55 (s), 126.96 (s), 127.44 (d), 127.97 (d), 128.26 (s), 128.77 (d), 130.45 (d), 132.42 (d), 135.85 (s), 141.39 (s), 144.07 (s), 144.61 (d), 151.52 (s), 151.97 (s); ^{29}Si NMR (CDCl_3 , 54 MHz) δ -24.87, 1.68, 1.78, 1.96. HRMS (EI, 70 eV): found m/z 776.4315 ($[\text{M}]^+$); calcd for $\text{C}_{42}\text{H}_{76}\text{Si}_7$ 776.4332. Anal. Calcd for $\text{C}_{42}\text{H}_{76}\text{Si}_7$: C, 64.86; H, 9.85. Found C, 64.60; H, 9.56.

Crystal Data of 12. Formula $\text{C}_{42}\text{H}_{76}\text{Si}_7$, $M = 777.66$, triclinic, space group $P\bar{1}$, $a = 13.220(2)$ Å, $b = 16.128(3)$ Å, $c = 12.486(3)$ Å, $\alpha = 93.33(2)^\circ$, $\beta = 97.11(1)^\circ$, $\gamma = 106.66(1)^\circ$, $V = 2518.4(8)$ Å³, $Z = 2$, $D_c = 1.025$ g cm⁻³, $R = 0.056$ ($R_w = 0.038$). Colorless and prismatic single crystals of **12** were grown by the slow evaporation of its $\text{CHCl}_3/\text{CH}_3\text{CN}$ solution. The intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 296 K. The structure was solved by direct method with SHELXS-86, and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located by calculation. The final cycles of the least-squares refinements were based on 5179 observed reflections ($I > 3.00\sigma(I)$) and 442 variable parameters.

Reaction of 1a with 1 Equiv Amount of Elemental Sulfur. **1a** (30 mg, 0.043 mmol) and elemental sulfur (1.4 mg, 0.044 mmol as S atom) were dissolved in C_6D_6 (0.7 mL). After the solution was transferred into an NMR tube, degassed, and sealed, the signal assignable to **13** ($\delta_{\text{Si}} = -67.62$) was observed by ^{29}Si NMR. However, purification of this reaction mixture by PTLC (hexane/chloroform = 2:1) gave only a hydrolyzed product (11.3 mg, 37%), and the rest was a complex mixture.

Reaction of 1a with an Excess Amount of Elemental Sulfur. **1a** (98.8 mg, 0.142 mmol) and elemental sulfur (50 mg, 1.56 mmol as S atom) were dissolved in benzene (4 mL). After removal of the solvent, the crude products were submitted to separation by WCC (hexane/chloroform = 2:1) and HPLC to afford 4,10b-dihydro-4-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-[2]benzosilino[2,1-*d*]-1,2,3,4-trithiasilole (**14**) as a white powder (23.0 mg, 20%). ^1H NMR (CDCl_3) δ -0.10 (s, 9H), -0.05 (s, 9H), 0.02 (s, 18H), 0.07 (s, 9H), 0.11 (s, 9H), 1.32 (s, 1H), 2.46 (s, 2H), 4.40 (s, 1H), 6.14 (d, $J = 13.8$ Hz, 1H), 6.29 (br s, 1H), 6.41 (s, 1H), 7.15–7.26 (m, 5H); ^{13}C NMR (CDCl_3 , 126 MHz) δ 0.55 (q), 0.73 (q), 0.89 (q), 0.98 (q), 1.30 (q), 29.2 (d), 29.50 (d), 30.89 (d), 44.11 (d), 118.56 (s), 122.70 (d), 126.66 (d), 127.79 (d), 127.97 (d), 128.26 (d), 131.20 (d), 132.13 (d), 134.58 (s), 136.00 (s), 144.15 (d), 147.18 (s), 153.57 (s), 153.95 (s); ^{29}Si NMR (CDCl_3 , 54 MHz) δ 1.99, 2.16, 2.57, 15.37. HRMS (FAB): observed m/z 791.2773, calcd for $\text{C}_{36}\text{H}_{67}\text{Si}_7\text{S}_3$ 791.2790. Anal. Calcd for $\text{C}_{36}\text{H}_{67}\text{Si}_7\text{S}_3$: C, 54.62; H, 8.40; S, 12.15. Found C, 53.91; H, 8.33; S, 10.32.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a** and **12**, and total electronic energies and atomic coordinations for all molecules used in Figure 2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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