Invited Paper

The Chemistry of Stable Silabenzenes

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Stable silabenzenes (**1a**; R = Tbt, **1b**; R = Bbt) were synthesized by taking advantage of extremely bulky and efficient steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis-[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt). The structure of Tbt-substituted **1a** was determined by X-ray crystallographic analysis, which demonstrated the complete delocalization of the π-electrons of the silabenzene ring. It was found that silabenzene **1a** reacted with C–C and C–O multiple bond compounds to give the corresponding [4+2]-cycloadducts via 1,4-addition, while **1a** underwent both 1,2- and 1,4-additions by the reaction with methanol. Silabenzene **1a** dimerized very gradually to afford its [4+2]-dimer, although **1b** showed no change under the same conditions. Photochemical reaction of **1a** gave the corresponding silabenzvalene isomer instead of the Dewar silabenzene isomer.

Keywords: Silabenzene; Kinetic stabilization; Silaaromatics; Delocalized π electrons; Silabenzvalene.

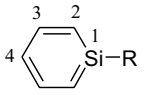
INTRODUCTION

Benzene, a 6π-electron ring system, is one of the most important and fundamental organic molecules.[1] Since silicon is located just under carbon in the periodic table and is expected to have similar characters to those of carbon, the chemistry of silabenzene (silicon analogues of benzene) has been much focused on and explored in recent decades.[2] Although aromatic characters of silabenzene were predicted by theoretical calculations,[2c,e] little experimental information has been obtained for silabenzene. Photoelectron, UV and IR spectra of silabenzene were measured in low-temperature argon matrices or in the gas phase.[3] Some trapping reactions which support the formation of silabenzene derivatives were also reported.[4]

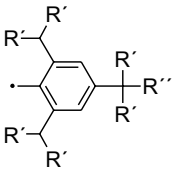
Silabenzene can be regarded as not only an aromatic compound but also a low-coordinated organosilicon compound. Non-conjugated doubly bonded compounds containing a silicon atom have already been synthesized as stable molecules by taking advantage of kinetic stabilization, namely, by introducing bulky substituents around the reactive double bonds.[5,6] Although applications of this method to stabilize silabenzene have also been reported, no silabenzene stable at ambient temperature has ever been reported until the start of our research. The meta-stable silabenzene described is 1,4-di-*tert*-butyl-2,6-bis(trimethylsilyl)-1-silabenzene, which is reportedly stable below –100 °C and observed by low-temperature NMR measurements.[4f] However, it was stable only below –100 °C in a special solvent (THF/ether/petroleum ether, 4:1:1) and clearly coordinated with the solvent (most likely THF) as judged by the relatively high field ^{29}Si chemical shift (δ_{Si} = 26.8). Although a more hindered silabenzene, 1-*tert*-butyl-2,6-bis-(dimetylisopropylsilyl)-4-trimethylsilyl-1-silabenzene, was generated under argon flow, it was stable only at –180 °C in argon matrix.[3f]

Although the successful syntheses of anion and dianion species of silacyclopentadienes[7] and cyclic diaminosilylenes[8] indicated the existence of "silicon-containing aromatic systems",[2e] synthesis of silicon analogues of simple benzenoid aromatic compounds still remains as an important subject in organosilicon chemistry. A highly efficient steric protection group is essential for the synthesis of stable silabenzenoid compounds, since only one substituent can be introduced on their reactive silicon center. The use of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and 2,6-bis[bis(trimethylsilyl)methyl]-4-

[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt hereafter) groups, which were developed by us[9] and successfully applied to stabilize a variety of low-coordinated main group element compounds,[10] brought good results. Thus, Tbt or Bbt-substituted silaaromatic compounds such as silabenzene,[11] 1- and 2-silanaphthalenes,[12,13] 9-silaanthracene,[14] 9-silaphenanthrene[15] were successfully synthesized and their detailed properties, especially their aromatic character, were revealed. Recently, the heavier analogues of silaaromatics, i. e., germa-[16] and stannaaromatics,[17] have also been obtained as stable "*heavy aromatics*". While we have reported the preliminary contributions on the synthesis of a stable silabenzene and its structural determination by X-ray crystallographic analysis,[11] we wish to describe here the details of the synthesis, structure, and reactivity of stable silabenzenes bearing 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) groups.[18]



1a; R = Tbt
1b; R = Bbt
1c; R = H
1d; R = Ph
1e; R = Tbtx

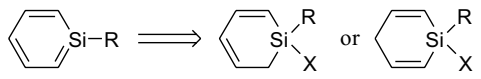


Tbt; R′ = $SiMe_3$, R′′ = H
Bbt; R′ = R′′ = $SiMe_3$
Tbtx; R′ = SiH_3, R′′ = H

RESULTS AND DISCUSSION

Synthesis of Silabenzenes

Many synthetic routes have been developed towards transient silabenzenes.[2] Taking the preparative scale synthesis and our successful synthesis of other metallaaromatics[11-17] into account, we selected halosilacyclohexadienes as the precursors of silabenzenes **1**.

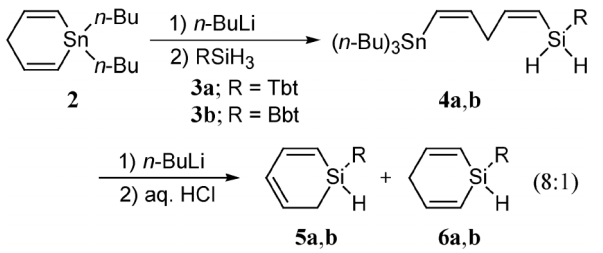


1
R = Tbt, Bbt

X = halogen

Although we first attempted the introduction of a Tbt group onto 1,1-dihydro- or 1,1-dihalo-1-silacyclohexa-2,4-diene, the substitutions did not occur efficiently.[19] After the examinations of several routes, we finally succeeded in the synthesis of the mixture of silacyclohexadienes **5** and **6** starting from stannacyclohexadiene **2** and bulky trihydrosilanes **3** (Scheme I) according to the method similar to that used for the synthesis of the substituted silacyclohexadienes.[20] The mixture of **5** and **6** was subjected to further reactions without separation since the mixture was inseparable by any chromatographic methods.

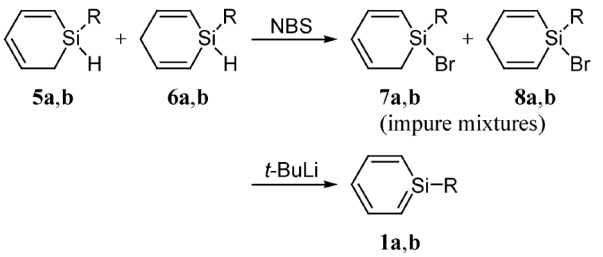
Scheme I



2
3a; R = Tbt
3b; R = Bbt
4a,**b**
5a,**b**
6a,**b**
(8:1)

The synthesis of silabenzenes **1** was attempted by using the same method as that for the stable 2-silanaphthalene,[13] namely, the bromination of hydrosilanes followed by the treatment with *t*-BuLi (Scheme II). However, the bromination of **5** and **6** did not take place efficiently and gave an impure mixture of **7** and **8**, the dehydrobromination of which resulted in the formation of only small amounts of silabenzenes **1** (~30% as judged by ^{1}H NMR).

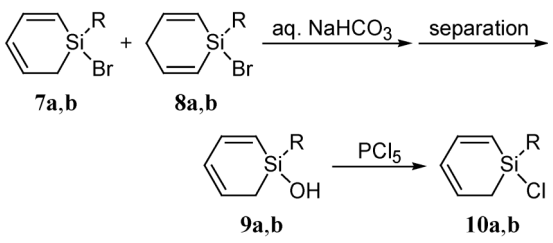
Scheme II



5a,**b**
6a,**b**
7a,**b**
8a,**b**
(impure mixtures)
1a,**b**

Although a mixture of **5** and **6** as well as that of **7** and **8** was inseparable, silanols **9** could be separated and purified from a crude mixture of the hydrolyzed products of **7** and **8**. The hydroxyl groups of **9** were easily converted to chlorosilanes **10** by the treatment with PCl_5 (Scheme III).

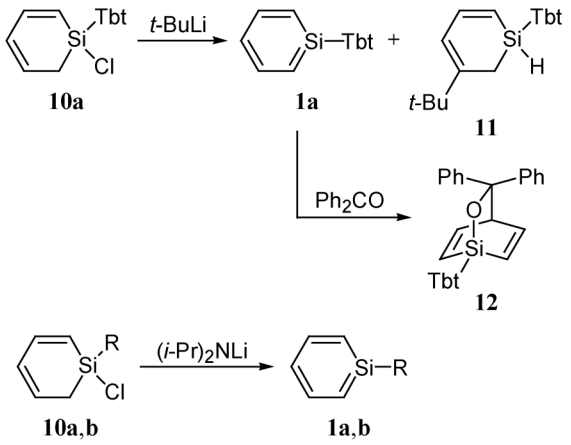
Scheme III



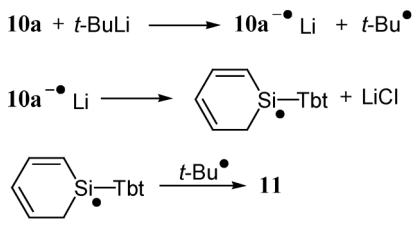
7a,**b**
8a,**b**
9a,**b**
10a,**b**

The treatment of **10a** with *t*-BuLi afforded silabenzene **1a** and a similar amount of a byproduct as indicated by the ^{1}H NMR spectrum. The addition of benzophenone to the reaction mixture followed by chromatographic separation gave the byproduct **11** (27%) along with **12** (20%), i.e., the benzophenone adduct of silabenzene **1a** (Scheme IV). The formation of **11** is most likely interpreted in terms of electron transfer from *t*-BuLi to **10** followed by a radical coupling reaction (Scheme V), although the mechanism is unclear at present. After examining several conditions, the formation of **11** was completely suppressed by using lithium diisopropylamide (LDA) as a base. Thus, the reactions of chlorosilanes **10a**,**b** with LDA at room temperature proceeded efficiently to give almost pure silabenzenes **1a**,**b** (96%).

Scheme IV



Scheme V



Although 1,4-di-*tert*-butyl-1-silabenzene was previously postulated as an initial product in a similar reaction of the corresponding chlorosilane with LDA, the isolated product was its dimer.[4c] In contrast, silabenzenes **1**, effectively protected by the extremely bulky Tbt or Bbt groups, have enough stability for the investigation of their detailed properties as described below.

NMR Spectra

^{29}Si, ^{13}C and ^{1}H NMR chemical shifts of silabenzenes **1a**,**b** are shown in Table 1.[21] The silabenzene rings were symmetric in terms of NMR spectra, which were assigned by 2D NMR techniques together with decoupling measurements. In Table 1 are also shown the calculated chemical shifts of the model compounds **1e** (the methyl groups of the Tbt group are replaced by hydrogens) and the real molecule **1a** for comparison. The agreement between the observed and calculated values is fairly good.

As shown in Table 1, ^{29}Si NMR signals of the central Si atom of silabenzenes **1a**,**b** were observed around 93 ppm. These values are in the low-field area characteristic of low-coordinate silicon compounds and are also similar to those of Tbt-substituted silaaromatics (87.3 ppm for 2-Tbt-2-silanaphthalene, 91.7 ppm for 1-Tbt-1-silanaphthalene, 87.2 ppm for 9-Tbt-9-silaanthracene, 86.9 ppm for 9-Tbt-9-silaphenanthrene). Although δ_{Si} values reported for stable Si–C doubly bonded compounds are widely scattered depending on the substituents, those of **1** are reasonably compared with that (δ_{Si} = 77.6) of $Mes_2Si{=}C(H)CH_2(t\text{-}Bu)$[22] and clearly different from that (δ_{Si} = 26.8) of previously reported marginally stable silabenzene, 1,4-di-*tert*-butyl-2,6-bis(trimethylsilyl)-1-silabenzene.[4f]

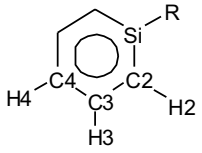
We have examined the delocalization of the double bonds of Tbt-substituted 2-silanaphthalene on the basis of the Si–C coupling constants (92 and 76 Hz),[13] which considerably exceed those of typical Si–C single bonds (~50 Hz).[23] The J_{Si-C2} values for silabenzenes **1a**,**b** were measured to be both 83 Hz. These values are consistent with the order of bond strengths (Si–C3 of 2-Tbt-2-silanaphthalene < 1-Tbt-1-silabenzene < Si–C1 of 2-Tbt-2-silanaphthalene) which is analogous to that of benzene and naphthalene. This order of bond strengths was also supported by the observed and calculated bond lengths.[13b] The J_{Si-C} values of silabenzene **1** are also similar to that of $(Me_3Si)_2Si{=}C(R)OSiMe_3$ (83–85 Hz),[24] which has a partial Si–C double bond character.[25]

The aromatic characters of silaaromatics have been discussed on the basis of the low-field shifts of the ^{1}H NMR signals.[13] Approximately 1 ppm low-field shifts were observed for the ring protons upon the aromatization of the silicon-containing six-membered ring.[13] In the case of silabenzene **1a** (Fig. 1), low-field shifts of approx. 1 ppm were also found upon aromatization. These shifts are similar to the difference of chemical shifts between cyclohexadiene (δ_H = 5.84) and benzene (δ_H = 7.34), supporting the aro-

Table 1. Observed and calculated NMR chemical shifts (ppm) of silabenzenes

Compound	Si	C2	C3	C4	H2	H3	H4
1a (R = Tbt, obsd)[a]	93.64	122.15	143.55	116.08	7.11	8.00	6.71
1b (R = Bbt, obsd)[a]	92.93	121.25	143.55	115.91	7.03	7.98	6.69
1e (R = Tbtx, calcd)[b]	89.88	126.67	148.52	121.50	6.99	8.08	6.78
1a (R = Tbt, calcd)[b]	96.33	127.98	148.13	119.91	6.81	7.99	6.63

[a] C_6D_6, room temperature.
[b] GIAO-B3LYP/6-311G(d)(6-311G(3d) on Si)//B3LYP/6-31G(d)



matic character of the silabenzene ring.

Structure

The D_{6h} symmetric hexagonal structure is one of the most important features of benzene. Although all structural optimization for silabenzenes indicated delocalized π-systems and aromaticity of silabenzenes,[2c,e] no structural analysis was performed due to their high instability. We have succeeded in the X-ray crystallographic analysis of the stable silabenzene **1a** for the first time and its structure was definitely determined (Fig. 2). The sum of the bond angles around the central Si atom and that of the interior bond angles of the silabenzene ring are 359.8(3)° and 720.0(9)°, respectively, indicating the planar geometry around the central silicon atom and the silabenzene ring. The lengths of two Si–C bonds in the silabenzene ring were found to be essentially equal to each other (1.765(4) and 1.770(4) Å) and in the middle between those of Si–C double and single bonds (1.70[26] and 1.89[27] Å, respectively). Furthermore, the C–C bond lengths (1.381(6) ~ 1.399(6) Å) in the silabenzene ring are almost equal to each other within the error of temperature factors, and also similar to the C–C length of benzene (1.39–1.40 Å).[1] Thus, it has experimentally been demonstrated that the silabenzene has a delocalized 6π-electron ring system similar to that of benzene. A slight difference between C3–C4 and C4–C5 lengths is probably due to the packing effect, which causes a close contact around *para*-positions of two silabenzene rings (Fig. 3).

Theoretical calculations at the level of B3LYP/6-311G(d,p) have predicted the Si–C bond length of parent silabenzene **1c** to be 1.771 Å, which is in good agreement with the observed value of **1a** as shown in Table 2. The calculated C–C bond lengths for **1c** (1.398 and 1.401 Å) are also close to those observed for **1a**. To evaluate the effect of bulky substituents, we calculated the geometry of the real molecule **1a** and the model compounds **1c-e**. At B3LYP/6-31G(d) level, the bond lengths of the model compound **1e**

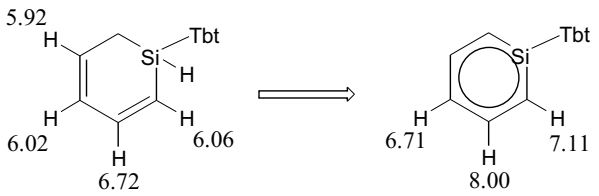


Fig. 1. Chemical shift changes of in ^{1}H NMR upon aromatization.

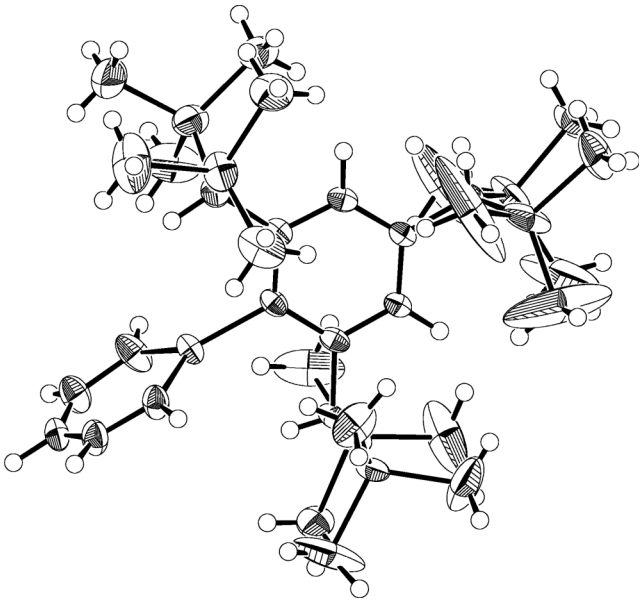


Fig. 2. Molecular structure of silabenzene **1a** (ORTEP, 50% probability).

Table 2. Observed and calculated bond lengths of silabenzenes

Compound	Method	Si–C2	C2–C3	C3–C4
1a (R = Tbt)	X-ray[a]	1.765(4)	1.391(6)	1.399(6)
		1.770(4)	1.397(6)	1.381(6)
1c (R = H)	B3LYP/6-311G(d,p)[b]	1.771	1.398	1.401
1c (R = H)	B3LYP/6-31G(d)[a]	1.773	1.400	1.403
1d (R = Ph)	B3LYP/6-31G(d)[a]	1.776	1.400	1.403
1e (R = Tbtx)	B3LYP/6-31G(d)[a]	1.777	1.401	1.402
1a (R = Tbt)	B3LYP/6-31G(d)[a]	1.780	1.401	1.402

[a] This work. [b] Ref. 2e.

(R = Tbtx) are almost the same as those of the parent compound **1c**. Thus, it can be concluded that an extremely bulky Tbt group exerts essentially no perturbation on the structure of the silabenzene ring.

UV Spectra

Tbt-substituted silabenzene **1a** showed absorption maxima in the UV-vis spectrum at 260 (sh), 301, 323, and 331 nm, which may be attributable to the several types of π-π* electron transitions. The comparison of the UV-vis spectra among benzene – silabenzene – 1,4-disilabenzene series was also reported.[28]

Reactivity

Only limited reactivities of silabenzenes were investigated using transient species. Although the 2-silanaphthalene was concluded to be highly aromatic, it reacted with various reagents at its 1,2-position like an unconjugated Si–C doubly bonded compound,[13] in contrast to the case of benzene, which is known to be inert toward some organic reagents such as alcohol, olefins, alkynes, and nitrile oxides. This reactivity can be explained by its structural similarity to naphthalene; the C1–C2 bond of naphthalene has a stronger double bond character than the C2–C3 bond. On the contrary, silabenzene **1a** has completely delocalized double bonds like benzene and its detailed reactivity is interesting.

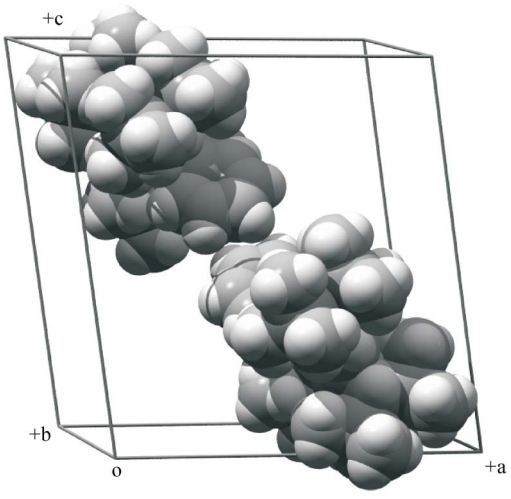
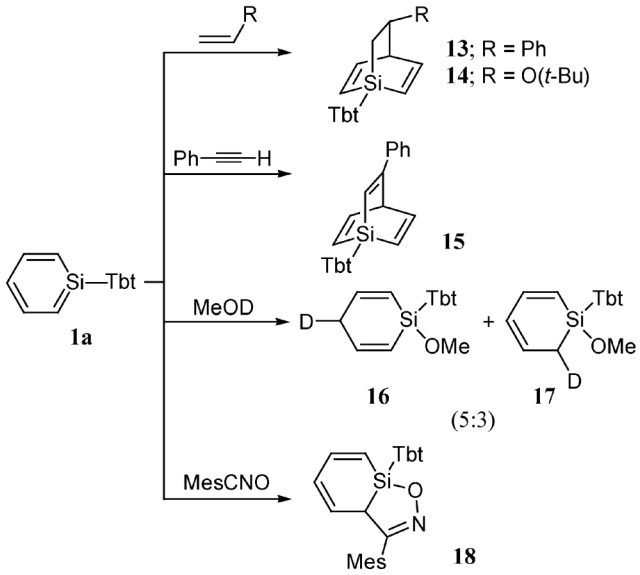


Fig. 3. Packing diagram of the silabenzene **1a**. Only two of four molecules in a unit cell are shown for clarity.

As mentioned above, silabenzene **1a** was trapped by benzophenone to afford the corresponding adduct **12** (Scheme IV). The structure of **12** was revealed by X-ray crystallographic analysis (Fig. 4), which clearly indicated that the silabenzene reacted with benzophenone via [4+2]-cycloaddition. Furthermore, C–C double and triple bond compounds were allowed to react with silabenzene **1a** to give the [4+2]-cycloadducts **13**–**15** as shown in Scheme VI. The structures of **13**–**15** were confirmed by X-ray crystallographic analyses (Fig. 5–7, respectively).

Scheme VI



Although the reaction of the previously reported silabenzenes with methanol afforded the corresponding 1,2-adduct,[3] the reaction of stable silabenzene **1a** with methanol gave both 1,4-adduct **16** and 1,2-adduct **17** in a ratio of 5:3. Mesitonitrile oxide reacted with silabenzene **1a** to afford the [3+2]-cycloadduct **18**, the structure of which was determined by X-ray crystallographic analysis (Fig. 8).

The products of these reactions indicate that silabenzene **1a** can undergo both 1,2- and 1,4-addition reactions.

These reactivities are quite different from that of the previously reported Tbt-substituted 2-silanaphthalene[13] and 9-silaanthracene,[14] which reacted selectively with some reagents only at 1,2-position and 9,10-position giving the corresponding adducts, respectively. Since these additions must accompany the destruction of the fused aromatic moiety, it should be energetically unfavorable. This type of energetic disadvantage for the 1,4-addition is not conceivable in the case of silabenzene.

Theoretical Investigation on Reactivity

To clarify the reactivity of silabenzene **1a**, we theoretically investigated the reaction pathways of addition reactions of a silabenzene. Addition reactions of the parent silabenzene **1c** with acetylene, nitrile oxide, and methanol

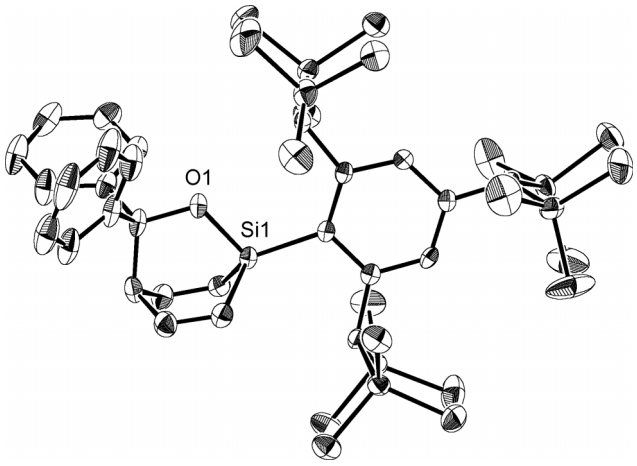


Fig. 4. Molecular structure of benzophenone adduct **12** (ORTEP, 50% probability). Hydrogen atoms are omitted for clarity.

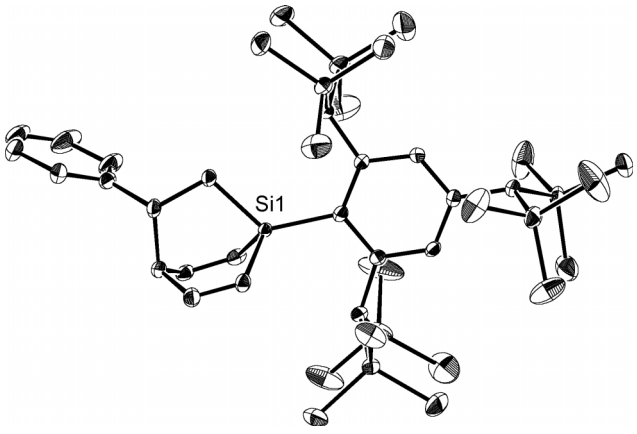


Fig. 5. Molecular structure of styrene adduct **13** (ORTEP, 50% probability). Hydrogen atoms, solvent molecules, and one of the disordered 8-phenyl-1-silabicyclo[2.2.2]octa-2,5-diene moieties are omitted for clarity.

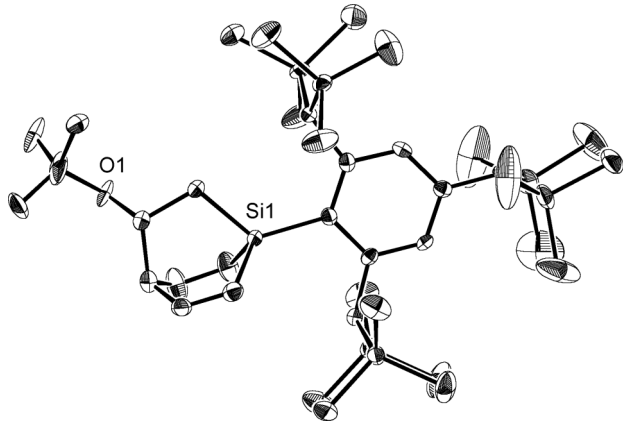


Fig. 6. Molecular structure of *tert*-butyl vinyl ether adduct **14** (ORTEP, 50% probability). Hydrogen atoms and one of the disordered oxygen atoms and *t*-Bu groups are omitted.

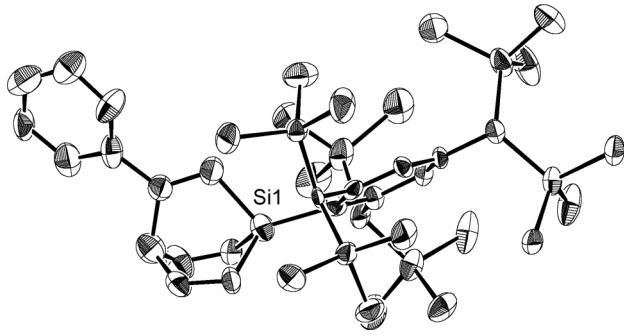


Fig. 7. Molecular structure of phenylacetylene adduct **15** (ORTEP, 50% probability). Hydrogen atoms are omitted.

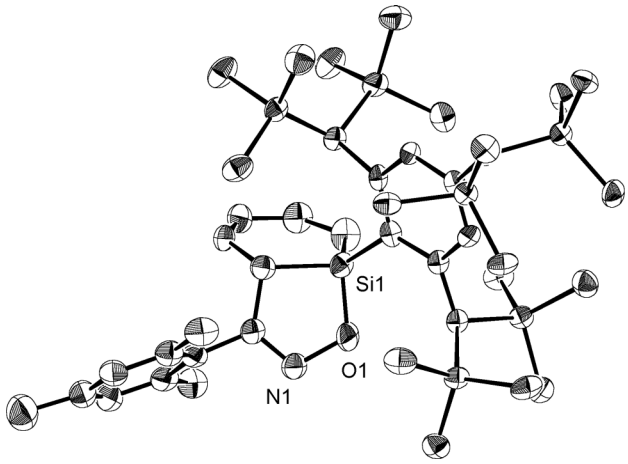


Fig. 8. Molecular structure of mesitonitrile oxide adduct **18** (ORTEP, 50% probability). Hydrogen atoms are omitted.

were selected as typical examples.

The free energy surface of a cycloaddition reaction of silabenzene **1c** with acetylene is shown in Fig. 9. The results suggested that the 1,4-addition, i.e., [4+2]-cycloaddition is more favorable than 1,2-addition, i.e., [2+2]-cycloaddition as judged by the lower energy of the transition state of the former than that of the latter by 15.5 kcal/mol, though the 1,2-adduct is thermodynamically more stable than the 1,4-adduct by 2.0 kcal/mol. The result of this calculation agrees with the experiments, where the reaction of **1a** with phenylacetylene afforded the corresponding 1,4-adduct exclusively.

In the case of the reaction of **1c** with nitrile oxide (Fig. 10), the calculations showed that the transition state for the 1,2-addition should be more favorable than the 1,4-addition, since the transition state for the 1,4-addition is less stable than that of the 1,2-addition by 12.9 kcal/mol. In this case, the 1,2-adduct is also more stable than the 1,4-adduct. The calculated free energy surface supports the experimental result of the exclusive 1,2-addition of **1a** with MesCNO.

On the other hand, the free energy surface for the addition reactions of **1c** with methanol (Fig. 11) seems to be inconsistent with the experimental result of the reaction of

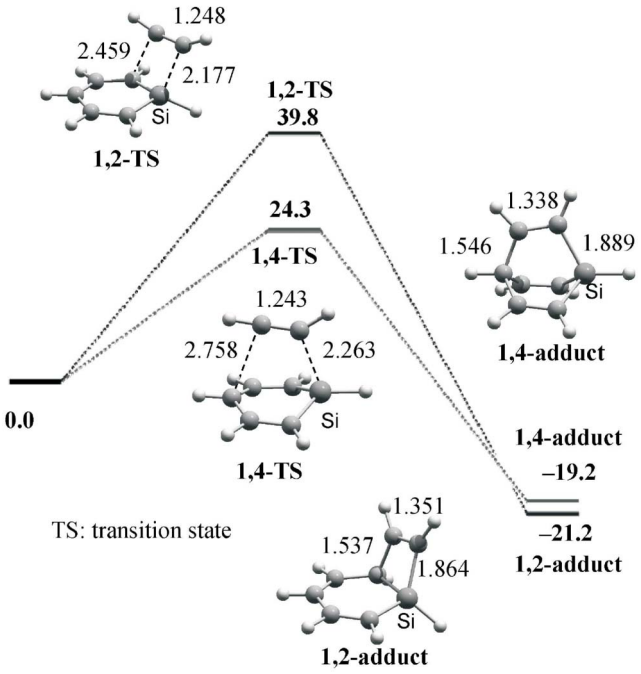


Fig. 9. Free energy surface (kcal/mol) in the reaction of silabenzene **1c** with acetylene. Selected bond lengths (Å) are shown. Caluclated at B3LYP/6-31G(d) level.

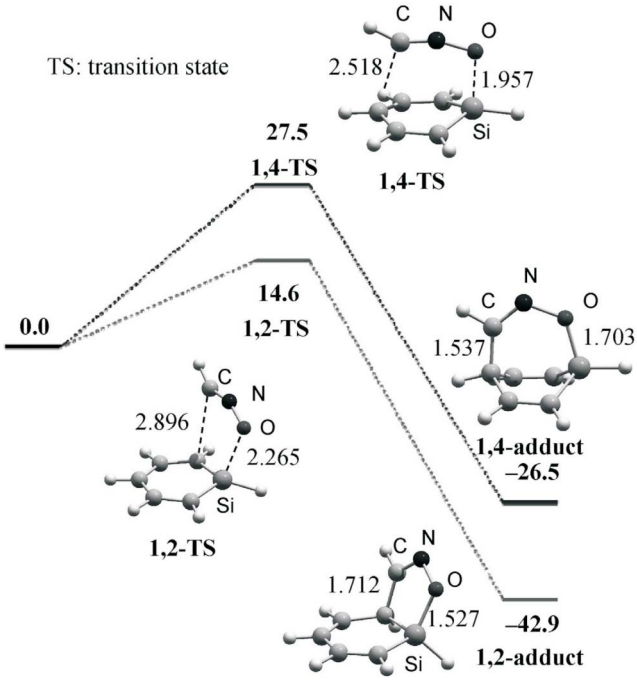


Fig. 10. Free energy surface (kcal/mol) in the reaction of silabenzene **1c** with HCNO. Selected bond lengths (Å) are shown. Calculated at B3LYP/6-31G(d) level.

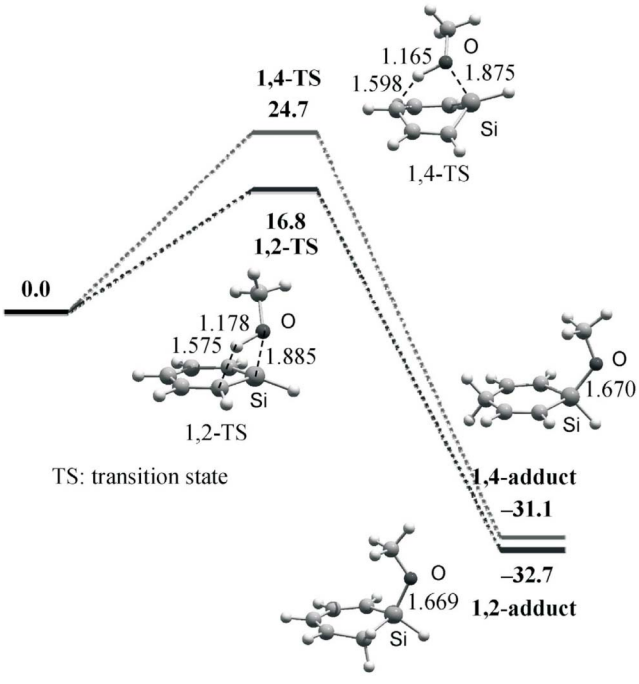


Fig. 11. Free energy surface (kcal/mol) in the reaction of silabenzene **1c** with a methanol monomer. Selected bond lengths (Å) are shown. Calculated at B3LYP/6-31G(d) level.

1a with methanol. That is, the calculations showed a lower transition state for the 1,2-addition than that for the 1,4-addition, though the treatment of silabenzene **1a** with MeOD afforded 1,4-adduct **16** as a major product along with 1,2-adduct **17** as a minor product (**16** : **17** = 5 : 3, *vide supra*). Furthermore, we have examined the theoretical calculations for the free energy surface of the reaction of **1c** with methanol trimer connected with hydrogen bondings as a model of methanol oligomer, since a methanol generally exists as an oligomer in solution due to hydrogen bondings (Fig. 12). Fig. 12 shows that the transition state for the 1,4-addition (1,4-TS) has a lower energy than that for the 1,2-addition (1,2-TS) by 4.6 kcal/mol in contrast to the case of the reaction of **1c** with a methanol monomer. That is, the selectivity between 1,2- and 1,4-additions of silabenzene and methanol should be susceptible to the situation of aggregation of methanol molecules with hydrogen bondings. The experimental results suggested that the methanol dominantly reacts with silabenzene **1a** as an oligomeric structure with hydrogen bondings.

The aromatic character of a silabenzene was also investigated on the basis of the reaction energies. Comparisons of the potential energy surfaces of silabenzene and silene in the addition reactions with acetylene and nitrile oxide are shown in Figs. 13 and 14, respectively. The activation energies are higher in the reactions of silabenzene,

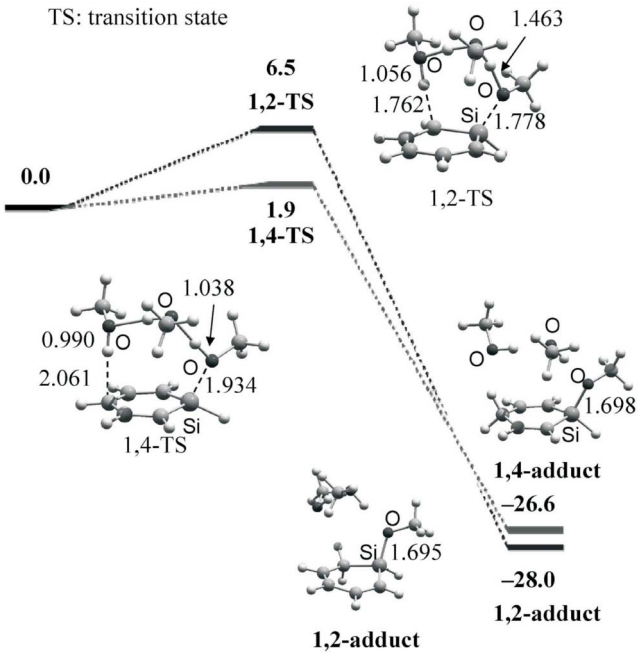


Fig. 12. Free energy surface (kcal/mol) in the reaction of silabenzene **1c** with a methanol trimer. Selected bond lengths (Å) are shown. Calculated at B3LYP/6-31G(d) level.

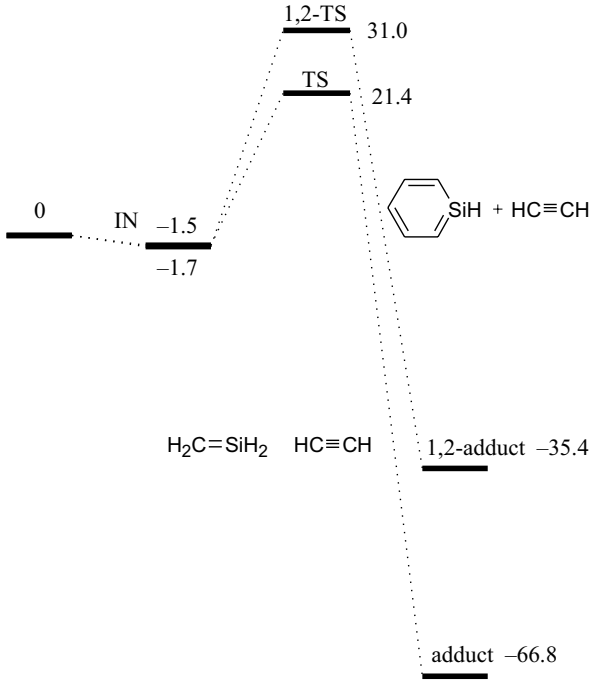


Fig. 13. Potential energy surface of the reactions of silabenzene and silene with acetylene calculated at B3LYP/6-31G(d) level.

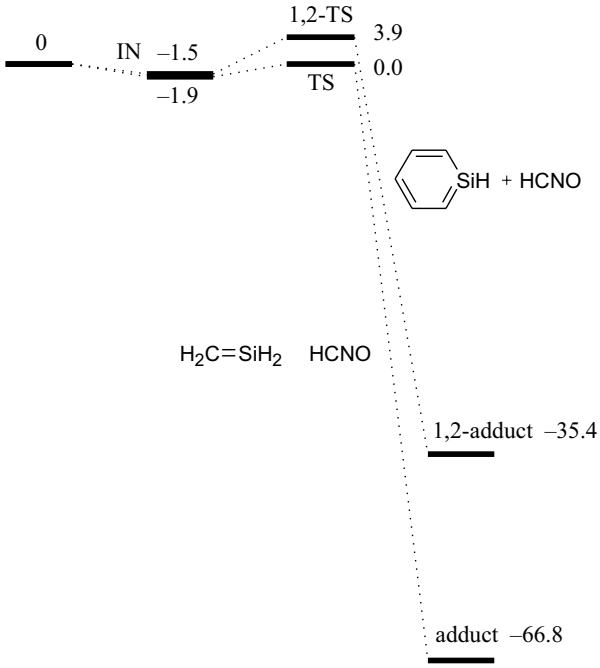


Fig. 14. Potential energy surface of the reactions of silabenzene and silene with HCNO calculated at B3LYP/6-31G(d) level.

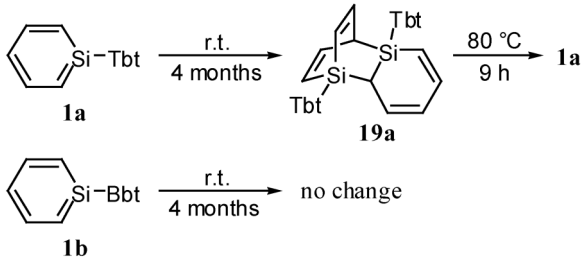
and there are large differences in the stability of the products. The adducts of silene are more stable than those of silabenzene, reflecting the loss of aromaticity in silabenzene in these addition reactions.

Stability

Silabenzene **1a** showed no change in solution even at 100 °C. Furthermore, the ^{29}Si NMR chemical shift of **1a** (δ_{Si} = 93.4) in THF/C_6D_6 (6:1) did not differ from that measured in C_6D_6 (δ_{Si} = 93.6). As mentioned above, the ^{29}Si NMR chemical shift of Märkl's silabenzene measured in THF/Et_2O/petroleum ether (4:1:1) is at much higher field (δ_{Si} = 26.8)[4f] than that of **1a**, indicating that it is coordinated with the solvent molecule, most likely with THF, and hence stabilized only in such a mixed solvent. The absence of such a complexation with the solvent in **1a** suggests the remarkable effectiveness of Tbt as a steric protection group.

Although we have reported that silabenzene **1a** is stable for many weeks,[11] **1a** was found to undergo gradual dimerization (~50% conversion after 4 months) at room temperature in benzene to afford the corresponding [4+2]-dimer **19a** (Scheme VII). The structure of **19a** was determined by X-ray analysis (Fig. 15). It is surprising that silabenzene **1a** dimerized even with an extremely bulky Tbt group. This fact strongly indicates the extremely high reactivity of silabenzene towards dimerization[29] and reasonably explains why no stable silabenzene had been reported before **1a** was synthesized. Interestingly, dimer **19a** was thermally labile to undergo dissociation into silabenzene **1a** on heating at 80 °C for 9 h. This result means that the dimer **19a** should be thermodynamically less stable than monomer **1a**, and the generation of **19a** at room temperature should be explained by the high crystallinity and low solubility of **19a** in benzene. Thus, Tbt group is a "marginal" substituent where both silabenzene and its dimer can be obtained. By contrast, Bbt-substituted silabenzene **1b** did not dimerize at all under the same conditions. Since Bbt group has one more trimethylsilyl group at its *para*-position, Bbt group may be slightly bulkier than Tbt group probably due to the buttressing effect.[30]

Scheme VII



Theoretical calculations on the dimerization reaction of parent silabenzene **1c** were performed. The potential energy surface of dimerization reactions of **1c** showed that the [4+2]-dimerization should be the most favorable among the [2+2]- and [4+2]-self-dimerization reactions as shown in Fig. 16, supporting the experimental results. In addition, calculations for the dimerization reactions of real molecules **1a**,**b** suggested that the activation energy of [4+2]-

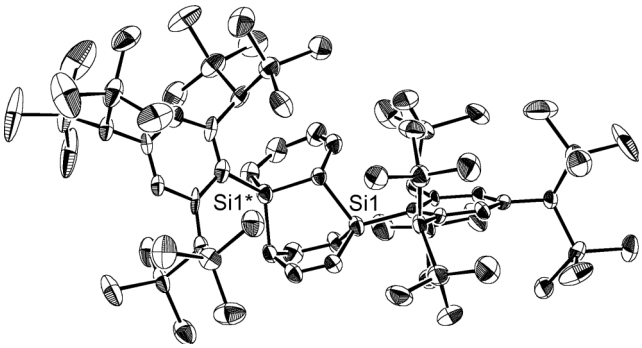


Fig. 15. Molecular structure of silabenzene dimer **19a** (ORTEP, 50% probability). Hydrogen atoms and one of the disordered parts are omitted.

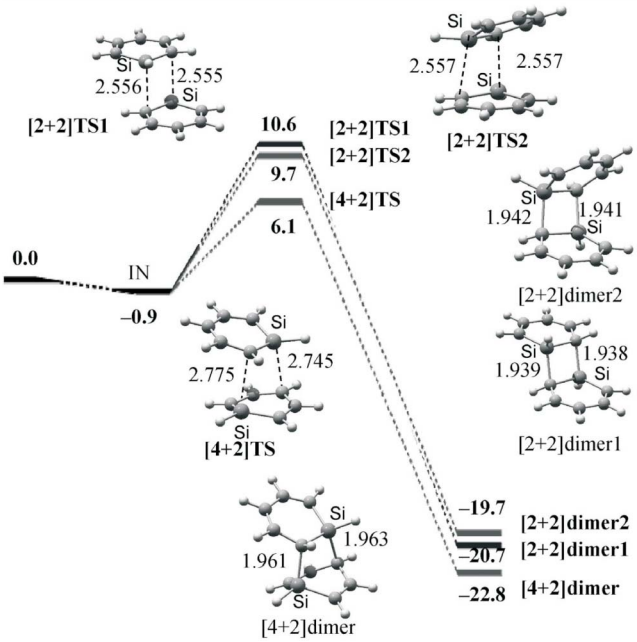


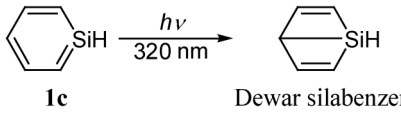
Fig. 16. Potential energy surface (kcal/mol) in the dimerization reactions of silabenzene **1c**. Selected bond lengths (Å) are shown. Calculated at B3LYP/6-31G(d) level.

dimerization reaction of Tbt-substituted silabenzene **1a** should be lower than that of Bbt-substituted silabenzene **1b**,[31] while [4+2]-dimer **19a** (dimer of **1a**) is thermodynamically more stable than **19b** (dimer of **1b**) (Fig. 17).

Photochemical Reaction

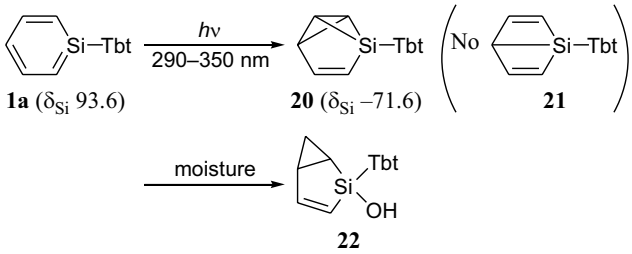
It is well established that photochemical reaction of benzene affords interesting isomers, such as Dewar benzene or benzvalene. Although the photochemical isomerization of the parent silabenzene to Dewar silabenzene has already been studied in an argon matrix, the characterization of the Dewar silabenzene was based only on the Si–H stretching frequency in its IR spectrum which shifted from that of Si(sp^2)–H to that of Si(sp^3)–H (Scheme VIII).[3e]

Scheme VIII



Photoirradiation of the stable silabenzene **1a** using a solution filter which is transparent at 290–350 nm[32] resulted in the formation of a new compound, which showed a ^{29}Si NMR signal of its central silicon atom at –71.6 ppm. This signal cannot be assignable to that of Dewar silabenzene, since it appears in a high field region characteristic not of four-membered ring silicon compounds but of three-membered ones.[33] Several new signals appeared in the ^{1}H NMR spectrum (two in the sp^3 region and two in the sp^2 region in 1:2:1:1 ratio). Furthermore, silanol **22** having a three-membered ring was isolated from the reaction mixture (the structure of **22** was determined by X-ray analysis, Fig. 18). Thus, the product of the photoirradiation of silabenzene **1a** is not Dewar silabenzene derivative **21** but silabenzvalene **20** (Scheme IX). No other isomer was observed.[34]

Scheme IX



Although no silabenzvalene derivative has been reported to the best of our knowledge, a stable disilabenzvalene bearing four trimethylsilyl and two phenyl groups was reported by Ando et al.[35] ^{29}Si NMR chemical shift corresponding to the two Si atoms of the disilabenzvalene was reported to be –61.9 ppm, which is very similar to that of silabenzvalene **20**. It was indicated by theoretical calcula-

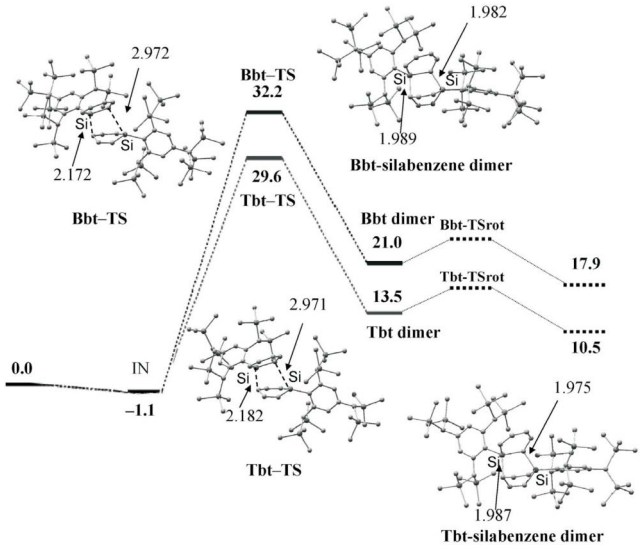


Fig. 17. Potential energy surface (kcal/mol) in the dimerization reactions of silabenzenes **1a,b**. Selected bond lengths (Å) are shown. Calculated at B3LYP/6-31G(d) level.

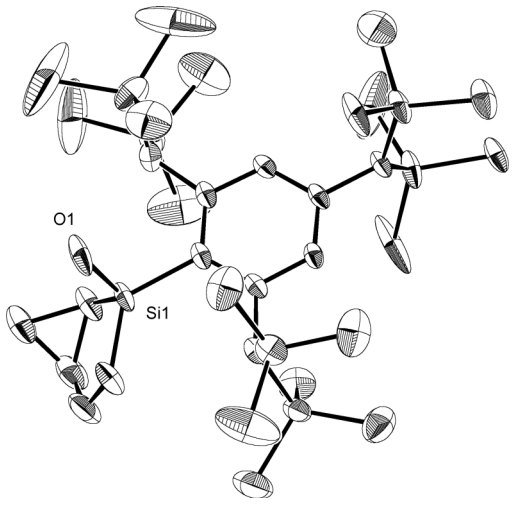


Fig. 18. Molecular structure of **22**(ORTEP, 50% probability). Hydrogen atoms, solvent molecules, and one of the disordered 2-hydroxy-2-silabicyclo[3.1.0]-hex-3-ene moieties and *p*-bis(trimethylsilyl)methyl groups of Tbt are omitted.

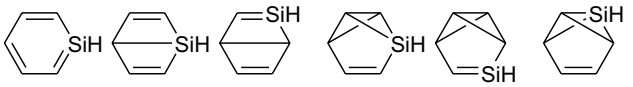


Fig. 19. Calculated relative energies of silabenzene isomers (B3LYP/6-31G(d), kcal/mol).

tions that the energy difference between the parent disilabenzvalene and its Dewar disilabenzene isomer should be small. In contrast, previous theoretical studies on silabenzene isomers were concentrated only on Dewar silabenzene and the possibility of silabenzvalene was not taken into consideration.[36] Although high-level calculations including a silaprismane isomer were recently reported, they still neglected a silabenzvalene isomer.[37] We performed, therefore, B3LYP/6-31G(d) calculations on all the conceivable silabenzene isomers. The possibility of the formation of silabenzvalene was supported by a small energy difference between Dewar silabenzene and silabenzvalene (Fig. 19), though further investigation on the transition states of the photochemical reaction is required to reveal the origin of the selectivity.

The use of stable silabenzene **1a** as a substrate enabled us to perform the detailed investigation on the photochemical reaction product of this unique class of ring systems, leading to the evidence for the photochemical valence isomerization of silabenzene into silabenzvalene. In view of the results here obtained, the previous report on the formation of Dewar silabenzene[3e] should be reinvestigated since the possibility of the formation of silabenzvalene was disregarded. It should be noted, however, that the effect of the large substituent of **1a** might not be negligible.

CONCLUSION

The stable silabenzenes were successfully synthesized by taking advantage of extremely bulky Tbt or Bbt groups. The synthesis of these fundamental silaaromatic compounds enabled us to compare carbon and silicon analogues in aromatic systems, and we found the structure of the silabenzene here revealed is very similar to that of benzene. Although the structural features and spectroscopic data indicate a similarity between the carbon and silicon analogues, the reactivities of aromatic and silaaromatic compounds are very different from each other. Even in the case substituted by an extremely bulky Tbt group, it is not sufficient to suppress the dimerization of the silabenzene completely. The high aromaticity and reactivity of silabenzenes here disclosed do not conflict with each other but rather indicate an intrinsic character of silaaromatics.

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. ^{1}H NMR (500, 400, or 300 MHz), ^{13}C NMR (126, 101, or 76 MHz), and ^{29}Si NMR (99, 68, or 59 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM-A500, JNM-EX400 or JNM-AL300 spectrometer. Unless otherwise noted, the spectra were measured at room temperature. In ^{1}H NMR spectra, signals due to $CHCl_3$ (7.25 ppm) and C_6D_5H (7.15 ppm) were used as references, and those due to $CDCl_3$ (77 ppm) and C_6D_6 (128 ppm) were used in ^{13}C NMR spectra. ^{29}Si NMR was measured with NNE or INEPT techniques using TMS as an external standard. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. High- and low-resolution mass spectral data were obtained on a JEOL JMS-SX102 and Shimadzu QP-5050A GC/MS spectrometer, respectively. SCC (short column chromatography) and FCC (flush column chromatography) were performed on Wakogel C-200 and Merck Silica Gel 60, respectively. GPLC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). All melting points were determined on a Yanaco micro-melting point apparatus and were 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),[9] 1-bromo-2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]benzene (BbtBr),[38] 1,1-dibutyl-1-stannacyclohexa-2,5-diene (**2**),[39] Tbt-substituted trihydrosilane (**3a**)[40] were prepared according to the reported procedures. Calculations were carried out with the Gaussian 98 program.[41]

Preparation of {2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}silane (3b)

A solution of BbtBr (12.0 g, 17.0 mmol) in THF (160 mL) was cooled to –78 °C, and *t*-BuLi (1.67 M in pentane, 25.5 mL, 42.6 mmol) was added dropwise to the solution. After the solution was stirred for 30 min, SiF_4 gas was bubbled into the solution until the color of the solution had al-

most disappeared. After the mixture was warmed to room temperature, the solvent was evaporated. Hexane (500 mL) was added to the residue and filtered using Celite®. Removal of the solvent afforded a crude product containing $BbtSiF_3$, which was dissolved in THF (140 mL) and treated with $LiAlH_4$ (1.94 g, 51.1 mmol). The mixture was refluxed for 12 h and quenched by the successive addition of AcOEt (40 mL), H_2O (50 mL), and 2 M HCl (80 mL) at 0 °C. After separation of the organic layer, the aqueous layer was extracted with hexane (100 mL, twice). The organic layers were combined and washed with aq. $NaHCO_3$ (100 mL, twice) and H_2O (100 mL). After the organic layers were dried over $MgSO_4$, the solvent was evaporated and the residue was reprecipitated from CH_2Cl_2/EtOH to afforded **3b** (7.01 g, 10.7 mmol, 63%). **3b**: colorless powder (from CH_2Cl_2/EtOH), mp. 165.5–170.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 36H), 0.24 (s, 27H), 2.15 (s, 2H), 4.23 (s, 3H), 6.73 (s, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.98 (q), 5.33 (q), 22.27 (s), 31.56 (d), 122.75 (s), 126.01 (d), 146.45 (s), 151.50 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –76.16, 0.64, 1.60. Anal. Calcd for $C_{30}H_{70}Si_8 \cdot H_2O$: C, 53.49; H, 10.77%. Found C, 53.70; H, 10.34%. LRMS (DI): *m*/*z* found 654 [M^+], calcd for $C_{30}H_{70}Si_8$ 654.

Preparation of Dihydro(5-tributylstannylpenta-1,4-dienyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane (4a)

To a solution of **2** (720 mg, 2.41 mmol) in Et_2O (15 mL) was added *n*-BuLi (1.65 M in hexane, 1.53 mL, 2.52 mmol) at –50 °C. After the solution was stirred for 2 h, a solution of **3a** (1.40 g, 2.41 mmol) in Et_2O (12 mL) was added to the reaction mixture. The solution was warmed to room temperature and stirred for 2 d. After evaporation of the solvent, removal of inorganic salts by SCC (hexane) followed by purification with GPLC (chloroform) and reprecipitation from CH_2Cl_2/CH_3CN afforded **4a** (1.41 g, 1.50 mmol, 60%). **4a**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 64.9–67.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (s, 36H), 0.03 (s, 18H), 0.88 (t, $^3J_{HH}$ = 7.3 Hz, 9H), 0.92–0.95 (m, 6H), 1.27–1.35 (m, 7H), 1.47–1.53 (m, 6H), 2.06 (s, 2H), 3.05 (t, $^3J_{HH}$ = 7.1 Hz, 2H), 4.78 (d, $^3J_{HH}$ = 4.0 Hz, 1H), 5.59 (dt, $^3J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 4.3 Hz, 1H), 5.91 (d, $^3J_{HH}$ = 12.2 Hz, 1H), 6.27 (br s, 1H), 6.35–6.40 (m, 2H), 6.48 (dt, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.54 (q), 0.68 (q), 0.83 (q), 10.27 (t), 13.70 (q), 27.32 (t), 29.22 (t), 29.74 (d), 30.07 (d), 30.48 (d), 40.49 (t), 121.39 (d), 123.03 (s), 123.29 (d), 126.20 (d), 130.12 (d), 144.77 (s), 145.77 (d), 148.32 (d), 151.57 (s), 151.77 (s). ^{29}Si NMR (99 MHz, $CDCl_3$) δ –64.29, 1.59, 1.87. HRMS (FAB): *m*/*z* calcd for $C_{44}H_{95}Si_7Sn$ 939.4841, found 939.4813 ([M+H]$^+$). Anal. Calcd for $C_{44}H_{94}Si_7Sn$: C, 56.30; H, 10.09. Found C, 56.00; H, 9.80.

Preparation of Dihydro{2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl}(5-tributylstannylpenta-1,4-dienyl)silane (4b)

Compound **4b** was synthesized with the same procedure as that for **4a**. The use of **2** (2.53 g, 8.46 mmol), *n*-BuLi (1.66 M, 5.21 mL, 8.65 mmol) and **3b** (5.55 g, 8.47 mmol) afforded **4b** (5.03 g, 4.98 mmol, 59%). **4b**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 72.0–75.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 36H), 0.25 (s, 27H), 0.88–1.05 (m, 15H), 1.25–1.37 (m, 6H), 1.46–1.59 (m, 6H), 2.16 (s, 2H), 3.06 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 4.81 (d, $^3J_{HH}$ = 3.9 Hz, 1H), 5.60 (dt, $^3J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.1 Hz, 1H), 5.93 (d, $^3J_{HH}$ = 12.5 Hz, 1H), 6.36–6.53 (m, 2H), 6.72 (s, 2H). ^{13}C NMR (76 MHz, r.t., $CDCl_3$) δ 1.20 (q), 5.35 (q), 10.28 (t), 13.70 (q), 22.23 (s), 27.31 (t), 29.22 (t), 31.08 (d), 40.62 (t), 122.77 (d), 125.87 (s), 125.94 (d), 130.25 (d), 145.66 (d), 146.35 (s), 148.88 (d), 151.46 (s). ^{29}Si NMR (60 MHz, r.t., $CDCl_3$) δ –63.32, 0.64, 1.60. Anal. Calcd for $C_{47}H_{102}Si_8Sn$: C, 55.85; H, 10.17. Found C, 55.76; H, 10.24.

Preparation of a Mixture of Silacyclohexadienes 5a and 6a

To a solution of **4a** (8.32 g, 8.87 mmol) in THF (150 mL) was added *n*-BuLi (1.67 M in hexane, 10.9 mL, 18.2 mmol) at –78 °C. After the solution was stirred at –78 °C for 2 h, the reaction was quenched by the addition of 2 M HCl (5 mL). Warming the mixture to room temperature followed by purification with SCC (hexane), GPLC (chloroform), and reprecipitation from CH_2Cl_2/CH_3CN afforded a mixture of 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,1-dihydro-1-silacyclohexa-2,4-diene (**5a**) and 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,1-dihydro-1-silacyclohexa-2,5-diene (**6a**) (4.52 g, 6.98 mmol, 79%, **5a**:**6a** = 1:0.13). **5a**: colorless powder (from CH_2Cl_2/CH_3CN). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.01 (s, 36H), 0.03 (s, 18H), 1.30 (s, 1H), 1.69 (m, 1H), 1.88 (m, 1H), 2.22 (br s, 1H), 2.24 (br s, 1H), 5.05 (t, $^3J_{HH}$ = 6.3 Hz, 1H), 5.92 (m, 1H), 6.02 (m, 1H), 6.06 (d, $^3J_{HH}$ = 13.7 Hz, 1H), 6.25 (br s, 1H), 6.37 (br s, 1H), 6.72 (dd, $^3J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.60 (q), 0.71 (q), 0.95 (q), 1.04 (q), 11.56 (t), 28.52 (d), 28.83 (d), 30.44 (d), 121.67 (d), 125.38 (d), 126.09 (d+s), 128.71 (d), 141.11 (d), 144.71 (s), 151.59 (s), 151.87 (s). ^{29}Si NMR (99 MHz,

$CDCl_3$) δ –45.85, 1.67, 1.78, 1.91. HRMS (EI): *m*/*z* calcd for $C_{32}H_{66}Si_7$ 646.3550, found 646.3555 ($[M]^+$). The spectral data of **6a** were not collected since this compound was obtained only as a mixture with **5a**.

Preparation of a Mixture of Silacyclohexadienes 5b and 6b

Silacyclohexadienes **5b** and **6b** were prepared by the same method as that for Tbt-substituted **5a** and **6a**. The use of **4b** (4.50 g, 4.45 mmol) and *n*-BuLi (1.66 M, 5.56 mL, 9.23 mmol) afforded 1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**5b**) and 1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]}-1-silacyclohexa-2,5-diene (**6b**) (2.68 g, 3.72 mmol, 83%, **5b**:**6b** = 1:0.13). **5b**: colorless powder (from CH_2Cl_2/CH_3CN). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 18H), 0.06 (s, 18H), 0.24 (s, 27H), 1.70 (m, 1H), 1.91 (m, 1H), 2.36 (s, 2H), 5.07 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 5.92 (m, 1H), 6.04 (m, 1H), 6.10 (d, $^3J_{HH}$ = 14.3 Hz, 1H), 6.68 (s, 2H), 6.73 (dd, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.5 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 1.26 (q), 1.44 (q), 5.39 (q), 11.65 (t), 22.14 (s), 29.69 (d), 125.64 (d), 126.13 (d), 126.30 (d), 128.54 (s), 128.67 (d), 140.89 (d), 146.42 (s), 151.47 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –44.61, 0.65, 1.50, 1.58. The spectral data of **6b** were not collected since this compound was obtained only as a mixture with **5b**.

Bromination of Silacyclohexadienes 5a and 6a

Silacyclohexadienes **5a** and **6a** (50 mg, 0.077 mmol) and NBS (14.2 mg, 0.0798 mmol) in CCl_4 (10 mL) were stirred vigorously with a magnetic stirrer at 0 °C in a 50 mL round-bottomed flask equipped with a $CaCl_2$ tube. After the disappearance of the starting materials (confirmed by TLC, after ca. 5 days), the solvent was removed and hexane (5 mL) was added to the residue. Removal of the succinimide by filtration followed by removal of the solvent afforded a crude mixture containing 1-bromo-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**7a**) and 1-bromo-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,5-diene (**8a**), though the total content of **7a** and **8a** was approx. 60% (estimated by ^{1}H NMR). Spectral data of **7a** and **8a** were not obtained since **7a** and **8a** decomposed under the purification conditions.

Reaction of Bromosilanes 7a and 8a with *t*-BuLi

The crude mixture of bromosilanes **7a** and **8a** obtained in the previous experiment was dissolved in cyclohexane-d_{12} (0.6 mL) and *t*-BuLi (0.355 M in hexane, 0.20 mL, 0.071 mmol) was added to the solution. The mixture was transferred into a 5 mm NMR tube, and it was degassed and sealed. Measurement of ^{29}Si NMR spectrum showed a signal at 92.51 ppm which is assignable to that of silabenzene **1a**. The yield of **1a** was estimated to be 30% by the ^{1}H NMR spectrum.

Preparation of 1-Hydroxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacylohexa-2,4-diene (9a)

A mixture of silacyclohexadienes **5a** and **6a** (300 mg, 0.463 mmol) and NBS (86.6 mg, 0.487 mmol) in CCl_4 (40 mL) was stirred vigorously at 5 °C in a 50 mL round-bottomed flask equipped with a $CaCl_2$ tube for 1 week. Removal of the solvent afforded a crude mixture containing bromosilanes **7a** and **8a**, which was dissolved in Et_2O (15 mL) and then treated with saturated aq. $NaHCO_3$ (2 mL). After the mixture was stirred for 2 h, the solvent and water were removed under vacuum. Purification by SCC ($CHCl_3$) and FCC (hexane/$CHCl_3$, 5:1) afforded pure **9a** (205 mg, 0.309 mmol, 67%). **9a**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 181.8–185.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 0.00 (s, 9H), 0.03 (s, 27H), 0.05 (s, 9H), 1.30 (s, 1H), 1.57 (br s, 1H), 1.82–1.85 (m, 2H), 2.47 (s, 2H), 5.95–5.99 (m, 1H), 6.08–6.13 (m, 1H), 6.23 (br s, 1H), 6.25 (d, $^3J_{HH}$ = 14.2 Hz, 1H), 6.35 (br s, 1H), 6.75 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.65 (q), 0.74 (q), 1.00 (q), 1.12 (q), 19.85 (t), 27.92 (d), 28.19 (d), 30.33 (d), 122.03 (d), 125.46 (d), 126.82 (s), 127.02 (d), 129.89 (d), 130.47 (d), 140.08 (d), 144.74 (s), 151.30 (s), 151.71 (s). ^{29}Si NMR (79 MHz, $CDCl_3$) δ 1.43, 1.57, 1.77, 2.14. HRMS (EI): *m*/*z* calcd for $C_{32}H_{66}OSi_7$ 662.6499, found 662.3487 ($[M]^+$). Anal. Calcd for $C_{32}H_{66}OSi_7 \cdot 0.5H_2O$: C, 57.15; H, 10.04. Found C, 56.86; H, 9.66.

Preparation of 1-Hydroxy-1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (9b)

Silanol **9b** was prepared by the same method as that for Tbt-substituted **9a**. The use of a mixture of **5b** and **6b** (300 mg, 0.417 mmol) and NBS (81.6 mg, 0.459 mmol) afforded **9b** (135 mg, 0.183 mmol, 44%). **9b**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 166.1–172.5 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 18H), 0.09 (s, 18H), 0.25 (s, 27H), 1.67 (br s, 1H), 1.76–1.95 (m, 2H), 2.62 (s, 2H), 5.95–6.01 (m, 1H), 6.08–6.14 (m, 1H), 6.29 (d, $^3J_{HH}$ = 14.1 Hz, 1H), 6.67 (s, 2H), 6.75 (dd, $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 5.9 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 1.39 (q), 1.56 (q), 5.45 (q), 19.91 (t), 22.05 (s), 28.85 (d), 125.49 (d), 126.78 (d), 129.50 (s), 130.05 (d), 130.43 (d), 139.85 (d),

146.49 (s), 151.28 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –13.07, 0.67, 2.04. Anal. Calcd for $C_{35}H_{74}OSi_8$: C, 57.14; H, 10.14. Found C, 56.84; H, 10.12.

Chlorination of Silanol 9a

A mixture of silanol **9a** (205 mg, 0.309 mmol) and PCl_5 (643 mg, 3.09 mmol) in Et_2O (25 mL) was refluxed for 15 h. After the removal of the solvent, hexane (40 mL) was added to the residue and filtered with Celite®. Removal of the solvent from the filtrate followed by purification using GPLC (toluene) afforded almost pure 1-chloro-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**10a**) (183 mg, 0.268 mmol, 89%). **10a**: white powder. ^{1}H NMR (300 MHz, C_6D_6) δ 0.15 (s, 18H), 0.20 (s, 18H), 0.21 (s, 18H), 1.46 (s, 1H), 2.18–2.34 (m, 2H), 2.62 (s, 2H), 5.80 (m, 1H), 5.91 (m, 1H), 6.41–6.51 (m, 3H), 6.61 (br s, 1H). ^{13}C NMR (76 MHz, C_6D_6) δ 0.90 (q), 0.95 (q), 1.01 (q), 1.75 (q), 21.76 (t), 29.13 (d), 29.38 (d), 31.04 (d), 122.79 (d), 125.17 (s), 125.95 (d), 127.80 (d), 128.75 (d), 129.17 (d), 139.42 (d), 146.43 (s), 152.43 (s), 152.96 (s). LRMS (DI): *m*/*z* found 680 ([M]$^+$), calcd for $C_{32}H_{65}ClSi_7$ 680. Chlorosilane **9a** was used without further purifications due to its gradual decomposition under ambient conditions.

Chlorination of Silanol 9b

Chlorination of silanol **9b** was performed by the same procedure as that for Tbt-substituted silanol **9a**. The use of **9b** (92.4 mg, 0.126 mmol) and PCl_5 (131 mg, 0.629 mmol) afforded 1-chloro-1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**10b**) (82.4 mg, 0.109 mmol, 87%). **10b**: colorless powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.06 (s, 18H), 0.11 (s, 18H), 0.25 (s, 27H), 2.09–2.28 (m, 2H), 2.52 (s, 2H), 5.99 (m, 1H), 6.08 (m, 1H), 6.12 (d, $^3J_{HH}$ = 5.1 Hz, 1H), 6.68 (m, 1H), 6.70 (s, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 1.55 (q), 1.65 (q), 5.48 (q), 21.37 (t), 22.39 (s), 29.55 (d), 125.55 (d), 127.13 (d), 127.19 (s), 128.68 (d), 128.96 (d), 138.68 (d), 147.97 (s), 151.81 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –0.79, 0.81, 1.63, 2.40. LRMS (DI): *m*/*z* found 752 ([M]$^+$), calcd for $C_{35}H_{73}ClSi_8$. Chlorosilane **9b** was used without further purifications due to its gradual decomposition under ambient conditions.

Synthesis and Trapping of Silabenzene 1a from Chlorosilane 10a and *t*-BuLi

In a glovebox filled with argon, chlorosilane **10a** (33.2 mg, 0.0487 mmol) was dissolved in cyclohexane (2 mL), and *t*-BuLi (0.589 M, 80.0 μL, 0.0471 mmol) was added to this solution. The solvent was removed by slow evaporation with standing for 12 h. C_6D_6 (0.7 mL) was added to the residue, and the solution was transferred into a 5 mm NMR tube. After the tube was degassed and sealed, a signal due to silabenzene **1a** was observed at 93.64 ppm in ^{29}Si NMR. The tube was opened in a glovebox and benzophenone (18 mg, 0.099 mmol) was added to the mixture. After removal of the solvent, separation of the mixture by SCC ($CHCl_3$), GPLC ($CHCl_3$) and FCC (hexane/$CHCl_3$ = 10:1) afforded 5-*tert*-butyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**11**) (9.1 mg, 0.013 mmol, 27%) and 8,8-diphenyl-1-{2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl}-7-oxa-1-silabicyclo-[2,2,2]octa-2,5-diene (**12**) (7.9 mg, 0.0095 mmol, 20%). **11**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 175.0–181.5 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.01 (s, 18H), 0.03 (s, 36H), 1.08 (s, 9H), 1.29 (s, 1H), 1.58–1.66 (m, 1H), 1.73 (dd, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H), 2.32 (br s, 1H), 2.34 (br s, 1H), 5.01–5.05 (m, 1H), 5.83 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 5.93 (d, $^3J_{HH}$ = 14.2 Hz, 1H), 6.24 (br s, 1H), 6.36 (br s, 1H), 6.74 (dd, $^3J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.50 (s), 0.68 (s), 0.85 (s), 1.07 (s), 11.66 (t), 28.72 (d), 29.03 (q), 30.37 (d), 37.46 (s), 117.62 (d), 121.66 (d), 122.65 (d), 125.30 (s), 126.52 (d), 141.85 (d), 144.65 (s), 150.32 (s), 151.71 (s), 151.94 (s). ^{29}Si NMR (79 MHz, $CDCl_3$) δ –38.47, 1.75, 1.85. HRMS (EI): *m*/*z* calcd for $C_{36}H_{74}Si_7$ 702.4176, found 702.4173 ([M]$^+$). Anal. Calcd for $C_{36}H_{74}Si_7$: C, 61.46; H, 10.06. Found C, 61.03; H, 10.46. **12**: white powder (from CH_2Cl_2/CH_3CN), mp. 196.0–199.0 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.07 (s, 36H), 0.08 (s, 18H), 1.39 (s, 1H), 2.44 (s, 1H), 2.95 (s, 1H), 4.80 (tt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 6.39 (br s, 1H), 6.45 (dd, $^3J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 1.3 Hz, 2H), 6.47 (br s, 1H), 6.99 (dd, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 7.0 Hz, 2H), 7.10 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.20 (t, $^3J_{HH}$ = 7.3 Hz, 4H), 7.50 (d, $^3J_{HH}$ = 8.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.75 (q), 0.81 (q), 1.17 (q), 27.31 (d), 27.82 (d), 30.76 (d), 48.21 (d), 83.60 (s), 119.72 (s), 122.11 (d), 126.70 (d), 126.80 (d), 127.64 (d), 136.12 (d), 145.96 (s), 147.21 (s), 147.62 (d), 152.43 (s), 152.68 (s) (one of the *m*-proton of Tbt group was not observed probably due to an overlapping with other peaks). ^{29}Si NMR (99 MHz, $CDCl_3$) δ –29.79, 1.85, 2.07. HRMS (FAB): *m*/*z* calcd for $C_{45}H_{75}OSi_7$ 827.4203, found 827.4227 ([M+H]$^+$). Anal. Calcd for $C_{45}H_{74}OSi_7 \cdot 0.5H_2O$: C, 64.59; H, 9.03. Found C, 64.73; H, 8.83.

Synthesis of Silabenzene 1a from Chlorosilane 10a and LDA

In a glovebox filled with argon, chlorosilane **10a** (144 mg, 0.212 mmol) was dissolved in hexane (5 mL), and LDA (2.0 M in heptane/THF/ethylbenzene, 0.123 mL, 0.246 mmol, Aldrich Chemicals Co.) was added to the solution. The solvent was removed under reduced pressure, and hexane (5 mL) was added to the residue. The mixture was left for 2 days and the precipitates were removed by decantation. Removal of the solvent afforded almost pure 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silabenzene (**1a**) (136 mg, 0.211 mmol, 96%). **1a**: colorless powder (from hexane), mp. 125.1–140.0 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.13 (s, 36H), 0.15 (s, 18H), 1.50 (s, 1H), 2.55 (br s, 1H), 2.66 (br s, 1H), 6.58 (br s, 1H), 6.71 (t, $^{3}J_{HH}$ = 8.3 Hz, 1H), 6.71 (br s, 1H), 7.11 (d, $^{3}J_{HH}$ = 12.2 Hz, 2H), 8.00 (dd, $^{3}J_{HH}$ = 12.2 Hz, $^{3}J_{HH}$ = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ 0.61 (q), 0.81 (q), 0.97 (q), 31.38 (d), 36.62 (d), 37.20 (d), 116.08 (d), 121.42 (d), 122.15 (d), 125.95 (d), 126.24 (s), 143.55 (d), 147.75 (s), 152.12 (s), 152.16 (s). ^{29}Si NMR (79 MHz, C_6D_6) δ 2.19, 2.54, 93.64. Anal. Calcd for $C_{32}H_{64}Si_7$: C, 59.55; H, 9.99. Found C, 58.48; H, 10.12.

Synthesis of Silabenzene 1b

Bbt-substituted silabenzene **1b** was synthesized by the same procedure as that for Tbt-substituted **1a**. The use of **10b** (96.9 mg, 0.129 mmol) and LDA (2.0 M, 0.077 mL, 0.15 mmol) afforded almost pure 1-{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1-silabenzene (**1b**). **1b**: colorless powder. mp. 127 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.15 (s, 36H), 0.35 (s, 27H), 2.79 (s, 2H), 6.69 (t, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.03 (s, 2H), 7.03 (d, $^{3}J_{HH}$ = 12.7 Hz, 2H), 7.98 (dd, $^{3}J_{HH}$ = 12.7 Hz, $^{3}J_{HH}$ = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ 1.17 (q), 5.43 (q), 23.14 (s), 38.94 (d), 115.91 (d), 121.25 (d), 125.88 (d), 129.15 (s), 143.55 (d), 149.31 (s), 151.72 (s). ^{29}Si NMR (79 MHz, C_6D_6) δ 1.11, 2.12, 92.93.

Reaction of Silabenzene 1a with Styrene

In a glovebox filled with argon, **1a** (34.9 mg, 0.0541 mmol) was dissolved in C_6D_6 (0.7 mL) and the solution was put into a 5 mm NMR tube. After styrene (0.03 mL) was added to the solution, the NMR tube was degassed and sealed. The disappearance of **1a** was confirmed by NMR measurements. Then, the tube was opened and the solvent was evaporated. A hexane solution of the residue was passed through the column of Florisil® and concentrated to give a crude mixture, the separation of which by GPLC (toluene) afforded 7-phenyl-1-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-1-silabicyclo[2.2.2]octa-2,5-diene (**13**) (11.6 mg, 0.0155 mmol, 29%). **13**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 147.8–150.0 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 36H), 0.06 (s, 18H), 0.98 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H), 1.35 (s, 1H), 1.43 (dd, $^{2}J_{HH}$ = 13.4 Hz, $^{3}J_{HH}$ = 10.0 Hz, 1H), 2.20 (br s, 1H), 2.53 (br s, 1H), 2.98 (m, 1H), 3.70 (m, 1H), 6.31 (br s, 1H), 6.40 (d, $^{3}J_{HH}$ = 11.9 Hz, 1H), 6.44 (br s, 1H), 6.60 (d, $^{3}J_{HH}$ = 12.1 Hz, 1H), 6.81 (dd, $^{3}J_{HH}$ = 12.1 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H), 7.14–7.27 (m, 6H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.76 (q), 1.10 (q), 20.26 (t), 28.53 (d), 28.77 (d), 30.49 (d), 43.50 (d), 46.73 (d), 121.89 (d), 122.96 (s), 125.77 (d), 126.83 (d), 127.79 (d), 128.07 (d), 133.04 (d), 135.78 (d), 145.17 (s), 145.82 (d), 147.95 (s), 150.16 (d), 152.21 (s), 152.66 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –37.44, 1.83, 1.96. Anal. Calcd for $C_{40}H_{72}Si_7$: C, 64.09; H, 9.68. Found C, 63.86; H, 9.38.

Reaction of Silabenzene 1a with *tert*-Butyl Vinyl Ether

In a glovebox filled with argon, **1a** (26.7 mg, 0.0414 mmol) was dissolved in C_6D_6 (0.7 mL) and the solution was put into a 5 mm NMR tube. After *tert*-butyl vinyl ether (0.03 mL) was added to the solution, the NMR tube was degassed and sealed. Although the NMR signals due to **1a** were observed just after the mixing, they disappeared after standing overnight. Then, the tube was opened and the solvent was evaporated. The hexane solution of the residue was passed through a column of Florisil® and concentrated to give a crude mixture, the separation of which by GPLC (toluene) afforded 7-*tert*-butoxy-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silabicyclo[2.2.2]octa-2,5-diene (**14**) (12.2 mg, 0.0164 mmol, 40%). **14**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 189.0-193.8 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 36H), 0.05 (s, 18H), 0.64 (dd, $^{2}J_{HH}$ = 13.0 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H), 1.20 (s, 9H), 1.33 (s, 1H), 1.39 (dd, $^{2}J_{HH}$ = 13.0 Hz, $^{3}J_{HH}$ = 9.0 Hz, 1H), 2.10 (br s, 1H), 2.14 (br s, 1H), 3.75 (m, 1H), 3.81 (m, 1H), 6.27 (br s, 1H), 6.34 (d, $^{3}J_{HH}$ = 11.9 Hz, 1H), 6.40 (br s, 1H), 6.57 (d, $^{3}J_{HH}$ = 11.9 Hz, 1H), 6.95–7.02 (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.72 (q), 0.76 (q), 1.00 (q), 1.09 (q), 24.34 (t), 28.25 (d), 28.51 (d), 28.66 (q), 30.46 (d), 48.07 (d), 70.26 (d), 73.74 (s), 121.82 (d), 122.68 (s), 126.71 (d), 134.70 (d), 135.32 (d), 145.15 (s), 145.21 (d), 147.15 (d), 152.25 (s), 125.63 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –39.12, 1.80, 1.91, 1.98. Anal. Calcd for $C_{38}H_{76}OSi_7$: C, 61.21; H, 10.27. Found C, 60.98; H, 10.02.

Reaction of Silabenzene 1a with Phenylacetylene

In a glovebox filled with argon, **1a** (27.7 mg, 0.0429 mmol) was dissolved in C_6D_6 (0.7 mL) and the solution was put into a 5 mm NMR tube. After phenylacetylene (0.024 mL) was added to the solution, the NMR tube was degassed and sealed. The NMR signals of **1a** were observed just after the mixing, but they disappeared after standing overnight. Then, the tube was opened and the solvent was evaporated. The hexane solution of the residue was passed through a column of Florisil® and concentrated to give a crude mixture, the separation of which by GPLC (toluene) afforded 3-phenyl-1-{2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}-1-silabicyclo[2.2.2]octa-2,5,7-triene (**15**) (6.5 mg, 0.0087 mmol, 20%). **15**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 169.4–174.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 36H), 0.08 (s, 18H), 1.38 (s, 1H), 2.35 (br s, 2H), 5.30 (m, 1H), 6.36 (br s, 1H), 6.49 (br s, 1H), 6.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 10.6 Hz, 1H), 7.15–7.43 (m, 5H), 7.49 (dd, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 6.9 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.77 (q), 1.03 (q), 28.97 (d), 29.13 (d), 30.62 (d), 51.76 (d), 121.55 (s), 121.95 (d), 124.89 (d), 126.86 (d), 127.29 (d), 128.39 (d), 131.49 (d), 137.32 (d), 141.96 (s), 145.50 (s), 151.07 (d), 152.44 (s), 152.79 (s), 162.56 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 1.49, 1.87, 2.06. Anal. Calcd for $C_{40}H_{70}Si_7 \cdot 0.5H_2O$: C, 63.50; H, 9.46. Found C, 63.22; H, 9.16.

Reaction of Silabenzene 1a with MeOD

In a glovebox filled with argon, silabenzene **1a** (23.2 mg, 0.0359 mmol) was dissolved in THF (3 mL), and MeOD (0.03 mL) was added to the solution. The mixture was stirred for 2 h and the solvent was evaporated. Separation of the mixture by FCC (hexane) afforded 1-methoxy-5-deuterio-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,5-diene (**16**) (4.3 mg, 0.0063 mmol), 1-methoxy-4-deuterio-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-silacyclohexa-2,4-diene (**17**) (9.4 mg, 0.014 mmol), and the mixture of **16** and **17**. The total yields of **16** and **17** were 49 and 29%, respectively. The D content of both **16** and **17** was 65% as judged by ^{1}H NMR. **16**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 187.4-189.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.01 (s, 18H), 0.00 (s, 18H), 0.03 (s, 18H), 1.28 (s, 1H), 2.61 (br s, 1H), 2.62 (br s, 1H), 2.92 (br s, 1H), 3.29 (s, 3H), 6.10 (dd, $^3J_{HH}$ = 14.7 Hz, $^4J_{HH}$ = 2.1 Hz, 1H), 6.20 (br s, 1H), 6.32 (br s, 1H), 6.83 (dd, $^3J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 3.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.63 (q), 0.72 (q), 0.98 (q), 27.24 (d), 27.47 (d), 30.27 (d), 33.22 (dt, $^1J_{CD}$ = 18.6 Hz), 49.48 (q), 122.02 (d), 125.42 (s), 127.02 (d), 128.07 (d), 144.41 (s), 145.85 (d), 151.85 (s), 152.26 (s). ^{29}Si NMR (99 MHz, $CDCl_3$) δ –28.99, 1.67. HRMS (EI): *m*/*z* calcd for $C_{33}H_{67}DOSi_7$ 677.3718, found 677.3734 ($[M]^+$). Anal. Calcd for $C_{33}H_{67}DOSi_7$: C, 58.42; H, 10.25. Found C, 58.12; H, 9.96. **17**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 160.0–168.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.02 (s, 18H), 0.03 (s, 36H), 1.29 (s, 1H), 1.69 (br s, 1H), 2.53 (s, 2H), 3.34 (s, 3H), 5.97 (m, 1H), 6.14 (d, $^3J_{HH}$ = 14.0 Hz, 1H), 6.14 (m, 1H), 6.21 (br s, 1H), 6.33 (br s, 1H), 6.86 (dd, $^3J_{HH}$ = 14.0, 6.1 Hz, 1H). ^{13}C NMR (60 MHz, $CDCl_3$) δ 0.65 (q), 0.72 (q), 0.75 (q), 1.00 (q), 1.14 (q), 17.02 (dt, $^1J_{CD}$ = 17.8 Hz), 27.70 (d), 27.92 (d), 30.30 (d), 49.63 (q), 122.07 (d), 125.66 (d), 126.30 (s), 127.04 (d), 127.80 (d), 130.88 (d), 141.27 (d), 144.57 (s), 151.57 (s), 151.98 (s). HRMS (EI): *m*/*z* calcd for $C_{33}H_{67}DOSi_7$ 677.3718, found 677.3723 ($[M]^+$). Anal. Calcd for $C_{33}H_{67}DOSi_7 \cdot 0.5H_2O$: C, 57.65; H, 10.26. Found C, 57.49; H, 9.61.

Reaction of Silabenzene 1a with Mesitonitrile Oxide

In a glovebox filled with argon, **1a** (27.7 mg, 0.0429 mmol) and mesitonitrile oxide (20.8 mg, 0.129 mmol) were dissolved in hexane (3 mL). Filtration of the mixture with Celite® followed by separation with GPLC (toluene) afforded 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-aza-3a,7a-dihydro-1-oxa-7a-silaindene (**18**) (20.8 mg, 0.0258 mmol, 60%). **18**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 192.9–201.2 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.04 (s, 18H), 0.05 (s, 9H), 0.06 (s, 9H), 0.08 (br s, 18H), 1.36 (s, 1H), 1.85 (br s, 1H), 1.97 (br s, 1H), 2.14 (s, 6H), 2.27 (s, 3H), 3.35 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 5.84 (dd, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 6.10 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 10.2 Hz, 1H), 6.23 (d, $^3J_{HH}$ = 14.3 Hz, 1H), 6.35 (br s, 1H), 6.45 (br s, 1H), 6.84 (s, 2H), 6.87 (dd, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.1 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.49 (q), 0.67 (q), 0.73 (q), 0.88 (q), 1.10 (q), 1.47 (q), 19.74 (q), 20.11 (q), 21.06 (q), 29.41 (d), 29.75 (d), 30.76 (d), 38.20 (d), 121.67 (d), 124.46 (d), 125.18 (d), 126.74 (d), 127.06 (d), 128.36 (d), 128.52 (d), 128.62 (d), 129.60 (d), 135.45 (s), 137.30 (s), 138.18 (s), 141.90 (d), 146.31 (s), 151.93 (s), 152.13 (s), 164.53 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 1.63, 1.86, 2.79, 6.47. Anal. Calcd for $C_{42}H_{75}ONSi_7 \cdot 0.5H_2O$: C, 61.85; H, 9.39. Found C, 61.95; H, 8.98.

Dimerization of Silabenzene 1a

In a glovebox filled with argon, **1a** (41.9 mg, 0.0649 mmol) was dissolved in C_6D_6 (0.7 mL) and the solution was put into a 5 mm NMR tube. After the tube was degassed and sealed, the tube was stored at room temperature and the

reaction was monitored by ^{1}H NMR measurements. After 4 months about half of **1a** was converted into dimer **19a**. After the removal of the solvent, hexane was added to the residue and the mixture was filtered with Celite®. Removal of the solvent followed by separation with GPLC (toluene) afforded 1,7-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,7-disilatricyclo[3.2.2.0^{1,6}]dodeca-2,4,8,11-tetraene (**19a**) (18.9 mg, 0.0146 mmol, 45%). **19a**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 152.1–154.4 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.016 (s, 18H), 0.031 (s, 18H), 0.037 (s, 9H), 0.043 (s, 18H), 0.07 (s, 27H), 0.10 (s, 9H), 0.14 (s, 9H), 1.25 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 1.29 (s, 1H), 1.34 (s, 1H), 2.04 (s, 1H), 2.13 (s, 1H), 2.33 (s, 1H), 2.55 (s, 1H), 4.14 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 5.54 (d, $^3J_{HH}$ = 13.8 Hz, 1H), 5.69 (dd, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 5.9 Hz, 1H), 6.26–6.47 (m, 8H), 6.84 (dd, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 7.7 Hz, 1H), 7.47 (dd, $^3J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 6.8 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.77 (q), 0.79 (q), 0.90 (q), 1.00 (q), 1.08 (q), 1.10 (q), 1.24 (q), 1.38 (q), 1.55 (q), 1.66 (q), 1.79 (q), 2.12 (q), 14.36 (d), 27.06 (d), 27.45 (d), 29.10 (d), 29.17 (d), 30.36 (d), 30.55 (d), 39.88 (d), 122.42 (d), 122.50 (d), 122.82 (d), 124.05 (d), 127.37 (d), 127.93 (d), 128.22 (d), 129.01 (s), 129.35 (d), 130.26 (d), 135.50 (d), 140.75 (d), 144.07 (s), 144.99 (s), 148.01 (d), 150.68 (d), 151.97 (s), 153.10 (s), 153.24 (s), 153.58 (s). ^{29}Si NMR (60 MHz, $CDCl_3$) δ –42.64, –24.12, 1.66, 1.72, 1.78, 1.84, 1.87, 1.95, 2.01, 2.08, 2.15, 2.23, 2.48. Anal. Calcd for $C_{64}H_{128}Si_{14}\cdot H_2O$: C, 58.73; H, 10.01. Found C, 58.88; H, 9.62.

Thermal Dissociation of Silabenzene Dimer 19a

In a glovebox filled with argon, the solution of **19** (11.4 mg, 0.00883 mmol) in C_6D_6 (0.7 mL) was put into a 5 mm NMR tube. After the tube was degassed and sealed, the tube was heated at 80 °C for 9 h during which time the reaction was monitored by ^{1}H NMR measurements. Almost quantitative conversion of **19** into silabenzene **1a** was observed after 9 h.

Photolysis of Silabenzene 1a

In a glovebox filled with argon, the solution of **1a** (25.9 mg, 0.0401 mmol) in C_6D_6 (0.8 mL) was put into a 5 mm NMR tube. The tube was degassed, sealed, and irradiated with a 400 W high pressure Hg lamp through a filter solution which is transparent between 290 and 350 nm (2 M $NiSO_4$, 1 M $CoSO_4$, 0.1 M $CuSO_4$ in 5% H_2SO_4). After irradiation for 30 h, a 1:5 mixture of silabenzene **1a** and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-silatricyclo[3.1.0.0^{2,6}]-hex-3-ene (**20**) was obtained (by ^{1}H NMR). The sealed tube was opened in a glovebox, and to the solution was added benzophenone (21.9 mg, 0.120 mmol). After evaporation of the solvent, hexane was added to the residue, and the solution was filtered with Celite®. Removal of the solvent followed by separation of the residue with GPLC (toluene) afforded 2-hydroxy-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-silabicyclo[3.1.0]hex-3-ene (**22**) (8.1 mg, 0.012 mmol, 30%). **20** (complete data could not be obtained since this compound was obtained only as a mixture with silabenzene **1a**): ^{1}H NMR (300 MHz, C_6D_6) δ 2.24 (m, 1H), 2.50 (d, $^3J_{HH}$ = 5.1 Hz, 2H), 5.82 (dd, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 9.3, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 22.98 (d), 39.81 (d), 120.89 (d), 161.19 (d). ^{29}Si NMR (79 MHz, C_6D_6) δ –71.60. **22**: colorless powder (from CH_2Cl_2/CH_3CN), mp. 170.6–172.2 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (br s, 18H), 0.04 (s, 18H), 0.05 (br s, 18H), 0.33 (m, 1H), 0.53 (m, 1H), 1.07 (m, 1H), 1.32 (s, 1H), 2.00 (m, 1H), 2.39 (br s, 1H), 2.44 (br s, 1H), 6.65 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 6.25 (br s, 1H), 6.38 (br s, 1H), 7.01 (dd, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 2.6 Hz, 1H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 0.49 (q), 0.69 (q), 0.75 (q), 1.09 (q), 2.27 (d), 20.52 (t), 24.12 (d), 28.12 (d), 28.38 (d), 30.43 (d), 121.85 (d), 126.76 (d), 127.41 (s), 128.94 (d), 144.99 (s), 150.88 (s), 151.30 (s), 153.53 (d). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 1.64, 1.72, 1.78, 2.04, 11.85. LRMS (DI): *m*/*z* found 662 ([M]$^+$). Anal. Calcd for $C_{32}H_{66}OSi_7$: C, 57.93; H, 10.03. Found C, 57.32; H, 9.60.

X-ray Crystallographic Analyses

Crystal data of **1a**, **12**–**15**, **18**, **19a**, and **22** are shown in Table 3. Crystals of all compounds suitable for X-ray analysis were obtained by slow evaporation of their solutions, and the solvents are also described in Table 3. Only crystals of **1a** were grown in a glovebox. All crystals were colorless. A crystal of **1a** was mounted inside a glass capillary, while the other crystals were mounted on glass fibers. All intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated MoKα radiation (λ = 0.71069 Å) at –180 °C to $2\theta_{max}$ = 55°. Empirical absorption corrections (symmetry related method) were performed with the ABSCOR program.[42] Equivalent reflections were merged. The structures were solved by direct methods (SIR92 or SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[43] Phenyl or methyne hydrogens of **1a** were refined isotropically; all the other hydrogens were placed using AFIX instructions. For **13**, **14**, **19a**, and **22** some restraints as shown below were applied to refine

Table 3. Crystal data of **1a**, **12**–**15**, **18**, **19a**, and **22**

	1a	**12**	**13**	**14**
empirical formula	$C_{32}H_{64}Si_7$	$C_{45}H_{74}OSi_7$	$C_{40}H_{72}Si_7 \cdot CH_2Cl_2$	$C_{38}H_{76}OSi_7$
formula weight	645.46	827.67	834.53	745.62
solvent	hexane	hexane	CH_2Cl_2/CH_3CN	hexane
crystal size (mm)	0.5 × 0.5 × 0.2	0.4 × 0.3 × 0.02	0.6 × 0.3 × 0.2	0.4 × 0.4 × 0.1
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$P2_1/n$
a (Å)	18.9186(3)	18.3020(6)	12.8367(3)	18.1163(4)
b (Å)	10.9969(2)	10.9614(3)	17.5750(7)	12.8263(3)
c (Å)	20.0757(4)	25.8847(7)	12.4173(4)	20.7598(5)
α (deg)	90	90	108.012(1)	90
β (deg)	99.2711(6)	106.916(2)	98.693(1)	99.8824(5)
γ (deg)	90	90	104.485(1)	90
V (Å^3)	4122.1(1)	4968.2(3)	2498.7(1)	4752.3(2)
Z value	4	4	2	4
D_{calc}	1.040	1.107	1.109	1.042
no. of reflections (all)	9446	11339	11333	10889
no. of parameters	411	497	597	471
no. of restraints	0	0	144	17
R_1 ($I > 2\sigma(I)$)	0.097	0.053	0.058	0.083
wR_2 (all data)	0.258	0.124	0.177	0.209
goodness of fit	1.043	0.796	1.059	1.303
	15	**18**	**19a**	**22**
empirical formula	$C_{40}H_{70}Si_7$	$C_{42}H_{75}ONSi_7$	$C_{64}H_{128}Si_{14}$	$C_{32}H_{66}OSi_7 \cdot 0.5C_6H_{12}$
formula weight	747.59	806.66	1290.92	705.56
solvent	hexane	heptane	CH_2Cl_2/CH_3CN	cyclohexane
crystal size (mm)	0.6 × 0.08 × 0.08	0.4 × 0.2 × 0.1	0.5 × 0.1 × 0.1	0.3 × 0.2 × 0.1
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	12.316(1)	11.042(1)	34.628(2)	38.407(1)
b (Å)	21.153(3)	26.030(3)	10.3929(5)	13.2176(4)
c (Å)	9.814(2)	9.315(1)	22.776(1)	18.4041(6)
α (deg)	91.418(6)	94.939(2)	90	90
β (deg)	111.384(4)	113.197(3)	95.510(2)	104.5197(7)
γ (deg)	78.145(3)	86.247(2)	90	90
V (Å^3)	2326.3(6)	2450.2(5)	8159.0(7)	9044.3(4)
Z value	2	2	4	8
D_{calc}	1.067	1.093	1.051	1.036
no. of reflections (all)	7847	9035	9233	10263
no. of parameters	443	476	686	553
no. of restraints	0	0	498	105
R_1 ($I > 2\sigma(I)$)	0.125	0.097	0.057	0.074
wR_2 (all data)	0.329	0.274	0.155	0.218
goodness of fit	1.743	1.446	0.930	1.293

disordered structures adequately.

Structural Refinement of 13

The 8-phenyl-1-silabicyclo[2.2.2]octa-2,5-diene moieties were disordered at two overlapped positions in a 0.718(3):0.282(3) ratio, which were restrained to be identical to each other using SAME, SIMU, and DELU instructions.

Structural Refinement of 14

The oxygen atoms and *t*-Bu groups were disordered at two positions in 0.591(7):0.409(7) and 0.533(9):0.467(9) ratios, respectively. The structures of disordered parts were restrained to be identical to each other using SADI instruc-

tions.

Structural Refinement of 19a

The central 1,7-disilatricyclo[3.2.2.$0^{1,6}$]dodeca-2,4,8,11-tetraene moieties and Tbt groups were disordered and their occupancies were fixed to 0.5. The structure of disordered Tbt groups were restrained to be identical to each other using SADI, SAME, SIMU, and DELU instructions.

Structural Refinement of 22

The central 2-hydroxy-2-silabicyclo[3.1.0]-hex-3-ene moieties, *p*-bis(trimethylsilyl) groups of Tbt, and one atom of solvent cyclohexane molecule were disordered in 0.481(3):0.519(3), 0.249(3):0.751(3), and 0.780(8):0.220(8), respectively. The structure of disordered parts were restrained to be identical to each other using SAME, SIMU, and DELU instructions.

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Supporting Information Available

Results of X-ray structural analyses of **1a**, **12**–**15**, **18**, **19a**, and **22** (CIF), and details of the theoretical calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES AND NOTES

1. Minkin, V. J.; Glukhovtsev, M. N.; Simkin, Y. B. *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.
2. For reviews on silaaromatic compounds, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Ed.; Wiley: New York, 1989; pp 1102–1108. (c) Apeloig Y. *ibid*., pp 151–166. (d) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem*. **1996**, *39*, 71. (e) Apeloig, Y.; Karni, M. In *The Chemistry of Organic Silicon Compounds, Volume 2*; Rappoport, Z.; Apeloig, Y.; Ed.; Wiley: New York, 1998; Chapter 1.
3. (a) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (b) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 52. (c) Kreil, C. L.; Chapman, O. L.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 841. (d) Maier, G.; Mihm, G.; Reisenauer, H. P. *Chem. Ber.* **1982**, *115*, 801. (e) Maier, G.; Mihm, G.; Baumgärtner, R. O. W.; Reisenauer, H. P. *Chem. Ber.* **1984**, *117*, 2337. (f) Jutzi, P.; Meyer, M.; Reisenauer, H. P.; Maier, G. *Chem. Ber.* **1989**, *122*, 1227.
4. (a) Barton, T. J.; Banasiak, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5199. (b) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246. (c) Märkl, G.; Hofmeister, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 789. (d) Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788. (e) Sekiguchi, A.; Tanikawa, H.; Ando, W. *Organometallics*, **1985**, *4*, 584. (f) Märkl, G.; Schlosser, W. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 963.
5. Recent reviews on low-coordinated organosilicon compounds: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 232. (b) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. For reviews of Si–C doubly bonded compounds, see ref. 1.
6. A stable tetrasila-1,3-butadiene has conjugated Si–Si double bonds. Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2503.
7. Reports on the delocalization of silole anions and dianions: (a) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (b) Goldfuss, B.; Schleyer, P. v. R. Hampel, F. *Organometallics*, **1996**, *15*, 1755. (c) Goldfuss, B.; Schleyer, P. v. R. *Organometallics*, **1997**, *16*, 1543. (d) Choi, S.-B.; Boudjouk, P.; Wei, P. *J. Am. Chem. Soc*. **1998**, *120*, 5814. (e) Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc*. **1998**, *120*, 8245.
8. (a) Arduengo, A. J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Hermann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641. (b) West, R.; Denk, M. *Pure. Appl. Chem.* **1996**, *68*, 785. (c) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (d) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (e) West, R.; Buffy, J. J.; Haaf, M.; Müller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1639.
9. Okazaki, R.; Tokitoh, N.; Matsumoto, T. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A.; Ed.; Thieme: New York, 1996; Vol. 2 (Auner, N., Klingebiel, U., Vol. Eds.), pp 260-269 references cited therein.
10. Examples for the applications of Tbt and Bbt groups: (a) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *227*, 78. (b) Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829. (c) Tokitoh, N. *J. Organomet. Chem.* **2000**, *611*, 217. (d) Okazaki, R.; Tokitoh,

N. *Acc. Chem. Res.* **2000**, *33*, 625. (e) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. -Eur. J.* **2003**, *9*, 3530. (f) Sasamori, T.; Mieda, E.; Takeda, N.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2005**, *44*, 3717. (g) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582.

11. (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 634. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648.
12. (a) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 4024. (b) Shinohara, A.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 977.
13. (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.
14. (a) Takeda, N.; Shinohara, A.; Tokitoh, N. *Organometallics* **2002**, *21*, 256. (b) Shinohara, A.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2003**, *125*, 10804.
15. Tokitoh, N.; Shinohara, A.; Matsumoto, T.; Sasamori, T.; Takeda, N.; Furukawa, Y. *Organometallics*, in press.
16. (a) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2001**, *20*, 5507. (b) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2002**, *124*, 6914. (c) Nakata, N.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2002**, 818. (d) Nakata, N.; Takeda, N.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2003**, *42*, 115. (e) Nakata, N.; Takeda, N.; Tokitoh, N. *Organometallics* **2003**, *22*, 481. (f) Nakata, N.; Takeda, N.; Tokitoh, N. *J. Organomet. Chem.* **2003**, *672*, 66. (g) Sasamori, T.; Inamura, K.; Hoshino, W.; Nakata, N.; Mizuhata, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Organometallics* **2006**, *25*, 3533.
17. Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1050.
18. Bbt group has almost the same steric protection ability as that of Tbt group, but sometimes shows different chemical or crystallographic behavior. For example, see: (a) Kano, N.; Tokitoh, N.; Okazaki, R. *Organometallics* **1998**, *17*, 1241. (b) Tokitoh, N.; Sasamori, T.; Okazaki, R. *Chem. Lett.* **1998**, 725. (c) Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Phys. Org. Chem.* **2003**, *16*, 450. (d) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661.
19. Wakita, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 687.
20. Märkl, G.; Baier, H.; Hofmeister, P.; Kess, F.; Soper, U. *J. Organomet. Chem.* **1979**, *173*, 125.
21. These values are slightly different from the previously reported values (in cyclohexane-d_{12})[11a] since these values were measured in C_6D_6.
22. Delpon-Lacaz, G.; Couret, G. *J. Organomet. Chem.* **1994**, *480*, C14.
23. Kalinowski, H-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy* translated by J. K. Becconsall; Wiley: New York, 1986; p 600.
24. Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994.
25. Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5668.
26. (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.
27. Sheldrick, W. M. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Ed.; Wiley: New York, 1989; p 246.
28. Maier, G.; Schöttler, Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4079.
29. Previous calculations indicated that dimerization of silabenzene is exothermic by $\Delta H = -21.5$ kcal/mol. Brown, E. C.; Borden, W. T. *Organometallics* **2000**, *19*, 2208.
30. The structural difference between Tbt and Bbt groups was revealed by X-ray analysis of TbtBr and BbtBr. Sasamori, T. *Dissertation*, Kyushu Univ., 2002.
31. It was found that the dimerization reaction pathway was followed by the rotation processes of Tbt and Bbt groups for dimers **19a,b** leading to the formation of the more stable geometries. Since the rotation barrier of the Tbt and Bbt group of **19a,b** should be smaller than the activation energies of the dimerization of silabenzenes **1a,b**, the rotational processes leading to the more stable geometries were not discussed here.
32. 2 M $NiSO_4$/0.8 M $CoSO_4$/0.1 M $CuSO_4$ in 5% H_2SO_4. Horspool, W. M. In *Synthetic Organic Photochemistry*; Horspool, W. M.; Ed.; Plenum Press: New York, 1984; p 493.
33. Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z.; Ed.; Wiley: New York, 1989; p 536.
34. Since prolonged irradiation afforded polymeric products, the possibility of the formation of unstable isomers cannot be completely excluded.
35. (a) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629. (b) Kabe, Y.; Ohkubo, K.; Ishikawa, H.; Ando, W. *J. Am. Chem. Soc.* **2000**, *122*, 3775.
36. Chandrasekhar, J.; Schleyer, P. v. R.; Baumgartner, R. O. W.; Reetz, M. T. *J. Org. Chem.* **1983**, *48*, 3453.
37. (a) Kiprof, P.; Brown, A. B. *Internet J. Chem.* **1999**, *2*, 23. (b) Dhevi, D. M.; Priyakumar, U. D.; Sastry, G. N. *J. Mol. Struct. (Theochem)* **2002**, *618*, 173. (c) Priyakumar, U. D.; Dinadayalane, T. C.; Sastry, G. N. *New J. Chem.* **2002**, *26*,

347. (d) Priyakumar, U. D.; Saravanan, D.; Sastry, G. N. *Organometallics* **2002**, *21*, 4823. (e) Priyakumar, U. D.; Sastry, G. N. *Organometallics* **2002**, *21*, 1493. (f) Priyakumar, U. D.; Punnagai, M.; Sastry, G. N. *J. Organomet. Chem.* **2004**, *689*, 1284.
38. Unno, M. Dissertation, The University of Tokyo, 1988.
39. Ashe III, A. J.; Chan, W.-T. *J. Org. Chem.* **1979**, *44*, 1409.
40. Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016.
41. Calculations were carried out using the Gaussian 98 program. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
42. Higashi, T. *ABSCOR: Program for Absorption Correction*; Rigaku Corporation, 1995.
43. Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.