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# Syntheses and structures of silicon analogues of cyclopropabenzenes

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## Abstract

The reactions of an overcrowded diaryldilithiosilane,  $\text{Tbt}(\text{Dip})\text{SiLi}_2$  ( $\text{Tbt} = 2,4,6\text{-tris}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$ ;  $\text{Dip} = 2,6\text{-diisopropylphenyl}$ ), with *o*-dibromobenzene and 1,2,4,5-tetrabromobenzene resulted in the synthesis and isolation of the first stable silacyclopropabenzene and bis(silacyclopropa)benzenes (IUPAC name is 4,8-disilatricyclo[5.1.0.0<sup>3,5</sup>]octa-1,3(5),6-triene), respectively. The crystallographic analyses and theoretical calculations revealed that the lengths of the juncture carbon–carbon bonds of the mono- and bis(silacyclopropa)benzenes were marginally in the range of carbon–carbon bond lengths of usual benzene rings. It is shown that this structural feature is attributable to a decrease in the strain energy of silacyclopropabenzene relative to the corresponding cyclopropabenzene, and the strain energy is a simple additive function of the number of the fused three-membered rings involving Si atom.

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## 1. Introduction

A variety of small ring species annelated with a benzene ring have been synthesized so far, and their unique structures and properties have been extensively studied [1]. Cyclopropabenzene derivatives are of interest in view of their molecular structure and reactivity due to the highly strained ring system. In particular, the structures of these compounds have attracted much attention from the viewpoint of the studies on the Mills–Nixon effect [2]. There has been no definitive evidence for the existence of Mills–Nixon effect, and it is a matter of controversy even now whether such an effect really exists or not [3]. On the other hand, silacyclopropabenzene, a silicon analog of cyclopropabenzene, has remained as an unprecedented ring system until recently. It is very difficult to apply the conventional synthetic methods useful in the prepara-

tion of silicon containing three-membered ring compounds or cyclopropabenzene. Moreover, there had been no example for heteracyclopropabenzene stable at room temperature, although some heteracyclopropabenzene such as aza- [4], thia- [5], seleno- [6], boro- [7], and silacyclopropabenzene [8] have been postulated as intermediates. Bis(silacyclopropa)benzenes, i.e. benzene derivatives bridged by two silylene units at the 1, 2 and 4, 5 positions of the benzene ring, are silicon analogues of bis(cyclopropa)benzenes, which have not been synthesized as stable compounds so far. Their synthesis is much more difficult to be accessible than that of silacyclopropabenzene.

We have recently reported the formation of the first diaryldilithiosilane,  $\text{Tbt}(\text{Dip})\text{SiLi}_2$  ( $\text{Tbt} = 2,4,6\text{-tris}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$ ;  $\text{Dip} = 2,6\text{-diisopropylphenyl}$ ), treatment of which with bifunctional electrophiles is potentially useful for the synthesis of a novel class of cyclic organosilicon compounds [9]. Furthermore, we preliminarily reported a simple and effective preparation of silacyclopropabenzene **1a** and bis(silacyclopropa)benzenes **7a,b** by taking advantage of the characteristic reactivity of the overcrowded dilithiosilane.

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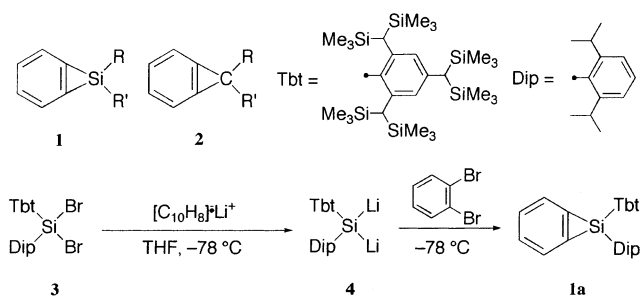
E-mail address: [tokitoh@boc.kuier.kyoto-u.ac.jp](mailto:tokitoh@boc.kuier.kyoto-u.ac.jp) (N. Tokitoh).

lane Tbt(Dip)SiLi<sub>2</sub> together with the first examples of the X-ray structural analysis of these silacyclopropabenzene derivatives [10]. In this paper, we present the details of the synthesis and properties of these silacyclopropabenzene derivatives.

## 2. Results and discussion

### 2.1. Synthesis of silacyclopropabenzene

Dilithiosilane **4** was generated by the exhaustive reduction of the corresponding overcrowded diaryldibromosilane **3** with lithium naphthalenide (5 molar amounts) in dry THF at  $-78\text{ }^{\circ}\text{C}$  under an Ar atmosphere. Dilithiosilane **4** thus generated was allowed to react with *o*-dibromobenzene (1.5 molar amounts) to give silacyclopropabenzene **1a** as stable colorless crystals in 34% yield (Scheme 1).

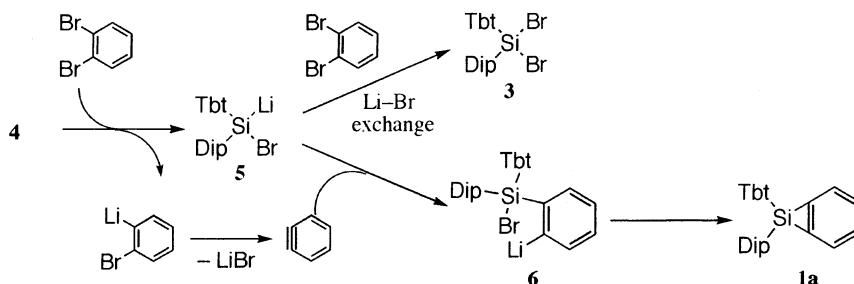


Interestingly, a considerable amount of starting material Tbt(Dip)SiBr<sub>2</sub> (**3**) (44%) was recovered in this reaction, although the quantitative generation of **4** from **3** had been confirmed by the trapping experiments using MeI and D<sub>2</sub>O [9]. Considering these trapping experiments, the recovery of **3** can be most likely interpreted in terms of the double lithium–bromine exchange reactions of **4** with *o*-dibromobenzene via silylenoid, Tbt(Dip)SiLiBr (**5**), which probably plays another important role for the formation of silacyclopropabenzene **1a** (Scheme 2). The initial formation of silylenoid **5** in this reaction was confirmed by the following trapping

experiments. After mixing dilithiosilane **4** with *o*-dibromobenzene in THF  $-78\text{ }^{\circ}\text{C}$  for 1 h, satd. NH<sub>4</sub>Cl aqueous solution was added to this mixture to afford only **1a** and **3**. However, it was found that the intermediary silylenoid **5** could be trapped with MeOD giving the expected product, Tbt(Dip)SiDBr, as a main product (23%), when the trapping reaction was performed at much lower temperature (at  $-110\text{ }^{\circ}\text{C}$ ) and just after the mixing of **4** and *o*-dibromobenzene (ca. 5 min). The following is a possible mechanism for the formation of **1a** on the basis of the trapping reactions mentioned above. At first, dilithiosilane **4** reacts with *o*-dibromobenzene to give Tbt(Dip)SiLiBr (**5**) and 1-bromo-2-lithiobenzene via Li–Br exchange reaction. Then, benzyne, a possible key intermediate of this reaction, might be generated by the elimination of LiBr from 1-bromo-2-lithiobenzene. The concomitantly formed reactive intermediates, i.e. silylenoid **5** and benzyne, react to afford the *o*-silylated phenyllithium **6**. The intramolecular cyclization of **6** gives the final product, silacyclopropabenzene **1a**. In this reaction mechanism, the competing Li–Br exchange reaction of Tbt(Dip)SiLiBr (**5**) with *o*-dibromobenzene is considered to afford Tbt(Dip)SiBr<sub>2</sub> (**3**). Chemical evidence for the presence of intermediate **6** has not been obtained yet at present. Silacyclopropabenzene **1a** was found to be thermally very stable even at its melting point ( $257\text{ }^{\circ}\text{C}$ ) in the solid state. A benzene solution of silacyclopropabenzene **1a** did not undergo any reaction in the presence of an excess amount of methanol at  $170\text{ }^{\circ}\text{C}$  (in a sealed tube) (Scheme 2).

### 2.2. NMR spectra of silacyclopropabenzene

Magnetic properties of rings are often used to describe their aromaticity. All the <sup>1</sup>H-NMR (in CDCl<sub>3</sub>) chemical shifts assigned to the central benzene ring protons of **1a** [7.35 (2H, AA'BB', *J* = 2.6, 5.0 Hz), 7.68 (2H, AA'BB', *J* = 2.6, 5.0 Hz)] were observed in the aromatic region, and the <sup>13</sup>C-NMR chemical shifts of the central benzene ring carbons of **1a** (135.0, 144.7, 150.0, 151.8, 152.0, and 154.4) were also located in the aromatic region. Although <sup>1</sup>H- and <sup>13</sup>C-NMR signals showed little downfield shifts compared to the signals of



cyclopropabenzene, these results indicate the aromatic character of the central benzene ring of **1a**. The  $^{29}\text{Si}$ -NMR spectrum showed four signals, of which the three signals at higher field (1.92, 2.41, and 2.66 ppm) were assigned belong to those of the  $\text{SiMe}_3$  of Tbt group and the other one observed at  $-103.8$  ppm was attributed to the signal for the Si atom of the silacyclopropene unit.

### 2.3. Structure of silacyclopropabenzene

When the bond lengths and angles of cyclopropabenzene rings are compared with those of usual benzene rings (the typical C–C lengths are 1.39–1.40 Å [11]), cyclopropabenzene shows an extreme shortening for the juncture bond (1.334 Å) along with a slight shortening for its neighboring bonds (1.363 Å [12]). The bond angles of the benzene ring in cyclopropabenzene ( $124.5$ ,  $122.4$ , and  $113.2^\circ$ ) deviate from that of ideal benzene ring ( $120^\circ$ ). The molecular structure of silacyclopropabenzene **1a** was definitively determined by the X-ray crystallographic analysis at  $-180^\circ\text{C}$  (Fig. 1). The selected bond lengths and angles of silacyclopropabenzene **1a** are listed in Table 1 together with those of the model molecule, silacyclopropabenzene (**1b**). Silacyclopropabenzene **1a** has a completely planar geometry for the central benzene ring. The sum of interior bond angles of the benzene ring of **1a** is  $720.0^\circ$ , and the sums of bond angles around the juncture carbon atoms (C1 and C6) are both  $360.0^\circ$ . The juncture bond length of **1a** [1.390(4) Å] is much longer than that of cyclopropabenzene [1.334(4) Å] [12], and the six C–C bond lengths of **1a** are almost equal to that of the usual benzene rings. Theoretical calculations for the model compound **1b** were also performed for comparison (Tables 1 and 2). The experimentally obtained bond lengths for **1a** are in good agreement with the theoretically calculated values

Table 1  
Observed and calculated bond lengths for silacyclopropabenzene and cyclopropabenzene

	Compound [E1RR']		
	<b>1a</b> [SiTbt(Dip)] <sup>a</sup>	<b>1b</b> [SiH <sub>2</sub> ] <sup>b</sup>	<b>2</b> [CH <sub>2</sub> ] <sup>c</sup>
C(1)–E(1)	1.826(2)	1.817	1.498(3)
E(1)–C(6)	1.828(3)	1.817	1.498(3)
C(1)–C(6)	1.390(4)	1.392	1.334(4)
C(5)–C(6)	1.388(4)	1.392	1.363(3)
C(1)–C(2)	1.394(4)	1.392	1.363(3)
C(2)–C(3)	1.381(4)	1.389	1.387(4)
C(3)–C(4)	1.383(4)	1.389	1.387(4)
C(4)–C(5)	1.403(5)	1.405	1.390(5)

<sup>a</sup> This work.

<sup>b</sup> This work at the B3LYP/6-311G (2d,p) level.

<sup>c</sup> Data were collected at  $-153^\circ\text{C}$ , see Ref. [13].

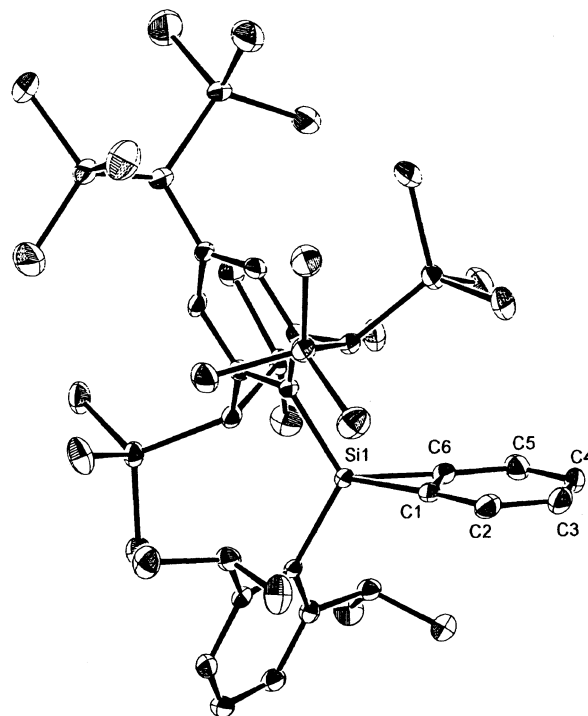


Fig. 1. ORTEP drawing of **1a** with thermal ellipsoid plots (50% probability).

for **1b**. These results strongly indicate that **1a** has no bond alternation in the central benzene ring. Thus, Mills–Nixon effect was not observed in the benzene ring of silacyclopropabenzene **1a**. The benzene skeleton of **1a** has merely distorted angles ( $117.3$ ,  $121.3$ ,  $121.5$ ,  $121.2$ , and  $121.4^\circ$ ). These bond angles indicate the less distorted benzene ring of **1a** than that of cyclopropabenzene. The remarkable structural difference between

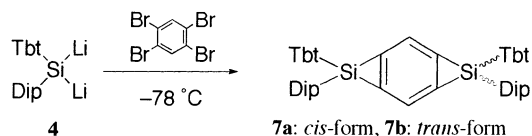
Table 2  
Observed and calculated bond angles for silacyclopropabenzene and cyclopropabenzene

	Compound [E1RR']		
	<b>1a</b> [SiTbt(Dip)] <sup>a</sup>	<b>1b</b> [SiH <sub>2</sub> ] <sup>b</sup>	<b>2</b> [CH <sub>2</sub> ] <sup>c</sup>
C(1)–E(1)–C(6)	44.7(1)	45.3	52.8(2)
E(1)–C(1)–C(6)	67.6(2)	67.5	63.6(1)
E(1)–C(6)–C(1)	67.7(1)	67.5	63.6(1)
C(1)–C(6)–C(5)	121.3(3)	121.9	124.5(2)
C(6)–C(1)–C(2)	121.5(2)	121.9	124.5(2)
C(1)–C(2)–C(3)	117.3(3)	116.5	113.2(2)
C(6)–C(5)–C(4)	117.3(3)	116.5	113.2(2)
C(2)–C(3)–C(4)	121.2(3)	121.6	122.4(2)
C(5)–C(4)–C(3)	121.4(3)	121.6	122.4(2)
E(1)–C(6)–C(5)	171.0(3)	170.7	171.7(2)
E(1)–C(1)–C(2)	170.9(2)	170.7	171.7(2)

<sup>a</sup> This work.

<sup>b</sup> This work at the B3LYP/6-311G (2d,p) level.

<sup>c</sup> Data were collected at  $-153^\circ\text{C}$ , see Ref. [13].



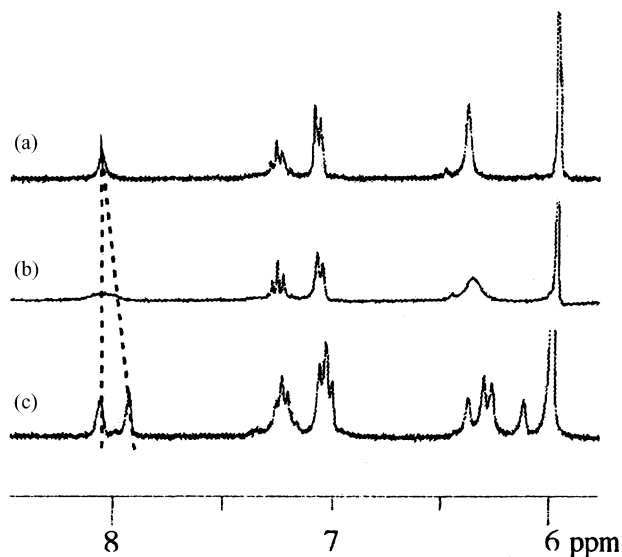
Scheme 3. Synthesis of bis(silacyclopropa)benzenes.

cyclopropabenzene **2** and its silicon analogue **1** is reasonably rationalized by their divergent ways of releasing the strain energy. Most of the molecular strain of the cyclopropabenzene skeleton mainly appears as the distortion of the juncture carbons from the ideal  $sp^2$  geometry. On the other hand, there should be another reducing mode of molecular strain, i.e. the expansion of the fused three-membered ring to the direction of its outer apex. Since C–Si bonds are much longer than C–C bonds, most of the molecular strain caused by the annelation might be inherently released in **1a,b** with this mode. These results are in good agreement with another theoretical study on the structure of silacyclopropabenzene [13].

#### 2.4. Synthesis of bis(silacyclopropa)benzene

Bis(silacyclopropa)benzenes **7a,b** were synthesized by the reaction of dilithiosilane **4** with 0.6 equivalent molar amount of 1,2,4,5-tetrabromobenzene in THF at  $-78\text{ }^\circ\text{C}$  (Scheme 3). The bis(silacyclopropa)benzenes have two stereoisomers, **7a** (*cis*-form) and **7b** (*trans*-form), and the yields of **7a** and **7b** are 3.4 and 1.9%, respectively. These compounds are very stable towards air and moisture. Their thermal stability is also shown in their high decomposition points (**7a**,  $340\text{ }^\circ\text{C}$ ; **7b**,  $351\text{ }^\circ\text{C}$ ).

This reaction resulted in the formation of two other products, i.e. Tbt(Dip)SiHBr (**8**) and silacyclopropaben-

Fig. 2. Variable-temperature  $^1\text{H-NMR}$  spectra of **7b** in tetrachloroethane- $d_2$ : (a) 120; (b) 90; and (c)  $25\text{ }^\circ\text{C}$ .

zene **1a**, in 44 and 9% yields, respectively. The formation mechanism of **7a** and **7b** can be explained in terms of a mechanism similar to that for the formation of silacyclopropabenzene **1a** by the reaction of dilithiosilane **4** and *o*-dibromobenzene. That is, dilithiosilane **4** initially reacts with 1,2,4,5-tetrabromobenzene to give Tbt(Dip)SiLiBr (**5**) and 1,2,4-tribromo-5-lithiobenzene via Li–Br exchange reaction, and then the resulting **5** adds to 4,5-dibromobenzene generated from 1,2,4-tribromo-5-lithiobenzene to afford the *o*-silylated phenyllithium **9**. The intramolecular cyclization of **9** and the subsequent similar condensation at the 3,4-positions of the resulting 3,4-dibromo-1-silacyclopropabenzene gives **7a** and **7b** (Scheme 4). Although the formation of the

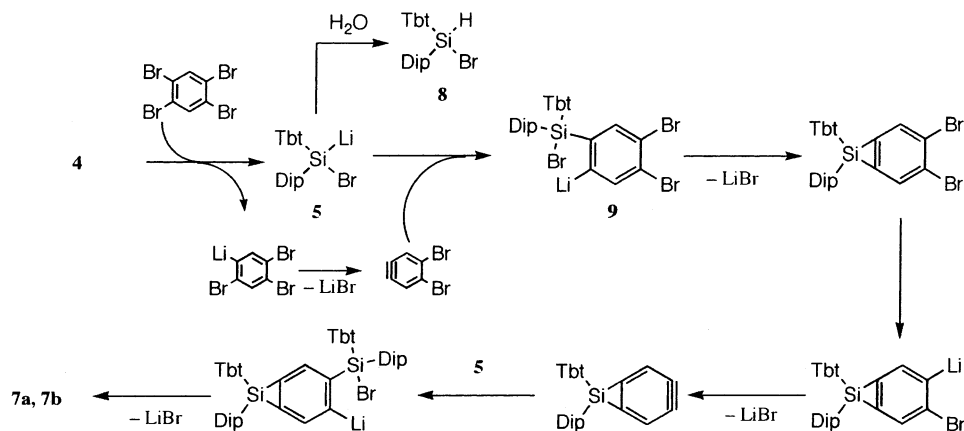
Table 3  
Observed and calculated structural parameters for bis(silacyclopropa)benzenes

	Theoretical Calculation				Observed	
	<b>7c</b> <sup>a</sup> R = H	<b>7d</b> <sup>a</sup> R = Ph	<b>7a</b> <sup>b</sup>	<b>7b</b> <sup>b</sup>	<b>7b</b> <sup>c</sup> Molecule A	<b>7b</b> <sup>c</sup> Molecule B
C(1)–C(6)	1.391	1.393	1.403	1.400	1.388(11)	1.389(11)
C(5)–C(6)	1.391	1.393	1.402	1.400	1.395(10)	1.405(11)
C(1)–C(2)	1.402	1.409	1.421	1.421	1.405(11)	1.398(11)
C(4)–C(5)	1.402	1.409	1.421	1.421	1.412(6)	1.380(11)
C(2)–C(3)	1.391	1.393	1.402	1.403	1.397(6)	1.414(10)
C(3)–C(4)	1.391	1.393	1.400	1.403	1.394(6)	1.389(11)
C(2)–C(1)–C(6)	123.4	123.0	122.6	122.8	123.2(4)	124.7(7)
C(1)–C(2)–C(3)	123.4	123.0	122.9	122.7	122.9(3)	121.2(7)
C(1)–C(6)–C(5)	113.1	114.0	114.4	114.6	113.3(4)	113.7(7)
C(2)–C(3)–C(4)	113.1	114.0	114.4	114.5	114.3(4)	114.8(7)
C(4)–C(5)–C(6)	123.4	123.0	123.0	122.8	122.9(4)	122.9(4)
C(3)–C(4)–C(5)	123.4	123.0	122.5	122.7	123.1(4)	122.7(4)

<sup>a</sup> Calculated level: B3LYP/6-311G(2d,p).

<sup>b</sup> Calculated level: B3LYP/6-31G\* for Si, 3-21G\* for C, H.

<sup>c</sup> Observed structure of **7b**: two independent molecules (molecule A and molecule B) were found in the unit cell.

Scheme 4. Reaction mechanism for the formation of bis(silacyclopropa)benzenes **7a,b**.

main product **8** can be interpreted in terms of the hydrolysis of remaining **5** during the work-up, the formation mechanism of **1a** in this reaction is not clear at present. The yields of bis(silacyclopropa)benzenes, **7a** and **7b**, were quite low but somewhat increased depending on the reaction temperature (**7a**: 1.3%, **7b**: 1.5% at  $-85\text{ }^{\circ}\text{C}$ , **7a**: 3.4%, **7b**: 1.9% at  $-78\text{ }^{\circ}\text{C}$ , **7a**: 2.4%, **7b**: 4.2% at  $-55\text{ }^{\circ}\text{C}$ ). The reaction at higher temperature such as  $0\text{ }^{\circ}\text{C}$  resulted in the formation of unidentified by-products, which are inseparable from **7a**. The formation of these by-products is probably due to the instability of dilithiosilane **4** and the increased reactivity of intermediates such as benzyne at higher temperature.

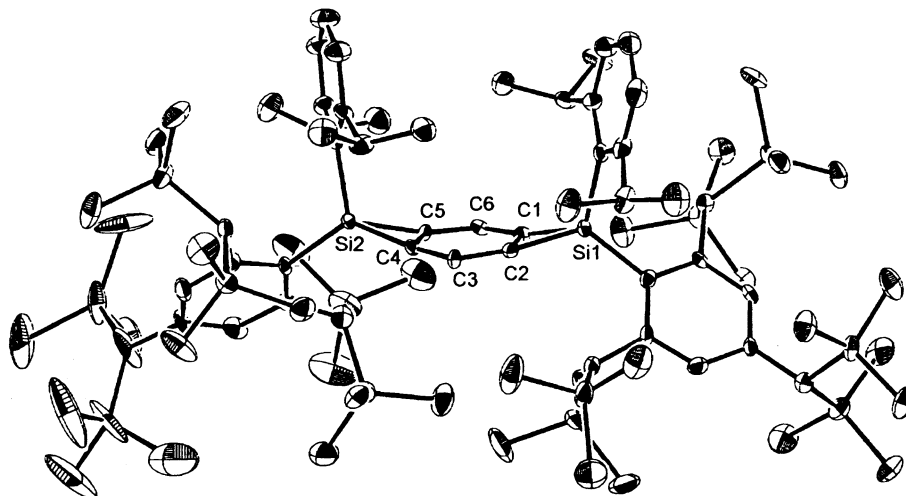
### 2.5. NMR spectra

The  $^1\text{H-NMR}$  spectrum of **7a** in  $\text{CDCl}_3$  at room temperature showed a singlet signal at 7.91 ppm, which is assigned to that of the two aromatic protons of the central benzene moiety. By contrast, the  $^1\text{H-NMR}$  spectrum of **7b** in  $\text{CDCl}_3$  at room temperature showed two signals at 7.92 and 8.11 ppm with equal intensity.

The measurement at  $90\text{ }^{\circ}\text{C}$  in tetrachloroethane- $d_2$  resulted in the coalescence of these signals to show only one signal at 8.00 ppm (Fig. 2). These  $^1\text{H-NMR}$  spectroscopic data strongly suggest the restricted rotations of the bonds between the carbon atoms of the Tbt and/or Dip groups and the Si atoms of the bis(silacyclopropa)benzene skeleton in **7b**, caused by the extreme steric congestion between the bulky Tbt and Dip groups. Therefore, **7b** is considered to have at least two conformers in solution. Bis(silacyclopropa)benzenes **7a** and **7b** exhibited very complicated  $^{13}\text{C-NMR}$  spectra, suggesting great steric congestion around the central silicon atoms. The  $^{13}\text{C-NMR}$  spectra of **7a** and **7b** were too complicated to be assigned even at  $120\text{ }^{\circ}\text{C}$ . The  $^{29}\text{Si-NMR}$  signals of the Si(1) and Si(2) atoms of **7a** and **7b** were not observed due to their low solubility in common NMR solvents.

### 2.6. Structures of bis(silacyclopropa)benzenes

Molecular structures of **7a** and **7b** were determined by X-ray crystallographic analysis at  $-180\text{ }^{\circ}\text{C}$  (Figs. 3 and

Fig. 3. ORTEP drawing of **7a** with thermal ellipsoid plots (50% probability).



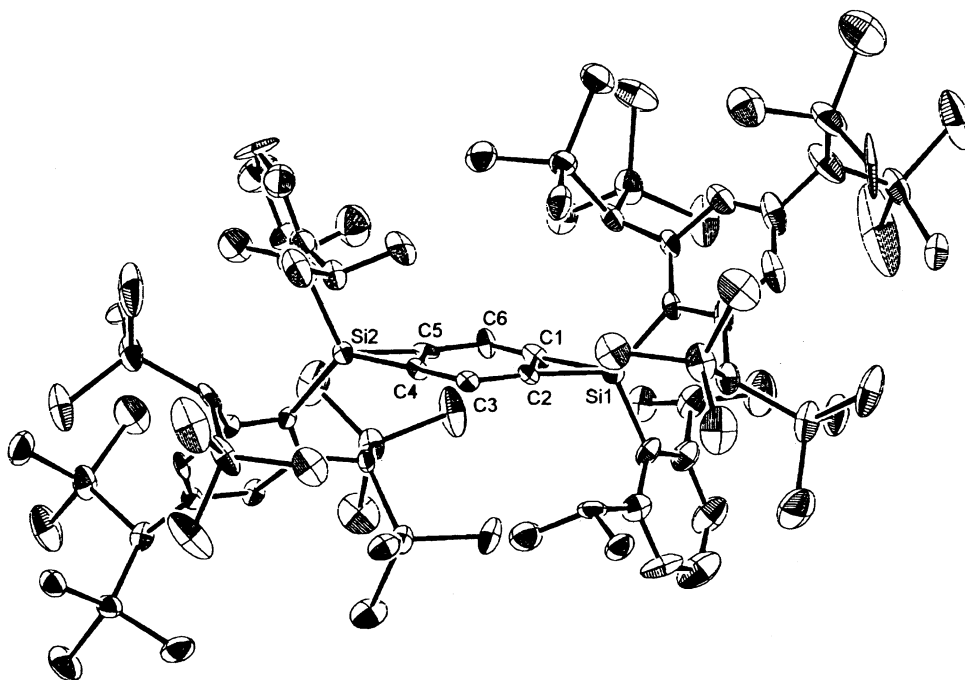


Fig. 4. ORTEP drawing of **7b** with thermal ellipsoid plots (50% probability).

4). The selected bond lengths and angles of **7a** and **7b** are listed in Table 3 together with the calculated values for the model molecules, [bis(silacyclopropa)benzenes (**7c**: R = H, **7d**: R = Ph)] and real molecules **7a** and **7b**. The experimentally obtained geometries for the bis(silacyclopropa)benzenes, **7a** and **7b**, have shown slightly squashed benzene rings, which are more perturbed than that of **1a**. The central benzene ring of **7b** has a completely planar geometry, where the sum of interior bond angles of the benzene ring is  $720.0^\circ$  and the sums of bond angles around the juncture carbon atoms (C1 and C6) are both  $360.0^\circ$ . The experimentally obtained geometry for **7b** are in good agreement with those theoretically calculated for **7b**, **7c**, and **7d**. On the other hand, the central benzene ring of **7a** has a bent structure. The dihedral angle between Si(1)–C(1)–C(2) and C(6)–C(1)–C(2)–C(3) planes and that between C(3)–C(4)–C(5)–C(6) and C(4)–Si(2)–C(5) planes are  $10.3$  and  $12.0^\circ$ , respectively. Moreover, the benzene ring is bent and the dihedral angle between C(6)–C(1)–C(2)–C(3) and C(3)–C(4)–C(5)–C(6) planes is  $4.7^\circ$ .

The optimized structures for **7b**, **7c**, and **7d** have an almost planar geometry for their central benzene rings, while the calculated structure for **7a** has a bent structure similar to the observed structure. From these results, we concluded that the bis(silacyclopropa)benzene skeleton intrinsically has a planar structure and the highly distorted benzene ring of **7a** is due to the steric repulsion between the two bulky Tbt groups situated in *cis*-form. All C–C bond lengths in the central benzene rings of **7a** and **7b** are almost equal to those of the usual benzene rings within the error of temperature factors. Thus,

bis(silacyclopropa)benzenes, **7a** and **7b**, have no distinct bond alternation for the central benzene ring moieties, and do not show the Mills–Nixon effect. In addition, the benzene skeletons of **7a** and **7b** have somewhat deviated bond angles ( $113.3$ – $114.4^\circ$  around the C(3) and C(6) carbons,  $122.5$ – $123.2^\circ$  around the C(1), C(2), C(4) and C(5) junction carbons). The deviation in bond angles of **7a,b** from that of usual benzene rings ( $120^\circ$ ) was larger than those of silacyclopropabenzene.

To the best of our knowledge, the synthesis of bis(cyclopropa)benzene has not been achieved yet. The absence of bis(cyclopropa)benzene is probably due to their severe distortion and the lack of suitable synthetic methods. The successful synthesis and isolation of bis(silacyclopropa)benzenes **7a,b** here described should be of particular note as the first stable examples of such tricyclic ring systems. The smaller ring strain of silacyclopropene than that of cyclopropene and the new synthetic strategy using a novel organosilicon reagent, dilithiosilane, are keys to a success.

### 3. Conclusion

We have succeeded in the syntheses of silacyclopropabenzene **1a** and bis(silacyclopropa)benzenes **7a,b**, the first examples of the stable heterocyclopropabenzenes, by taking advantage of a dilithiosilane **4** bearing bulky substituents, and the isolations of these novel silacyclopropabenzenes as stable crystalline compounds. The X-ray crystallographic analysis revealed that these new classes of annelated benzene derivatives are much less

distorted compared with those of their carbon analogues. This small distortion in the benzene ring can be interpreted in terms of the release of strain in the silacyclopropabenzene ring by the expansion of the fused three-membered ring to the direction of its outer apex due to the longer Si–C bonds than C–C bonds. These results were in good agreement with theoretical calculations of some model molecules and real molecules. Thus, the annelation of silacyclopropane ring brings about less effect in the geometrical change for the central benzene ring.

## 4. Experimental

### 4.1. General procedure

All experiments were performed under an argon atmosphere unless otherwise noted. THF was dried by standard methods and freshly distilled prior to use.  $^1\text{H}$ - (300 MHz),  $^{13}\text{C}$ - (75 MHz) and  $^{29}\text{Si}$ -NMR (57 MHz) spectra were measured in  $\text{CDCl}_3$  or  $d_2$ -tetrachloroethane with JEOL JNM AL-300 spectrometer. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Preparative gel permeation liquid chromatography (GPC) was performed on LC-908 and LC-918 apparatus (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform for LC-918, toluene for LC-908). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Electronic spectra were recorded on a JASCO Ubest-50 UV–vis spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)-methyl]benzene (TbtBr) [14] and **3** [15] were prepared according to the reported procedures.

### 4.2. Theoretical calculations

The geometries of silacyclopropabenzene and the related reference molecules were optimized by using the GAUSSIAN 98 program [16] at B3LYP/6-311G(2d,p) levels of density functional theory. Theoretical calculations for model molecules **7c,d** were carried out using the GAUSSIAN 98 program [16] with density functional theory at the B3LYP level [17]. The triple zeta basis set ([3s3p]) augmented by two sets of d polarization functions for Si (d exponents 0.424 and 0.118) was used with effective core potential [18]. The 6-311G(2d,p) basis sets were used for C and H. Theoretical calculations for real molecules **7a,b** were carried out with B3LYP/6-31G(d) for Si, 3-21G(d) for C and H.

### 4.3. X-ray structural determination

Crystallographic data of **1a** and **7a,b** were collected in Table 4. Single crystals of **1a** were grown by the slow evaporation of its saturated solution in hexane in refrigerator, while single crystals of **7a,b** were grown in  $\text{CHCl}_3$  and EtOH, respectively. The intensity data for **1a** ( $2\theta \leq 55.0^\circ$ ) were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo– $\text{K}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) at 93 K. The structure was solved by direct methods with SIR-92 [19] and expanded using Fourier techniques (DIRDIF-94 [20]). The refinements of the structure were carried out by the full-matrix least-squares procedures on  $F^2$  (SHELXL-97 [21]). All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for **1a** were performed using the teXsan [22] crystallographic software package of Molecular Structure Corporation. The intensity data of **7a,b** were collected on a Rigaku/MS Mercury CCD diffractometer with graphite monochromator Mo– $\text{K}\alpha$  radiation ( $\lambda = 0.71071 \text{ \AA}$ ) to  $2\theta_{\text{max}} = 50^\circ$  at 93 K. The structures were solved by direct methods (SIR-97 [23]) and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELXL-97 [21]). All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. In the case of **7a**, the overlapped and disordered trimethylsilyl groups of *p*-substituent of the Tbt group were restrained to be identical to each other using the SADI, DFIX, SIMU, and DELU instructions. The occupancies of fragments for **7a** were refined with constraints that their sum is 1

Table 4  
Crystallographic data for compounds **1a**, **7a** and **7b**

	<b>1a</b>	<b>7a</b>	<b>7b</b>
Formula	$\text{C}_{45}\text{H}_{80}\text{Si}_7$	$\text{C}_{84}\text{H}_{154}\text{Si}_{14}$	$\text{C}_{84}\text{H}_{154}\text{Si}_{14}$
Formula weight	740.02	1557.33	1557.33
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)	$Cc$ (#9)
<i>a</i> (Å)	11.9775(4)	12.9649(17)	42.518 (5)
<i>b</i> (Å)	22.9899(6)	15.990(2)	13.0980 (11)
<i>c</i> (Å)	9.9059(4)	48.414(5)	38.871(5)
$\alpha$ (°)	95.675(2)	90	90
$\beta$ (°)	107.6040(7)	90	112.970(4)
$\gamma$ (°)	76.798(2)	90	90
<i>V</i> (Å <sup>3</sup> )	2529.9(2)	10037(2)	19931(4)
<i>Z</i>	2	4	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.073	1.031	1.038
Crystal size (mm)	0.40 × 0.40 × 0.35	0.40 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Independent reflections	11383	17320	23748
Parameters	548	985	1858
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.053	0.0746	0.0946
<i>wR</i> <sub>2</sub> (all data)	0.151	0.1873	0.1807
Goodness-of-fit	0.98	1.131	1.098

(0.58:0.42). In the case of **7b**, the refinements were performed using TWIN instructions, and two independent molecules (molecules A and B) were found in the unit cell. The structures of the overlapped and disordered trimethylsilyl groups of *p*-substituent of the Tbt group for the molecules A and B of **7b** were restrained to be identical to each other using the SADI, DFIX, SIMU, ISOR, and DELU instructions. The occupancies of each fragment for **7b** were refined with constraints that their sum is 1 (0.62:0.38 for molecule A and 0.65:0.35 for molecule B, respectively)

#### 4.4. Synthesis of silacyclopropabenzene

A THF solution of lithium naphthalenide (1.0 M, 3.75 mL, 3.75 mmol, 5 molar amounts) was added at  $-78^{\circ}\text{C}$  to THF (7 mL) solution of Tbt(Dip)SiBr<sub>2</sub> (**3**) (676 mg, 0.75 mmol). After stirring for 1 h at this temperature, *o*-dibromobenzene (181  $\mu\text{L}$ , 1.50 mmol) was added to the reaction mixture. After warming to room temperature and removal of solvent, hexane (10 mL) was added to the residue. The mixture was extracted with hexane several times, and the mixture was filtered with Celite<sup>®</sup>. The residue was subjected to GPLC (CHCl<sub>3</sub>) followed by PTLC (hexane) gave silacyclopropabenzene **1a** (208 mg, 0.25 mmol, 34% yield) and Tbt(Dip)SiBr<sub>2</sub> (**3**) (297 mg, 0.33 mmol, 44%). **1a**: colorless crystals; m.p. 256.9–257.5  $^{\circ}\text{C}$ ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$   $-0.08$  (36H, s),  $0.06$  (18H, s),  $0.88$  (6H, d,  $J = 6.4$  Hz),  $1.31$  (1H, s),  $1.33$  (6H, d,  $J = 6.4$  Hz),  $2.64$  (1H, br s),  $2.72$  (1H, br s),  $3.81$  (2H, sept,  $J = 6.4$  Hz),  $6.22$  (1H, br s),  $6.37$  (1H, br s),  $7.10$  (2H, d,  $J = 6.8$  Hz),  $7.28$  (1H, t,  $J = 6.8$  Hz),  $7.35$  (2H, AA'BB',  $J = 2.6, 5.0$  Hz),  $7.68$  (2H, AA'BB',  $J = 2.6, 5.0$  Hz); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$   $0.86$  (q),  $0.97$  (q),  $1.18$  (q),  $22.48$  (q),  $27.14$  (br d),  $27.72$  (q),  $30.56$  (d),  $34.09$  (d),  $122.84$  (d),  $122.97$  (d),  $125.11$  (s),  $126.59$  (d),  $128.27$  (d),  $130.06$  (d),  $130.16$  (d),  $135.02$  (s),  $144.68$  (s),  $150.00$  (s),  $151.75$  (s),  $152.03$  (s),  $154.35$  (s); <sup>29</sup>Si-NMR (CDCl<sub>3</sub>)  $\delta$   $-104.83, 1.92, 2.41, 2.66$ ; UV-vis (hexane)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ )  $305$  ( $2.0 \times 10^4$ ),  $296$  ( $1.8 \times 10^4$ ),  $264$  ( $1.5 \times 10^5$ ),  $234$  ( $4.3 \times 10^5$ ),  $209$  ( $3.6 \times 10^5$ ); FAB-MS  $m/z$  (%)  $816.5$  ( $\text{M}^+$ , 15),  $73$  ( $\text{Me}_3\text{Si}^+$ , 100); Anal. Calc. for C<sub>45</sub>H<sub>80</sub>Si<sub>7</sub>: C, 66.10; H, 9.86. Found: C, 65.94; H, 9.58%.

#### 4.5. Synthesis of bis(silacyclopropa)benzene

A THF solution of lithium naphthalenide (2.36 M, 0.53 mL, 1.25 mmol, 5 molar amounts) was added at  $-78^{\circ}\text{C}$  to THF (3 mL) solution of **3** (227 mg, 0.25 mmol). After it had been stirred for 1 h at this temperature, powder of 1,2,4,5-tetrabromobenzene (58 mg, 0.15 mmol) was added to the reaction mixture. After removal of solvent, hexane (5 mL) was added to the residue, and the mixture was extracted with hexane several times. The mixture was filtered with Celite<sup>®</sup>, the

residue was subjected to GPLC (CHCl<sub>3</sub>) followed by PTLC (hexane) gave silacyclopropabenzene **1a** (10.4 mg, 12.7  $\mu\text{mol}$ , 9% yield), Tbt(Dip)SiHBr (**8**) (44% yield, determined by <sup>1</sup>H-NMR), bis(silacyclopropa)benzenes **7a** (6.6 mg, 4.2  $\mu\text{mol}$ , 3.4% yield) and **7b** (3.8 mg, 2.4  $\mu\text{mol}$ , 1.9% yield). **7a**: m.p.  $340^{\circ}\text{C}$  (decomp.); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 K)  $\delta$   $-0.37$  (s, 18H),  $-0.33$  (s, 9H),  $-0.30$  (s, 9H),  $0.02$  (s, 36H),  $0.20$  (s, 9H),  $0.22$  (s, 9H),  $0.29$  (s, 18H),  $1.05$ – $1.21$  (m, 8H),  $1.24$ – $1.41$  (m, 18H),  $2.21$  (br s, 2H),  $3.37$  (br s, 2H),  $3.59$  (s, 2H),  $4.12$  (br s, 2H),  $6.18$  (s, 1H),  $6.30$  (s, 1H),  $6.39$  (s, 1H),  $6.41$  (s, 1H),  $6.82$  (d,  $J = 7.8$  Hz, 2H),  $7.01$  (d,  $J = 7.8$  Hz, 2H),  $7.11$  (t,  $J = 7.8$  Hz, 2H),  $7.91$  (s, 2H); UV-vis (hexane)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ )  $310$  ( $1.0 \times 10^5$ ),  $295$  ( $2.0 \times 10^5$ ),  $263$  ( $5.0 \times 10^5$ ),  $237$  ( $9.8 \times 10^5$ ),  $213$  ( $7.6 \times 10^5$ ). **7b**: m.p.  $351^{\circ}\text{C}$  (decomp.); <sup>1</sup>H-NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 363 K)  $\delta$   $-0.78$  (s, 9H),  $-0.22$  (s, 9H),  $0.04$  (s, 54H),  $0.08$  (s, 18H),  $0.22$  (s, 18H),  $1.13$ – $1.60$  (m, 26H),  $2.31$  (brs, 2H),  $3.48$  (br s, 4H),  $4.35$  (br s, 2H),  $6.32$  (br s, 4H),  $7.02$  (d,  $J = 7.8$  Hz, 4H),  $7.22$  (t,  $J = 7.8$  Hz, 2H),  $8.00$  (s, 2H); FAB-MS  $m/z$   $1557.0$  ( $\text{M}^+$ ); UV-vis (hexane)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ )  $310$  ( $6.0 \times 10^4$ ),  $293$  ( $2.7 \times 10^5$ ),  $268$  ( $3.7 \times 10^5$ ),  $237$  ( $9.1 \times 10^5$ ),  $213$  ( $7.0 \times 10^5$ ); The <sup>13</sup>C-NMR spectra of **7a** and **7b** were too complicated to be assigned even at  $120^{\circ}\text{C}$ . The <sup>29</sup>Si-NMR signals of the Si(1) and Si(2) atoms of **7a** and **7b** were not observed due to their low solubility.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 206102, 200048 and 200049 for **1a**, **7a** and **7b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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