

The First Examples of Stable Benzenes Fused with Two Three-membered Rings: Synthesis and Structures of the Two Stereoisomers of Bis(silacyclopropa)benzenes¹

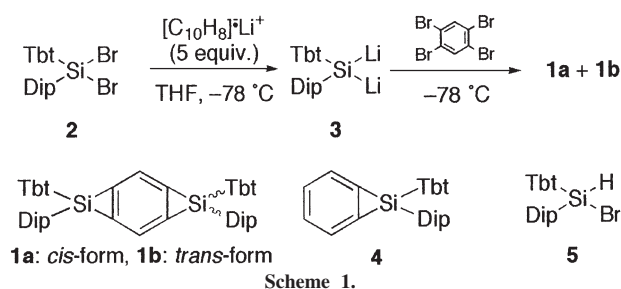
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Two stereoisomers of the first stable bis(silacyclopropa)benzenes (**1a**, **1b**) were successfully synthesized by the reaction of Tbt(Dip)SiLi₂ (**3**) [Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl] with 1,2,4,5-tetrabromobenzene. The molecular structures of **1a** and **1b** were discussed on the basis of the X-ray structural analyses.

Ever since Kekulé structure of benzene was recognized, chemists have been thinking about the effect of strained small rings annelated to benzene (Mills-Nixon effect³). In particular, highly strained bis(cyclopropa)benzenes, in which two cyclopropene skeletons are fused to the benzene ring, have attracted theoretical and experimental interests from the viewpoint of this effect.⁴ Nevertheless, the synthesis of bis(cyclopropa)benzenes has not been achieved yet,⁵ and very little has been known about the chemistry of these peculiar, distorted tricyclic compounds. The absence of these ring systems is probably due to their severe distortion and the lack of suitable synthetic methods.

On the other hand, we have recently succeeded in the synthesis and isolation of the first stable sila- and germacyclopropabenzene, which are also the first stable heteracyclopropabenzene, via the reaction of dilithiosilane **3** and dilithiogermene with *o*-dibromobenzene, respectively.^{6–8} In addition, we found that the benzene nuclei of sila- and germacyclopropabenzene are much less distorted by the annelation than those of cyclopropabenzene. With these results in hand, we expected that silicon analogues of bis(cyclopropa)benzenes, bis(silacyclopropa)benzenes, can be synthesized as stable compounds. Here, we describe the synthesis of the first bis(silacyclopropa)benzenes, which have two stereoisomers (**1a**: *cis*-form, **1b**: *trans*-form), by the reaction of **3** with 1,2,4,5-tetrabromobenzene and their X-ray crystallographic analyses together with the theoretical studies on the structures of **1a** and **1b**.



Dilithiosilane Tbt(Dip)SiLi₂ (**3**) was generated by the exhaustive reduction of Tbt(Dip)SiBr₂ (**2**) with an excess amount of lithium naphthalene (5 molar amounts) at –78 °C in THF under an Ar atmosphere.⁶ Dilithiosilane **3** was allowed to react with 0.6 equivalent of 1,2,4,5-tetrabromobenzene at –78 °C for 15 h under an Ar atmosphere, and the products were separated by gel

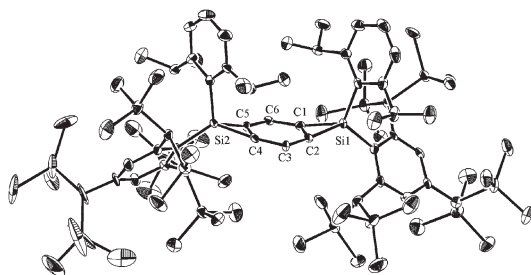
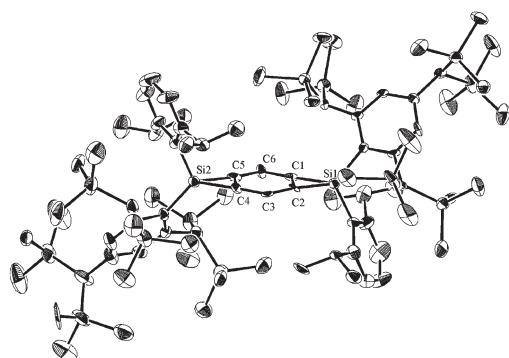
permeation chromatography using toluene as an eluent and the successive preparative thin layer chromatography (silica gel, eluent; hexane) to give the first bis(silacyclopropa)benzenes, **1a** and **1b**, as colorless crystals in 3.4 and 1.9% yields, respectively. Both products are very stable towards air and moisture. As for other products, Tbt(Dip)SiHBr (**5**) and silacyclopropabenzene **4** were also obtained in 44 and 9% yields, respectively (Scheme 1). The formation of **1a** and **1b** can be explained in terms of a mechanism similar to that for the formation of monometalla-(cyclopropa)benzenes.^{7,8} That is, dilithiosilane **3** initially reacts with 1,2,4,5-tetrabromobenzene to give Tbt(Dip)SiLiBr (**6**)⁹ and 1,2,4-tribromo-5-lithiobenzene (**7**) via Li-Br exchange reaction, and then the resulting **6** adds to 4,5-dibromobenzene generated from **7** to afford the *o*-silylated phenyllithium 2-[Tbt(Dip)(Br)Si]-4,5-Br₂C₆H₂Li (**8**). The intramolecular cyclization of **8** and the subsequent similar condensation at the 3,4-positions of the resulting 3,4-dibromosilacyclopropabenzene gives **1a** and **1b**. The formation of main product **5** is interpreted in terms of the hydrolysis of remaining **6** in the work-up. On the other hand, 3,4-dibromosilacyclopropabenzene was not observed in this reaction, and the formation mechanism of silacyclopropabenzene **4** is not clear at present. Although the yields of **1a** and **1b** are quite low, the achievement in the synthesis of these new class of annelated benzene rings is interesting in the viewpoint of structural chemistry, organometallic synthesis and aromatic compound chemistry.

The ¹H NMR spectrum of **1a** in CDCl₃ showed a singlet signal at 7.91 ppm,¹⁰ which is assigned to that of the two aromatic protons of the central benzene skeleton. By contrast, the ¹H NMR spectrum of **1b** in CDCl₃ showed two signals at 7.92 and 8.11 ppm with the same intensity. The measurement at 90 °C in tetrachloroethane-*d*₂ resulted in the coalescence of these signals to show only one signal at 8.00 ppm. These spectroscopic results strongly suggest the restricted rotations of the bonds between the carbon atoms of Tbt and/or Dip groups and the Si atoms of the bis(silacyclopropa)benzene skeleton in **1b**, caused by the extreme steric congestion between the bulky Tbt and Dip groups. Molecular structures of **1a** and **1b** were determined by X-ray crystallographic analysis at –180 °C (Figures 1 and 2).¹¹ Bis(silacyclopropa)benzenes, **1a** and **1b**, have slightly squashed benzene rings, which are more perturbed than that of **4**. The bis(silacyclopropa)benzene skeleton for **1b** was found to have an almost planar geometry. As for the structure of **1b**, the sums of bond angles around C1, C2, C4, and C5 are almost 360° and the sum of the interior bond angles in the benzene ring is 720.0°. By contrast, the skeleton for **1a** was obviously nonplanar. 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°, 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°. The C–C bond lengths in the central benzene rings of **1a** and **1b** are almost similar

Table 1. Observed and calculated bond distances (Å) and angles (°) in the benzene rings of bis(silacyclopropa)benzenes

Compound	a a'	b b'	c c'	α α'	β β'	γ γ'
1a^a	1.409(5)	1.415(6)	1.397(6)	123.2(4)	113.3(4)	122.9(4)
	1.414(6)	1.412(6)	1.394(6)	122.9(3)	114.3(4)	123.1(4)
	1.403	1.421	1.402	122.6	114.4	123.0
1a^b	1.402	1.421	1.400	122.9	114.4	122.5
1c^c (R = H)	1.391	1.402	1.391	123.4	113.1	123.4
1d^c (R = Ph)	1.393	1.409	1.393	123.0	114.0	123.0

^aObserved. ^bCalculated level: 6–31 G* for Si, 3–21 G* for C, H. ^cCalculated level: TZ(2d) for Si, 6–311 G** for C, H.

**Figure 1.** ORTEP drawing of bis(silacyclopropa)benzene **1a** (*cis*-isomer) with thermal ellipsoid plots (50% probability).**Figure 2.** ORTEP drawing of bis(silacyclopropa)benzene **1b** (*trans*-isomer) with thermal ellipsoid plots (50% probability).

to each other within the error of temperature factors, and also comparable to the C–C bond lengths of usual benzene rings (about 1.39–1.40 Å).¹² Thus, bis(silacyclopropa)benzenes, **1a** and **1b**, have no distinct bond alternation for the central benzene ring moieties. In order to discuss these molecular structures in detail, theoretical calculations for the model molecules (**1c**: R = H, **1d**: R = Ph) and the real molecule **1a** were performed. These results are summarized together with the observed values for **1a** in Table 1. Bis(silacyclopropa)benzene rings of the calculated model molecules, **1c** and **1d**, are almost planar, and the C–C bond lengths in the central benzene rings of **1c** and **1d** are consistent with those of usual benzene rings. In addition, the calculated structure for **1a** is compatible with the observed structure for **1a**. These results strongly suggest that the bis(silacyclopropa)benzene ring intrinsically has planar structure and the highly distorted benzene ring of **1a** is probably due to the steric repulsion between the two bulky Tbt groups situated in *cis*-form.

The results here described are of great interest as the first example of the synthesis and structural characterization of bis(silacyclopropa)benzenes. Further works on the elucidation of

the reactivity of **1a** and **1b** are currently in progress.

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References and Notes

- IUPAC name is 4,8-disilatricyclo[5.1.0.0^{3,5}]octa-1,3(5),6-triene.
- The initial part of this work was done at Institute for Fundamental Research of Organic Chemistry, Kyushu University.
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- The stability of **6** has been reported in ref. 6. Silylenoid **6** can survive at –78 °C without undergoing α -elimination of lithium bromide giving the corresponding silylene or intermolecular substitution reaction leading to oligo- or polysilanes.
- 1a**: mp 340 °C (decomp.); ¹H NMR (CDCl₃, 273 K) δ –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 (brs, 2H), 3.37 (brs, 2H), 3.59 (s, 2H), 4.12 (brs, 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). **1b**: mp 351 °C (decomp.); ¹H NMR (C₂D₂Cl₄, 363 K) δ –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 (brs, 4H), 4.35 (brs, 2H), 6.32 (brs, 4H), 7.02 (d, *J* = 7.8 Hz, 4H), 7.22 (t, *J* = 7.8 Hz, 2H), 8.00 (s, 2H); The ¹³C NMR spectra of **1a** and **1b** were too complicated to be assigned even at 120 °C. At present, the ²⁹Si NMR signals of the Si(1) and Si(2) atoms of **1a** and **1b** were not observed due to their low solubility.
- Crystallographic data for **1a**: The structure was solved by direct method (SIR-97)¹³ and refined by full-matrix least-squares procedures on F² for all reflections (SHELX-97).¹⁴ C₈₄H₁₅₄Si₁₄, *M_r* = 1557.33, orthorhombic, space group *P*2₁2₁2₁ (#19), *a* = 12.9649(17) Å, *b* = 15.990(2) Å, *c* = 48.414(5) Å, *V* = 10037(2) Å³, *Z* = 4, *D*_{calcd} = 1.031 g/cm³, μ = 0.215 mm^{–1}, *R*₁(*I* > 2σ(*I*)) = 0.0746, *wR*₂(all data) = 0.1873, *T* = 93(2) K, GOF = 1.131, (CCDC 200048); **1b**: C₈₄H₁₅₄Si₁₄, *M_r* = 1557.33, monoclinic, space group *C*c (#9), *a* = 42.518(5) Å, *b* = 13.0980(11) Å, *c* = 38.871(5) Å, β = 112.970(4)°, *V* = 19931(4) Å³, *Z* = 8, *D*_{calcd} = 1.038 g/cm³, μ = 0.217 mm^{–1}, *R*₁(*I* > 2σ(*I*)) = 0.0946, *wR*₂(all data) = 0.1807, *T* = 93(2) K, GOF = 1.098, (CCDC 200049). In the case of **1b**, two independent molecules (molecule A and molecule B) were found in the unit cell. Only molecule A is shown in Figure 2.
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