The First Stable Heteracyclopropabenzene: Synthesis and Crystal Structure of a Silacyclopropabenzene

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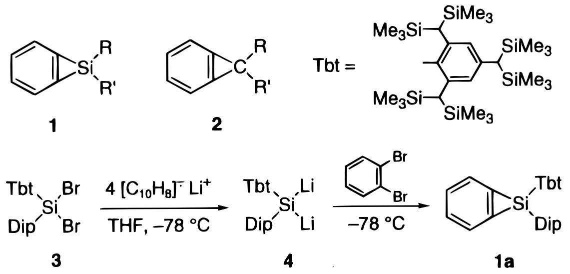
Silicon-containing three-membered-ring systems have attracted much attention in organosilicon chemistry from the viewpoints of their strained molecular structures and unique reactivities, and extensive studies have already been reported on a variety of ring systems, e.g., silacyclopropanes,[1] silacyclopropenes,[1a,b,2] and a bis(alkylidene)silacyclopropane.[3] On the other hand, silacyclopropabenzene **1** still remains as an unprecedented ring system of this class probably due to the lack of suitable synthetic methods,[4] since the conventional synthetic methods for cyclopropabenzenes **2**[5] or Si-containing three-membered rings[1−3] are very difficult to apply to the construction of a silacyclopropene ring system fused with a benzene ring. There have been no examples of stable heteracyclopropabenzenes so far, though benzothiirene and benzoselenirene have been postulated and detected as transient species in low-temperature matrices.[6]

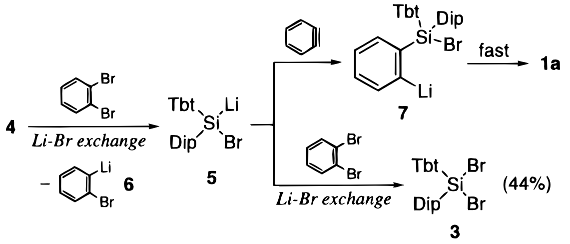
Meanwhile, we have recently reported the formation of the first diaryldilithiosilane **4**, Tbt(Dip)SiLi$_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl), treatment of which with bifunctional electrophiles is potentially useful for the synthesis of a novel class of cyclic organosilicon compounds.[7] Here, we present the synthesis and isolation of the first stable silacyclopropabenzene **1a** (R = Tbt, R′ = Dip) by taking advantage of this new silyl dianion species **4** together with the crystallographic structural analysis of **1a**.

Treatment of **4**, generated from **3** (676 mg, 0.75 mmol) and lithium naphthalenide (1.0 M, 3.75 mL, 5 molar amounts) in THF,[7] with 1 equiv of *o*-dibromobenzene at −78 °C resulted in the isolation of **1a** as stable colorless crystals in 34% yield (Scheme 1).[8] Compound **1a** should be noted as the first stable example of not only a sila- but also a heteracyclopropabenzene. Interestingly, a considerable amount of starting material **3** (44%) was recovered in this reaction, although the quantitative generation of **4** from **3** has already been confirmed by the trapping experiments.[7] The recovery of **3** can be most likely interpreted in terms of the double lithium−bromine exchange reactions of **4** with *o*-dibomobenzene via silylenoid, Tbt(Dip)SiLiBr (**5**),[9] which plays another important role for the formation of **1a** (Scheme 2).

Scheme 1



Scheme 2



Although a silyl monoanion has been known to react with an aryl halide to give the corresponding substitution product,[10] the formation of **1a** in the reaction of **4** with *o*-dibromobenzene may not be such a simple substitution but rather based on more complicated reaction processes, i.e., the addition of silylenoid **5** to benzyne, which is generated by the α,β-elimination[11] of LiBr from *o*-bromophenyllithium (**6**) initially formed via lithium−bromine exchange of **4** with *o*-dibromobenzene, followed by intramolecular cyclization of the resulting *o*-silylated phenyllithium **7** (Scheme 2). Thus, the unique reactivity of dilithiosilane **4** resulted in the concurrent generation of quite different reactive species such as silylenoid **5** and benzyne in the reaction system under very mild conditions.

Silacyclopropabenzene **1a** was found to be thermally very stable even after being heated to its melting point (257 °C) in the

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(8) **1a**: colorless crystals; mp 256.9−257.5 °C; ^{1}H NMR (CDCl$_3$) δ −0.08 (36H, s), 0.06 (18H, s), 0.88 (6H, d, J = 6.4 Hz), 1.31 (1H, s), 1.33 (6 H, d, J = 6.4 Hz), 2.64 (1H, br s), 2.72 (1H, br s), 3.81 (2H, sept, J = 6.8 Hz), 6.22 (1H, br s), 6.37 (1H, br s), 7.10 (2H, d, J = 7.3 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); ^{13}C NMR (CDCl$_3$) δ 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); ^{29}Si NMR (CDCl$_3$) δ −104.83, 1.92, 2.41, 2.66; UV−vis (hexane) λ_{max}/nm (ϵ) 305 (2000), 296 (1800); FAB-MS *m*/*z* (%) 816.5 (M$^+$, 15), 73 (Me$_3$Si$^+$, 100). Anal. Calcd for $C_{45}H_{80}Si_7$: C, 66.10; H, 9.86. Found: C, 65.94; H, 9.58.

(9) The stability of **5** has been reported in ref 7. Silylenoid **5** can survive at −78 °C and shows neither α-elimination of lithium bromide giving the corresponding silylene nor intermolecular substitution reaction leading to oligo- or polysilanes.

(10) The reaction mechanism of a monosilylanion with an aryl halide is still controversial, however, a single electron-transfer process can be considered as the most plausible reaction pathway. (a) Shippey, M. A.; Dervan, P. B. *J. Chem. Soc.* **1977**, *42*, 2654. (b) Watanabe, H.; Higuchi, K.; Kobayashi, M.; Hara, M.; Koike, Y.; Kitahara, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 534. (c) Gilman, H.; Wu, T. C. *J. Am. Chem. Soc.* **1951**, *73*, 4031.

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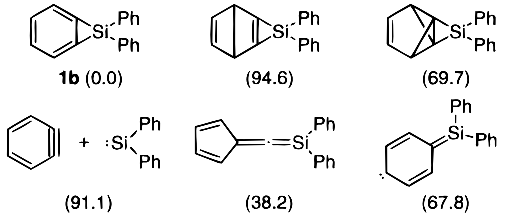


Figure 1. Relative energies (kcal/mol) of silacyclopropabenzene **1b** and its itomsers in the brackets at the B3LYP/6-31G (d) level.

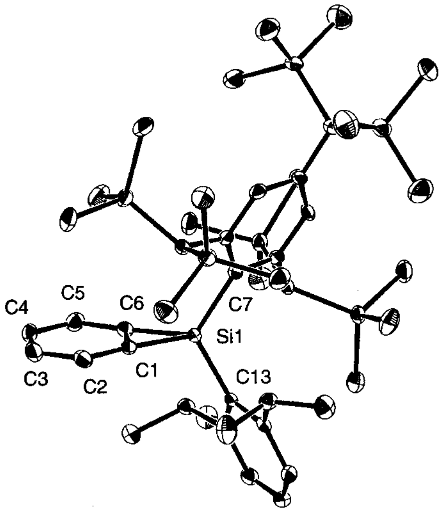
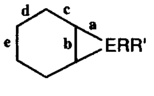
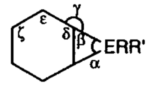


Figure 2. ORTEP drawing of silacyclopropabenzene **1a** with a thermal ellipsoid plot (50% probability).

solid state or thermolysis in the presence of methanol (in benzene at 170 °C, in a sealed tube). The surprising stability of **1a** was supported by theoretical calculations on the relative energies of model compound **1b** (R = R′ = Ph), and its possible isomers, which revealed that **1b** is the most stable of all isomers including the combination of benzyne and diphenylsilylene (Figure 1).[12]

The molecular structure of **1a** was determined by X-ray crystallographic analysis at −180 °C (Figure 2)[13] to reveal completely planar geometry for its silacyclopropabenzene skeleton. Although **1a** has a slightly squashed benzene moiety, the sum of interior bond angles of the benzene ring is 720.0° and the sums of bond angles around the juncture carbon atoms (C1 and C6) are both 360.0°. The selected bond lengths and angles of **1a** are listed in Table 1 together with those for the parent silacyclopropabenzene **1c** theoretically optimized and those of parent cyclopropabenzene **2a** (R = R′ = H).[15]

Table 1. Observed and Calculated Structural Parameters for Silacyclopropabenzenes (**1a** and **1c**) and Cyclopropabenzene (**2a**)

		Compound [ERR′]		
		1a [SiTbt(Dip)][a]	**1c [SiH$_2$]**[b]	**2a [CH$_2$]**[c]
bond length / Å 	**a**	1.826(2), 1.828(3)	1.817	1.498(3)
	b	1.390(4)	1.392	1.334(4)
	c	1.388(4), 1.394(4)	1.392	1.363(3)
	d	1.381(4), 1.383(4)	1.389	1.387(4)
	e	1.403(5)	1.405	1.390(5)
bond angle / deg 	α	44.7(1)	45.3	52.8(2)
	β	67.6(2), 67.7(1)	67.5	63.6(1)
	γ	170.9(2), 171.0(3)	170.7	171.7(2)
	δ	121.3(3), 121.5(2)	121.9	124.5(2)
	ε	117.3(3), 117.3(3)	116.5	113.2(2)
	ζ	121.2(3), 121.4(3)	121.6	122.4(2)

[a] This work. [b] This work at the B3LYP/6-311G (2d,p) level. [c] Data were collected at −153 °C, see ref 16.

It is well-known that annelation of a small ring to an aromatic system usually causes the deformation of the aromatic ring.[16] In comparison with the typical C−C distances in benzene (ca. 1.39−1.40 Å),[17] an extreme shortening of the juncture bond **b** along with a slight shortening of its neighboring bond **c** is observed for **2a**.[15] The angles of δ, ζ, and ϵ observed for **2a** also considerably deviate from the ideal value (120°) for a typical bond angle of an sp^2 carbon. Despite such distortion, the conclusion on the structure of **2a** was that the aromatic π-electron delocalization is still retained in the benzene ring.[15]

Interestingly, X-ray crystallographic analysis of **1a** revealed that the silacyclopropabenzene skeleton of **1a** showed no distinct bond shortening for any C−C bonds in the benzene moiety, and only a slight distortion for the inner bond angles (average δ = 121.4°, ϵ = 117.3°, and ζ = 121.3°). Thus, the juncture bond length of **1a** [1.390(4) Å] is much longer than that of **2a** and the mean length [1.390 Å] of the six C−C bonds of **1a** is almost equal to that of the nonperturbed benzene ring. The structural features for **1a** are nearly consistent with calculated geometrical parameters for the parent silacyclopropabenzene **1c**. These results strongly indicate that the benzene nucleus in silacyclopropabenzene **1a** is much less perturbed by annelation than that in the case of cyclopropabenzene **2a**.

The remarkable structural difference between 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. To compensate this localized distortion, the benzene moiety is deformed at the sacrifice of its equilateral hexagon as observed in **2a**. 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 **1** with this mode.

Further application of dilithiosilane **4** to the synthesis of other novel silacyclic systems and the synthesis of heteracyclopropabenzenes of other heavier group 14 elements is currently in progress.

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Calculations were carried out using the Gaussian 98 program.

(13) Crystallographic data for **1a**: The structure was solved by direct method (SIR-92) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[14] $C_{45}H_{80}Si_7$, MW = 817.73, triclinic, space group P-1 (#2), a = 11.9775(4) Å, b = 22.9899(6) Å, c = 9.9059(4) Å, α = 95.675(2)°, β = 107.6040(7)°, γ = 76.798(2)°, V = 2529.9(2) Å^3, Z = 2, D_{cal} = 1.073 g cm^{-3}, μ = 2.16 cm^{-1}, R_1 (wR_2) = 0.053 (0.151), T = 93 K, GOF = 0.98. Full details of crystallographic analysis of **1a** are described in the Supporting Information.

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