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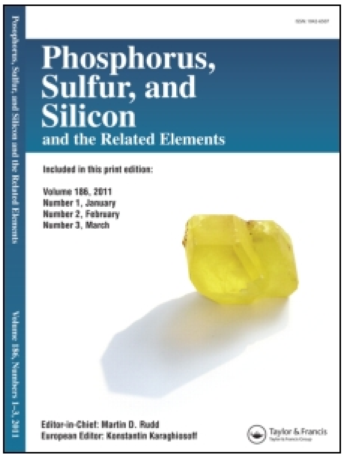

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Syntheses, Structures, and Reactivities of Novel Silacyclic Systems: the First Stable Silabenzene and Silacyclopropabenzene

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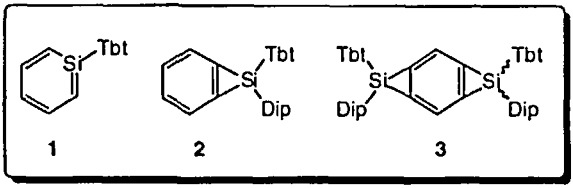
The first stable silabenzene and silacyclopropabenzenes were synthesized by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). The molecular geometries of these novel conjugated ring systems containing a silicon atom were definitively determined by X-ray crystallographic analysis. Their spectral data such as ^{1}H, ^{13}C, and ^{29}Si NMR, FT-Raman, and UV-vis spectra and the theoretical calculations revealed their unique properties.

Keywords: silabenzene; silacyclopropabenzene; bis(silacyclopropa)-benzene; steric protection; X-ray structural analysis

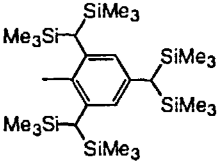
INTRODUCTION

In the last two decades, kinetic stabilization has played an important role in the synthesis and isolation of a variety of heavier main group element compounds having an exotic structure and novel bonding such as heavier congeners of carbenes and doubly bonded systems of heavier group 14, 15 and 16 elements. In the course of our study on the sterically congested molecules, we have developed an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted as Tbt hereafter), and applied it to the kinetic stabilization of highly reactive species of heavier main group elements.

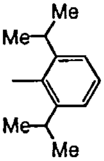


1 **2** **3**

Tbt =



Dip =

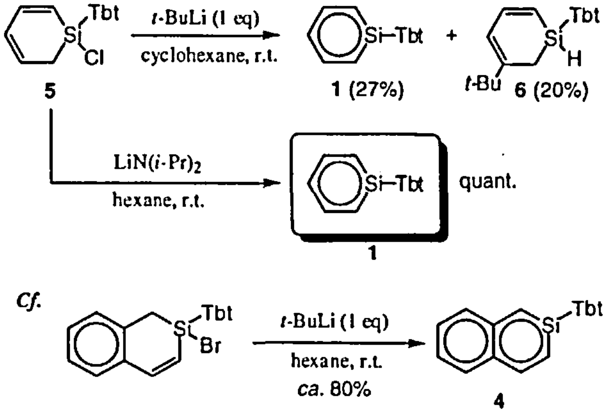


In this paper the synthesis and isolation of the first stable silabenzene 1 and silacyclopropabenzenes 2 and 3 are described as further application of Tbt group to the kinetic stabilization of novel conjugated ring systems containing a silicon atom.

RESULTS AND DISCUSSION

1) Synthesis, Structure and Reactivity of Stable Silabenzene.

Benzene, a 6π electron ring system, is the simplest and most fundamental species in aromatic compounds which play important roles in organic chemistry. From the viewpoint of similarity and difference between carbon and silicon, the chemistry of silabenzene, a silicon analogue of benzene, has attracted much attention and been explored extensively [1]. Although aromatic character of silabenzene has been theoretically predicted and some silabenzenes were observed spectroscopically in the gas phase or low-temperature matrices, their high reactivity prevented the syntheses of silabenzenes as stable molecules. Märkl et al. previously reported the synthesis of 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene, but it was reportedly stable only below −100 °C in solution (THF/Et_2O/petroleum ether, 4:1:1) and stabilized by coordination of a solvent Lewis base judging from its relatively high field ^{29}Si NMR chemical shift (δ_{Si} = 26.8) [2]. In contrast, we have recently succeeded in the synthesis of the first stable silabenzenoid compound, 2-silanaphthalene **4** (δ_{Si} = 87.3 in C_6D_6) by protecting its reactive silicon center with an extremely bulky substituent, Tbt group [3]. The crystallographic structural analysis and the spectral data for **4** revealed the planar geometry of the 2-silanaphthalene ring system and its high aromaticity [3]. We report here the synthesis and characterization of the stable silabenzene **1** bearing Tbt group as the more fundamental silaaromatic ring system.



Scheme 1.

Although silabenzene **1** was synthesized as a stable compound by the reaction of the corresponding chlorosilane precursor **5** with *t*-BuLi as in the case of 2-silanaphthalene **4**, the isolation of **1** was prevented by the competitive formation of undesired by-product **6** (Scheme 1) [4]. After examination of several reaction conditions, we have found that the use of lithium diisopropylamide (1 equiv. in hexane at r. t.) as a base instead of *t*-BuLi results in the exclusive formation of silabenzene **1** in high yield, which allowed us to isolate **1** as stable crystallines after the removal of inorganic salts from the reaction mixture [5]. X-ray structural analysis (at –180 °C) using a single crystal of silabenzene **1**, which was obtained by careful recrystallization from hexane, revealed the completely planar geometry around the central silicon atom and silabenzene ring [5].

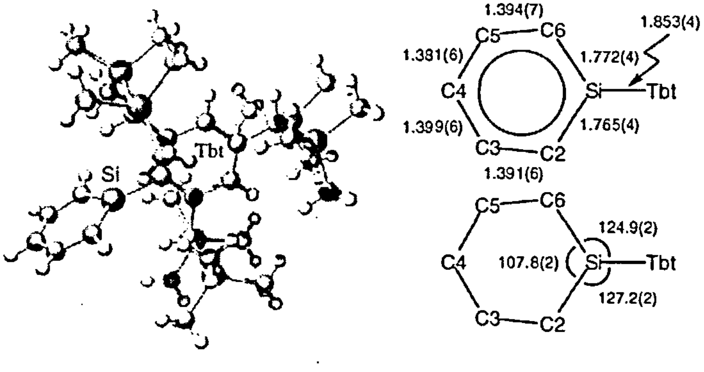
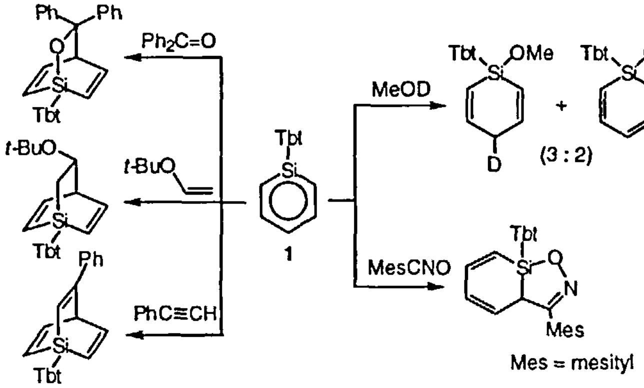


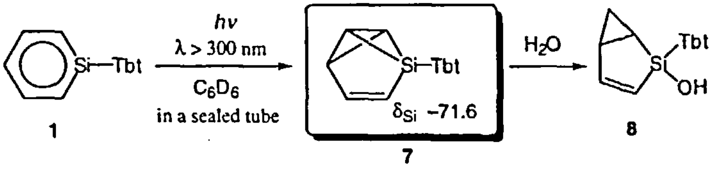
Fig. 1. Molecular structure of silabenzene **1** and selected bond lenghts (Å) and angles (deg).

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 and 1.89 Å, respectively) [6]. 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 bond length of benzene (1.39–1.40 Å) [7]. Thus, it has experimentally been demonstrated that silabenzene has a delocalized 6π electron ring system similar to that of benzene. The experimentally determined structural parameters are in good agreement with those obtained by theoretical calculations [7].



Scheme 2.

Although the silabenzene here synthesized is considerably hindered by the steric protection group, it still has an enough space for the reactions with alcohol, olefin, acetylene, ketone, and nitrile oxide to give the corresponding adducts in good yields (Scheme 2). In contrast to the case of 2-silanaphthalene 4 [3], silabenzene was found to undergo 1,4-addition in preference to 1,2-addition [4].



Scheme 3.

Interestingly, irradiation of a benzene solution of silabenzene **1** (δSi = 91.3) with the light of 290-350 nm resulted in the formation of an unprecedented valence isomer, silabenzvalene **7** (δSi = -71.6) [5]. Unfortunately, the isolation and characterization of **7** has not been achieved yet, separation of the reaction mixture in the open air afforded silanol **8** having a three-membered ring, the formation of which also suggests that the product of the photoirradiation of silabenzene **1** is not a Dewar silabenzene but silabenzvalene **7**.

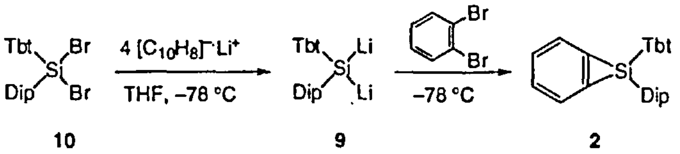
2) Synthesis and Characterization of the First Stable Silacyclopropabenzenes.

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, silacyclopropenes, and a bis(alkylidene)silacyclopropane. On the other hand, silacyclopropabenzene still remains as an unprecedented ring system of this class probably due to the lack of suitable synthetic methods, since the conventional synthetic methods for cyclopropabenzenes or Si-containing three-membered rings are very difficult to be applied to the construction of a silacyclopropene ring system fused with a benzene ring.

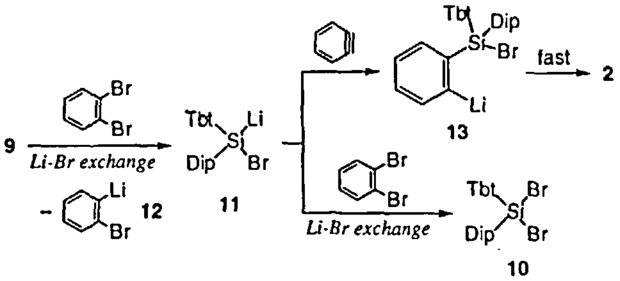
Meanwhile, we have recently reported the formation of the first diaryldilithiosilane **9**, Tbt(Dip)SiLi$_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl), treatment of which with bifunctional electrophiles is potentially useful for the synthesis of a novel class of cyclic organosilicon compounds [8]. Here, we present the synthesis and isolation of the first stable silacyclopropabenzene **2** and bis(silacyclopropa)benzenes **3** by taking advantage of this new silyl dianion species **9**.

Treatment of **9**, generated from **10** and an excess amounts of lithium naphthalenide in THF, with one equivalent of *o*-dibromobenzene at

–78 °C resulted in the isolation of **2** as stable colorless crystals in 34% yield (Scheme 4) [9]. Compound **2** should be noted as the first stable example of not only a sila- but also a heteracyclopropabenzene. Interestingly, a considerable amount of starting material **10** (44%) was recovered in this reaction, although the quantitative generation of **9** from **10** has already been confirmed by the trapping experiments [8]. The recovery of **10** can be most likely interpreted in terms of the double lithium-bromine exchange reactions of **9** with *o*-dibromobenzene via silylenoid, Tbt(Dip)SiLiBr (**11**), which plays another important role for the formation of **2** (Scheme 5).



Scheme 4.



Scheme 5.

Although a silyl monoanion has been known to react with an aryl halide to give the corresponding substitution product [10], the formation of **2** in the reaction of **9** with *o*-dibromobenzene may be not such a simple substitution but based on more complicated reaction processes, *i. e.*, the addition of silylenoid **11** to benzyne, which is generated by the α, β-elimination of LiBr from *o*-bromophenyllithium (**12**) initially formed via lithium-bromine exchange of **9** with *o*-dibromobenzene, followed by intramolecular cyclization of the resulting *o*-silylated phenyllithium **13** (Scheme 5). Thus, the unique reactivity of dilithiosilane **9** resulted in the concurrent generation of quite different reactive species such as silylenoid **11** and benzyne in the reaction system under very mild conditions [9].

Silacyclopropabenzene **2** was found to be thermally very stable even after heating up to its melting point (257 °C) in the solid state or thermolysis in the presence of methanol (in benzene at 170 °C, in a sealed tube). The surprising stability of **2** was supported by theoretical calculations on the relative energies of the diphenyl-substituted model compound and its possible isomers, which revealed that silacyclopropabenzene isomer is the most stable of all isomers including the combination of benzyne and diphenylsilylene [9].

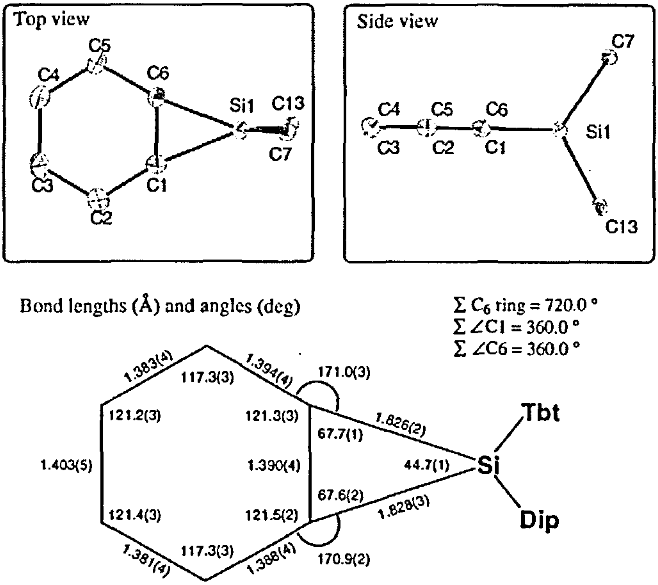
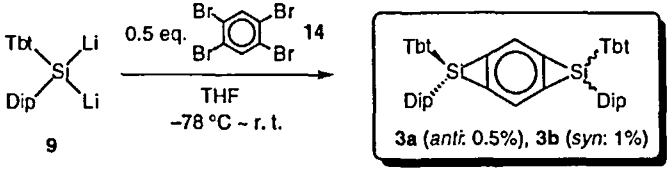


Fig. 2. Geometry of silacyclopropabenzene **2**.

The molecular structure of **2** was determined by X-ray crystallographic analysis at –180 °C (Fig. 2) to reveal completely planar geometry for its silacyclopropabenzene skeleton. Although **2** 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°.

It is well-known that annelation of a small ring to an aromatic system usually causes the deformation of the aromatic ring [11]. Interestingly, X-ray crystallographic analysis of **2** revealed that its silacyclopropabenzene skeleton showed no distinct bond shortening for any C–C bonds in the benzene moiety, but only a slight distortion for the inner bond angles.

The successful isolation of silacyclopropabenzene **2** prompted us to examine the reaction of dilithiosilane **9** with 1,2,4,5-tetrabromobenzene **14** in the hope of obtaining the corresponding bisadduct. When **14** was treated with 2 molar amount of dilithiosilane **9** in THF at –78 °C, the expected bisadducts, *i. e.*, *anti*-substituted bis(silacyclopropa)benzene **3a** and its *syn*-isomer **3b**, were obtained though in low yields (Scheme 6). The formation of **3a,b** should be noted not only as the novel silacyclopropane derivatives but also as the first examples of bis(cyclopropa)benzene ring system.



Scheme 6.

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Research from the Ministry of Education, Science, Sports, and Culture, Japan. Shin-Etsu Chemical, Central Glass, and Tosho Akzo Co. Ltds. are also acknowledged for a gift of organosilanes, tetrafluorosilane, and alkyllithiums, respectively.

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