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Generation of Stannabenzenes and Their Properties[†]

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Summary: Stannabenzenes ***3****, neutral stannaaromatic compounds having the simplest aromatic unit, were successfully generated by the reaction of the corresponding bromostannanes* ***5-Br*** *with lithium diisopropylamide in hexane at −40 °C. The generation of* ***3*** *was indicated by the formation of the [4 + 2] dimer* ***6*** *at room temperature. The thermal stability of* ***3*** *was completely different from that of the sila- and germabenzenes bearing the same substituent. The structural and electronic properties of stannabenzene were estimated by theoretical calculations.*

Benzene is representative of aromatic compounds, which are important from the viewpoints of not only fundamental chemistry but also application toward organic synthesis and material science.[1] Its chemical behavior, structure, and energetic and magnetic features have been widely studied from both experimental and theoretical standpoints, and such findings have contributed to understand the concept "aromaticity".[1,2] Although a variety of heterabenzene, in which one carbon atom of benzene is replaced with a heteroatom, have been synthesized and focused for a long time to discuss "aromaticity", the benzene analogues of heavier group 14 elements (Si, Ge, Sn, and Pb) have been recognized as highly reactive species.[3] For example, the parent silabenzene (SiC_5H_6) has been generated by flash thermolysis and studied in the gas phase and in low-temperature matrices, but it was found to oligomerize above 80 K.[4] This result is in sharp contrast with the high thermal stability of phosphabenzene, containing a phosphorus atom, which is an element in the same row as silicon.[5]

Recently, the chemistry of heteraaromatic compounds of heavier group 14 elements has experienced remarkable development, among which was our success in the synthesis and isolation of the first stable examples for neutral sila and germa aromatic compounds,[6,7] including sila-[8] and germabenzenes,[9] by taking advantage of the kinetic stabilization afforded by an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). Quite recently, our group and Sekiguchi's have reported the synthesis and isolation of 1,2-disilabenzenes by the reaction of stable disilynes (−Si≡Si−) with acetylenes.[10] In view of the recent progress in the chemistry of sila and germa aromatic compounds, the synthesis of stannaaromatic compounds is of great interest from the standpoint of systematic elucidation of the properties of heteraaromatic systems of heavier group 14 elements.

In comparison with sila and germa aromatic compounds, stanna aromatic compounds are still elusive and their properties have not been disclosed so far. Saito et al. have reported the synthesis of a series of stannole anions and dianions, i.e., ionic stanna aromatic compounds, as stable compounds along with their full characterization.[11] However, stable and neutral stanna aromatic compounds are limited to our 2-stannanaphthalene **1**,[12] which is kinetically stabilized by the combination of a Tbt group on the tin atom and a *t*-Bu group on the adjacent carbon atom. On the other hand, 9-Tbt-9-stannaphenanthrene (**2**) was found to undergo ready [2 + 2] dimerization at ambient temperature, most likely due to insufficient steric protection.[13] In the case of 2-stannanaphthalene, two Sn−C bonds in the ring were nonequivalent, reflecting the bond-alternating nature of the parent naphthalene skeleton. In order to investigate the effect of the tin−carbon bond in the aromatic ring, the synthesis of a stannabenzene essentially having no bond alternation is of great

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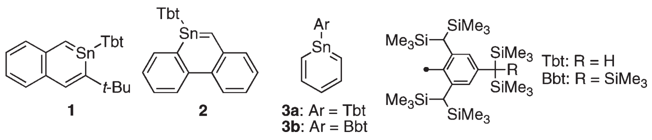
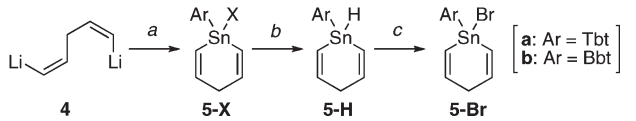
Chart 1



Scheme 1. Synthesis of Bromostannanes 5-Br[a]



[a] Conditions: (*a*) $ArSnX_3$ (X = Cl and Br), Et_2O, −50 °C, 1 h; (*b*) $LiAlH_4$, THF, 0 °C, 1 h, 20% (**5a-H** from **4**), 18% (**5b-H** from **4**); (*c*) NBS, benzene, room temperature, 1 h, 100% (**5a-Br**), 88% (**5b-Br**).

importance. Here, we report the generation and properties of stannabenzenes **3**, having the simplest aromatic unit: i.e., a benzene skeleton (Chart 1).

At first, the Tbt-substituted 1-bromo-1-stannacyclohexa-2,5-diene **5a-Br**, a suitable precursor of **3a**, was prepared by the synthetic route shown in Scheme 1. (1*Z*,4*Z*)-1,5-Dilithiopenta-1,4-diene (**4**) was prepared according to the reported procedure[14] and isolated by filtration of its hexane suspension under an inert atmosphere. Since the initial starting material ($TbtSnCl_3$) contained a considerable amount of bromostannanes due to the ready halogen-exchange reactions with LiBr inevitably generated in the preparation of TbtLi (TbtBr + 2 *t*-BuLi → TbtLi + LiBr + isobutane + isobutylene), the initially generated halostannanes were subjected to $LiAlH_4$ reduction followed by rebromination with NBS in order to prepare the corresponding pure bromostannanes. Even with the pure $TbtSnBr_3$ thus prepared,[12c] the reaction of $TbtSnBr_3$ with **4** did not afford the desired product **5a-Br** exclusively but a complicated mixture containing **5a-Br**. After chromatographic separation, the molecular structure of **5a-Br** was confirmed by its spectral data and finally established by X-ray crystallographic analysis (Figure 1).

The synthesis of **3a** was attempted by the dehydrobromination of **5a-Br** with lithium diisopropylamide (LDA) at −40 °C and then at room temperature, resulting in the formation of **6a**, the [4 + 2] dimer of stannabenzene **3a**, almost quantitatively (the isolated yield was 53% due to decomposition during the purification) (Scheme 2). The molecular structure of **6a** was fully established by the results of spectroscopic analysis. Although its dimeric structure was unambiguously confirmed by X-ray crystallographic analysis, the detailed structural parameters of **6a** could not be discussed due to the low quality of the crystals and severe disorder in the central part (see Figure S1, Supporting Information). In any event, the formation and isolation of **6a** strongly suggested the generation of **3a** as a transient species.

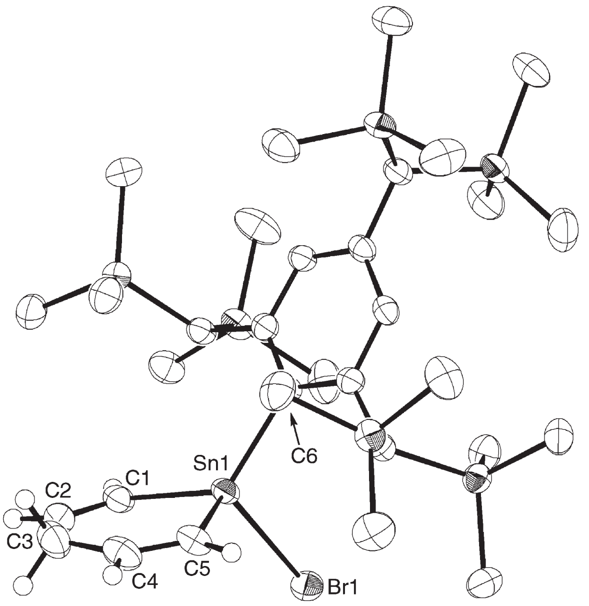
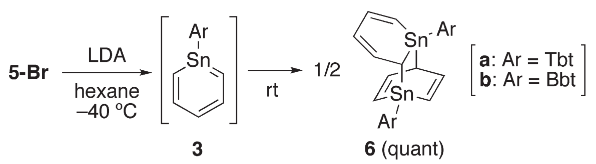


Figure 1. Thermal ellipsoid plot of **5a-Br** (50% probability). Hydrogen atoms, except for those on the SnC_5 ring, were omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1−C1 = 2.115(3), Sn1−C5 = 2.124(3), Sn1−C6 = 2.150(2), Sn1−Br1 = 2.5329(3), C1−C2 = 1.330(4), C2−C3 = 1.506(4), C3−C4 = 1.498(4), C4−C5 = 1.330(4); C1−Sn1−C5 = 96.58(11), C1−Sn1−C6 = 121.99(9), C5−Sn1−C6 = 118.80(9), C1−Sn1−Br1 = 105.60(7), C5−Sn1−Br1 = 106.89(8), C6−Sn1−Br1 = 105.63(6), C2−C1−Sn1 = 119.9(2), C1−C2−C3 = 130.1(3), C4−C3−C2 = 121.8(2), C5−C4−C3 = 130.8(3), C4−C5−Sn1 = 119.2(2).

Scheme 2. Generation of Stannabenzenes 3



In the case of 1-silanaphthalene,[15] the Tbt-substituted species was marginally stable enough in solution to make observation of its NMR spectra possible and underwent gradual dimerization at room temperature. On the other hand, the Bbt-substituted 1-silanaphthalene was found not to dimerize under the same conditions. This result prompted us to change the steric protection group from Tbt to Bbt in order to improve the stability of stannabenzene. The corresponding Bbt-substituted precursor **5b-Br** could be synthesized by a method similar to that for the synthesis of **5a-Br** (Scheme 1). Contrary to our expectation, the reaction of **5b-Br** with LDA also readily afforded the [4 + 2] dimer **6b** at room temperature, similarly to the case for the Tbt-substituted system (Scheme 2). When several trapping reactions of **3b** by 2,3-dimethyl-1,3-butadiene at −78 °C were tried, dimer **6b** had already formed. Although further investigations are needed, the stability of stannabenzenes is considered to be quite low.

Thus, the extremely high reactivity of stannabenzenes is in sharp contrast with the considerable thermal stability of Tbt-substituted sila- and germabenzenes (stable at 100 °C in C_6D_6).[8,9] To evaluate the differences in thermal stability among sila-, germa-, and stannabenzenes, theoretical calculations were performed. In Table 1, selected parameters for the optimized structures of **3a**,**b** are shown together with the related parameters of Tbt-substituted sila- and germabenzenes experimentally observed. The SnC_5 rings of **3a**,**b** have perfectly planar geometries (sum of the internal angles of SnC_5 rings 720°) similar to those of Tbt-substituted sila- and

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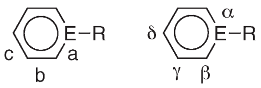
Table 1. Selected Structural Parameters of Metallabenzenes[a]

compd	a/Å	b/Å	c/Å	α/deg	β/deg	γ/deg	δ/deg
TbtSiC_5H_5 (obsd)[b]	1.765(4)	1.391(6)	1.399(6)	107.8(2)	117.7(3)	126.3(4)	124.1(4)
	1.770(4)	1.394(7)	1.381(6)		118.0(3)	126.1(4)	
TbtGeC_5H_5 (obsd)[c]	1.829(2)	1.389(3)	1.389(3)	105.81(9)	117.88(15)	126.55(19)	125.48(18)
	1.827(2)	1.396(3)	1.385(3)		117.82(16)	126.55(19)	
3a (calcd)[d]	2.026	1.396	1.407	100.97	117.12	128.49	127.87
3b (calcd)[d]	2.026	1.397	1.407	103.89	116.67	126.81	129.14
HSnC_5H_5 (calcd)[d]	2.018	1.396	1.406	102.01	116.42	128.47	128.20
HSnC_5H_5 (calcd)[e]	2.019	1.389	1.402	102.39	115.87	128.73	128.42

[a]



[b] Reference 8. [c] Reference 9. [d] Calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level. [e] Calculated at the B3LYP/6-311+G(2d,p) (TZ(2d) on Sn) level.

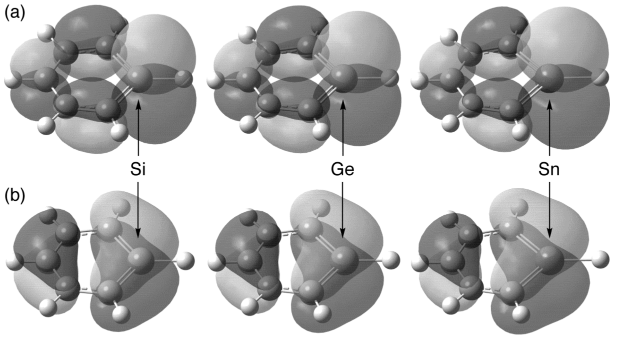


Figure 2. LUMOs (a) and HOMOs (b) of HEC_5H_5 (E = Si, Ge, Sn) calculated at the B3LYP/6-311+G(2d,p) (TZ(2d) on Si, Ge, Sn) level.

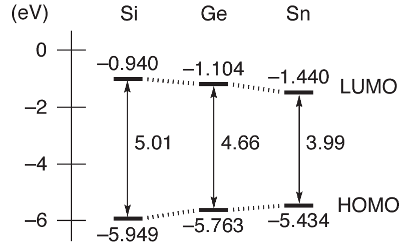


Figure 3. Energy levels of HOMOs and LUMOs of HEC_5H_5 (E = Si, Ge, Sn) calculated at the B3LYP/6-311+G(2d,p) (TZ(2d) on Si, Ge, Sn) level.

germabenzenes, implying efficient conjugation in the SnC_5 rings. The lengths of the two Sn−C bonds in each stannabenzene ring of structurally optimized **3a**,**b** were found to be equal to each other and similar to those of the reported all-carbon-substituted Sn−C double bonds (2.003(5),[16] 2.016(5) Å[17]) and the shorter Sn−C bond of the isolated 2-stannanaphthalene (2.029(6) Å[12]). Furthermore, the C−C bond lengths in the stannabenzene rings of structurally optimized **3a**,**b** are almost equal to each other and are also almost similar to the C−C length of the parent benzene (1.39−1.40 Å).[1] Thus, it has been theoretically demonstrated that the stannabenzene skeleton should have a delocalized six-π-electron ring system similar to that of benzene. On the other hand, the difference between the Sn−C and Ge−C bond lengths was found to be 0.198 Å, which is much longer than those between the Ge−C and Si−C bond lengths (0.06 Å). This marked elongation may result in the insufficient protection of the reactive Sn center of the stannabenzene skeleton.

The aromaticity of stannabenzene was evaluated by NICS calculations (GIAO-B3LYP/6-311+G(2d,p) (TZV on Sn)//B3LYP/6-31G(d) (LANL2DZ on Sn)).[18] The NICS(1) value of the parent stannabenzene is −8.1, the absolute value of which is slightly small as compared with those for sila- and germabenzenes (−8.5) and is estimated as about 80% of that of benzene (−10.0). In Figures 2 and 3, the energy levels and shapes of the HOMOs and LUMOs are summarized for the parent metallabenzenes. While the shapes of their HOMOs and LUMOs resemble each other, the coefficients on the E atoms slightly get larger, following the order of Si to Sn. The HOMO−LUMO energy gaps, correlating with the reactivity of the Diels−Alder type dimerization, change dramatically (Figure 3), and the difference between the cases of Si and Sn is about 1 eV. These results reasonably explain the high reactivity of stannabenzenes.

Furthermore, the energy differences between the monomer and dimer of Tbt-substituted sila- and stannabenzenes were calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level. Although a detailed investigation of the transition states in the dimerization reaction of **3a** has not yet been achieved, the formation of **6a** was found to be exothermic (−11.7 kcal/mol), in contrast to the endothermic dimerization of Tbt-substituted silabenzene (+10.5 kcal/mol).[8c] In the case of the silabenzene dimer, the steric repulsion between the two Tbt groups is not negligible. In the case of **6a**, on the other hand, elongation of the bond lengths around the tin atoms was considered to allow more facile formation of its dimer. As a result of the combination of structural demand and electronic features, stannabenzene might undergo ready dimerization, showing a striking difference from sila- and germabenzenes.

In summary, we have succeeded in the generation of stannabenzenes **3** for the first time and revealed their high reactivity. With the hope of isolating **3** as a stable compound, further investigation into the introduction of additional substituent(s) to the stannabenzene skeleton and the cooperative stabilization method (the contribution of kinetic and thermodynamic stabilization) is currently in progress.

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Supporting Information Available: Text, figures, and tables giving details of preparation procedures, characterization data, X-ray analyses of **5a-Br** and **6a**, and theoretical calculations and CIF files giving the X-ray crystallographic data of **5a-Br** and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.