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A Stable Neutral Stannaaromatic Compound: Synthesis, Structure and Complexation of a Kinetically Stabilized 2-Stannanaphthalene

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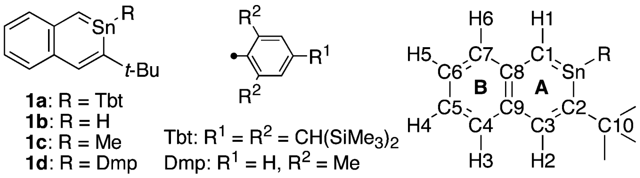
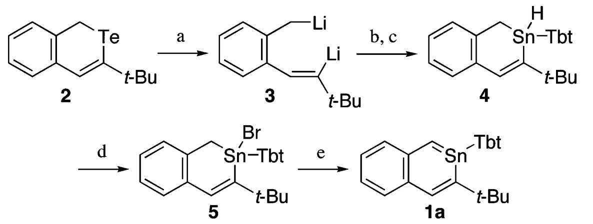
Aromatic hydrocarbons such as benzene and naphthalene are among the most fundamental class of organic compounds and play very important roles in organic chemistry. By contrast, the chemistry of metallaaromatic compounds of heavier group 14 elements, i.e., heavier congeners of the cyclic conjugated systems with $[4n + 2]$-π-electrons, showed a marked development only in the past decade, and the examples for the isolation of stable systems are limited to those containing Si or Ge atom.[1] Recently, we have succeeded in the synthesis and isolation of the first stable examples for neutral sila- and germaaromatic compounds by taking advantage of kinetic stabilization afforded by an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt).[2] In view of the recent progress in the chemistry of sila- and germaaromatic compounds, the synthesis of stannaaromatic compounds is of great interest from the standpoint of systematic elucidation of the properties of metallaaromatic systems of heavier group 14 elements. Although some stannole anions and dianions, i.e., ionic stannaaromatic compounds, have been synthesized as stable compounds and fully characterized,[3] neutral stannaaromatic compounds are still elusive, and their properties have not been disclosed yet so far. The main reason for the lack of neutral stannaaromatic compounds is probably due to the difficulty in their synthesis and isolation as a result of the extremely high reactivity of Sn−C double bonds.[4] In fact, 9-Tbt-9-stannaphenanthrene was found to undergo ready dimerization at ambient temperature most likely due to the insufficient steric protection.[5] Here, we report the synthesis of the first stable neutral stannaaromatic compound, 2-stannanaphthalene **1a**, 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 (Chart 1).

Chart 1



1,2-Dihydro-2-stannanaphthalene **4** was prepared by taking advantage of (*E*)-*o*-(2′-lithiovinyl)benzyllithium **3**, which can be readily generated from isotellurochromene **2** according to the method reported by Sashida.[6] The following bromination of **4** with NBS afforded bromostannane **5**, a suitable precursor of 2-stannanaphthalene **1a** (Scheme 1). 2-Stannanaphthalene **1a** was synthesized as pale-yellow crystals by the dehydrobromination of bromostannane **5** with LDA in hexane at −40 °C (Scheme 1). 2-Stannanaphthalene **1a** is thermally stable under an inert atmosphere either in the solid state (decomposed at 144 °C) or in solution (C_6D_6, at 80 °C for 1 h in a sealed tube).

Scheme 1. Synthesis of 2-Stannanaphthalene **1a**[a]



[a] Conditions (a) *n*-BuLi (2.0 equiv), THF, −78 °C; (b) $TbtSnX_3$ (X = Cl or Br, ca. 1 equiv), THF, −78 °C; (c) $LiAlH_4$ (excess), THF, 0 °C, 37% (from **2**); (d) NBS (1.1 equiv), benzene, rt, 91%; (e) LDA (1.1 equiv), hexane, −40 °C to room temperature, 63%.

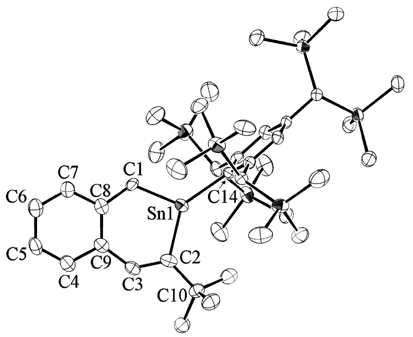


Figure 1. ORTEP drawing (50% probability) of **1a** with nonhydrogen atoms. Selective bond lengths (Å) and angles (deg): Sn1−C1 2.029(6), Sn1−C2 2.081(6), Sn1−C14 2.132(5), C2−C3 1.372(9), C2−C10 1.522(9), C3−C9 1.443(9), C4−C9 1.417(9), C4−C5 1.356(9), C5−C6 1.415(10), C6−C7 1.361(9), C7−C8 1.419(9), C8−C9 1.436(9), C1−C8 1.394(8), C1−Sn1−C2 100.0(3), C1−Sn1−C14 123.0(2), C2−Sn1−C14 137.0(2), Sn1−C2−C3 114.3(5), C2−C3−C9 132.7(6), C3−C9−C8 126.7(6), C1−C8−C9 124.6(6), Sn1−C1−C8 121.4(5), C5−C4−C9 123.5(7). C4−C5−C6 119.0(6), C5−C6−C7 119.5(7), C6−C7−C8 123.0(6), C7−C8−C9 117.5(6), C4−C9−C8 117.4(6).

The molecular structure of **1a** was determined by X-ray crystallographic analysis (Figure 1), which revealed the planarity of the 2-stannanaphthalene unit and the completely trigonal planar geometry around the tin atom. In addition, the benzene ring of the Tbt group was found to be almost perpendicular to the 2-stannanaphthalene plane; hence, it is considered that there is very little conjugative interaction between the two aromatic units. The lengths of the two endocyclic Sn−C bonds [2.029(6) and 2.081(6) Å] are shorter than those of typical single bonds (av 2.14 Å).[7] In particular, the former Sn−C bond length is close to the Sn−C double bond length of the previously reported stannene, $Tbt(Mes)Sn{=}CR_2$ [CR_2 = fluorenylidene; 2.016(5) Å],[8] which is stabilized by the conjugation of the Sn−C double bond with the fluorenylidene moiety. The C−C bond lengths of the 2-stannanaphthalene ring of **1a** [1.356(9)−1.443(9) Å] are also roughly intermediate between those of C−C double and single bonds. These results suggest that the π-electrons are delocalized in the 2-stannanaphthalene skeleton of **1a**. Furthermore, theoretical calculations for the model molecules **1b**−**d** supported the experimental results, indicating the effective

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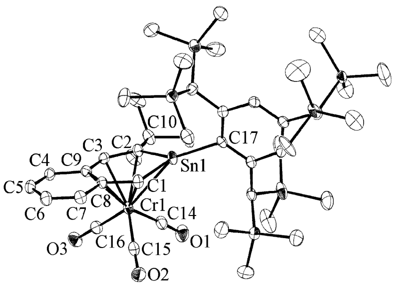
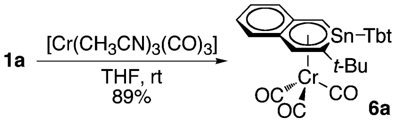


Figure 2. ORTEP drawing (30% probability) of **6a** with nonhydrogen atoms. Selective bond lengths (Å) and angles (deg): Sn1−C1 2.035(5), Sn1−C2 2.093(4), Sn1−C17 2.128(4), C2−C3 1.379(6), C2−C10 1.533(6), C3−C9 1.443(6), C4−C9 1.439(6), C4−C5 1.353(6), C5−C6 1.408(7), C6−C7 1.363(6), C7−C8 1.448(6), C8−C9 1.427(6), C1−C8 1.425(6), Sn1−Cr1 2.7537(8), C1−Sn1−C2 94.36(18), C1−Sn1−C17 124.63(18), C2−Sn1−C17 140.05(17), Sn1−C2−C3 118.3(3), C2−C3−C9 132.5(4), C3−C9−C8 124.5(4), C1−C8−C9 123.1(4), Sn1−C1−C8 125.9(4), C5−C4−C9 122.1(4). C4−C5−C6 119.8(4), C5−C6−C7 120.8(5), C6−C7−C8 121.5(5), C7−C8−C9 117.2(4), C4−C9−C8 118.5(4).

Scheme 2. Synthesis of **6a**



π-conjugation in the Sn-containing aromatic ring systems (Table S1, Supporting Information).

The ^{119}Sn NMR spectrum of **1a** in C_6D_6 showed a signal at 264 ppm, which is characteristic of the low-coordinated tin atom.[9] All the ^{1}H NMR signals of the 2-stannanaphthalene ring protons of **1a** (7.05−9.28 ppm) were observed in the aromatic region, and the ^{13}C NMR signals of the stannanaphthalene ring carbons (120.0−174.0 ppm) were located in the sp^2 region. Thus, these results clearly indicate the delocalized π-electronic system of **1a** even in solution.

The Raman spectrum of **1a** (Figure S1, Supporting Information) showed planar skeletal vibration as the most intense Raman signal at 1331 cm^{-1}, which corresponds to those of 1382, 1368, and 1360 cm^{-1} for naphthalene, 2-silanaphthalene,[2a] and 2-germanaphthalene,[2g] respectively. The calculated vibration modes of **1c** resemble considerably those of naphthalene, suggesting the structural similarity between 2-stannanaphthalene **1a** and naphthalene.[10]

Tbt-substituted sila- and germabenzene are known to behave as well as the conventional arene systems in the complexation with transition metal carbonyl complexes.[11] Similarly, the ligand exchange reaction of **1a** with [Cr(CH$_3$CN)$_3$(CO)$_3$] at room temperature in THF resulted in the regioselective formation of the first η^6-2-stannanaphthalene chromium complex **6a** as brown crystals in 89% yield (Scheme 2). The X-ray crystallographic analysis of **6a** (Figure 2) revealed that **6a** still keeps the planarity for the 2-stannanaphthalene moiety [sum of the interior bond angles in the ring **A** (Chart 1): 718.7°] and the trigonal planar geometry around the tin atom (sum of the bond angles: 359.0°). The lengths of the two endocyclic Sn−C bonds of **6a** [2.035(5) and 2.093(4) Å] are slightly longer than those of **1a** [2.029(6) and 2.081(6) Å]. In ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of **6a**, the signals corresponds to the atoms in the ring **A** (δ_{Sn}: 106, δ_{H1}: 5.07, δ_{H2}: 6.44, δ_{C}: 88.4−131.3) were shifted upfield relative to those for the free **1a** (δ_{Sn}: 264, δ_{H1}: 9.28, δ_{H2}: 8.75, δ_{C}: 120.0−174.0). The IR spectrum (KBr) of **6a** showed the presence of three intense ν(CO) bands at 1941, 1862, and 1851 cm^{-1}, which were observed in the region similar to those of [η^6-(naphthalene)Cr(CO)$_3$] [1941 and 1864 cm^{-1} (KBr)[12]]. The result suggests that **1a** has coordination ability as an arene ligand as well as that of naphthalene.

In summary, we have succeeded in the synthesis and characterization of 2-stannanaphthalene **1a**, the first example of a stable, neutral aromatic compound containing a tin atom. The results of spectroscopic and crystallographic structural analyses and theoretical calculations strongly suggest that **1a** has a delocalized 10-π-electron ring system as does naphthalene. These findings are of great importance for the chemistry of aromatic compounds containing heavier group 14 elements.

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Supporting Information Available: Experimental procedures and spectral data for new compounds, crystallographic data for **1a** and **6a**, Tables S1 and S2, Figure S1, UV/vis spectrum of **1a** (Figure S2), and the optimized structures of **1b**−**d** (Tables S3-S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The assignments of the ^{1}H, ^{13}C, and ^{119}Sn NMR signals are listed in Table S2 (Supporting Information) along with the calculated values for **1b**−**d**. The observed values are in good agreement with the calculated ones.

(10) This strongest vibrational frequency observed for **1a** is in good agreement with the theoretically calculated one [1378 cm^{-1} for **1b**, computed at the B3LYP/6-31G(d) (LANL2DZ on tin atom) level].

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