Bull. Chem. Soc. Jpn. Vol. 83, No. 7, 825–827 (2010)

Synthesis and Structures of Lithium Salts of Stannole Anions

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Received March 2, 2010
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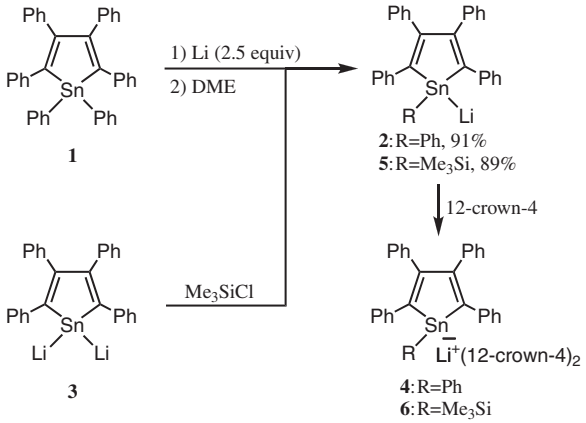
1-Lithio-1-phenyl- and 1-lithio-1-trimethylsilylstannoles were synthesized and the corresponding lithium salts of stannole anions were characterized by X-ray diffraction analysis. The five-membered rings of the two lithium salts are planar with remarkable alternation of the C–C bonds, suggesting that they are both non-aromatic. Theoretical calculations are also carried out to discuss their electronic nature.

The cyclopentadienyl anion has long played important roles in organic chemistry because of its aromatic character and its usefulness as a ligand of a wide variety of metal complexes.[1] Meanwhile, heavier group 14 metallole anions, which are heavier congeners of cyclopentadienyl, have recently received considerable attention because of their aromaticity and their potential as electron-rich ligands of transition-metal complexes.[2] The synthesis and molecular structures of alkali-metallated siloles and germoles have been already reported, these siloles and germoles being non-aromatic.[3] Most recently, heavier congeners of cyclopentadienyl anions bearing a Si_2GeC_2[4] or a Si_3C_2[5] ring have been prepared and found to have considerable aromatic character. With regard to alkali-metallated stannoles, which are tin-analogs of the cyclopentadienyl anion, our 1,2-dilithiobistannole and 1,3-dilithioterstannole are the only two examples of X-ray characterized lithiostannoles,[6,7] even though we have already reported the preparation and reactions of several lithiostannoles.[8] To provide more insight into the structures of stannole anions, we report herein the molecular structures of two lithium salts of stannole anions bearing a phenyl and a silyl group on the tin atoms. Theoretical calculations are also carried out to discuss their electronic nature.

The reduction of hexaphenylstannole **1**[9] with 2.5 equivalents of lithium in THF afforded a mixture of phenyllithium and lithiostannole **2**. To remove phenyllithium, the reaction solution was refluxed. However, further reduction of lithiostannole **2** to dilithiostannole **3**[10] occurred, even though phenyllithium decomposed.[11] Instead of refluxing, DME was added to the mixture, leading to the complete decomposition of phenyllithium, and **2** did not change. After filtration to remove unreacted lithium, **2** was isolated in 91% yield (Scheme 1). Recrystallization of **2** in the presence of 12-crown-4 provided single crystals of lithium salt **4** suitable for X-ray diffraction analysis.



Scheme 1. Preparation of lithiostannoles and their lithium salts.

To prepare trimethylsilyl-substituted lithiostannole **5**, reaction of dilithiostannole **3** with chlorotrimethylsilane was examined. When a deep-red THF solution of **3** was treated with chlorotrimethylsilane, the color of the solution did not change remarkably. However, the ^{119}Sn NMR spectrum of the resulting mixture showed only one new signal at −183.4 ppm with a coupling constant of 156 Hz, and the signal for **3**[10] disappeared completely, suggesting the formation of 1-lithio-1-trimethylsilylstannole **5**. After filtration to remove materials soluble in hexane, **5** was isolated in 89% yield (Scheme 1). Recrystallization of **5** in the presence of 12-crown-4 provided single crystals of lithium salt **6** suitable for X-ray diffraction analysis.

The molecular structures of lithium salts of stannole anions **2** and **5** were established by X-ray diffraction analysis. The ORTEP drawings of lithium salts **4** and **6** are shown in Figures 1 and 2. Each of the lithium atoms in both compounds is coordinated with two 12-crown-4 molecules. The distances between the tin and the lithium atoms in **4** and **6** are more than 6.5 Å, suggesting that both of them have solvent-separated ion pairs with no interactions between them. The five-membered rings of **4** and **6** are almost planar, as found for dilithiostannole **3**.[10] In contrast to **3** with no alternation of the C–C bonds in the stannole ring, **4** and **6** have remarkable alternation of the C–C bonds in the stannole rings. For example, the C–C bonds in the stannole ring of **4** are 1.363(2), 1.493(3), and 1.364(2) Å. The stannole rings of **4** and **6** have therefore 1,3-butadiene character. It is of considerable interest to note that the angle between the vector from the centroid[12] of the stannole ring of **6** to the tin atom and the Sn–Si bond is about 89°, which is smaller than the corresponding angles of 102 and 111° in **4** and 1,2-dilithiobistannole,[4] respectively. Similar trends were found in the structures of germole anions.[3b] On the other hand, theoretical calculations of $C_4H_4SnH^-$ have predicted that the corresponding angle is 98°.[13]

In order to understand the small angle around the tin atom of the lithium salt of stannole anion **6**, theoretical calculations were carried out using the Gaussian03 program package.[14] The geometry of $C_4H_4Sn(SiH_3)^-$ was fully optimized with hybrid

Published on the web June 30, 2010; doi:10.1246/bcsj.20100057

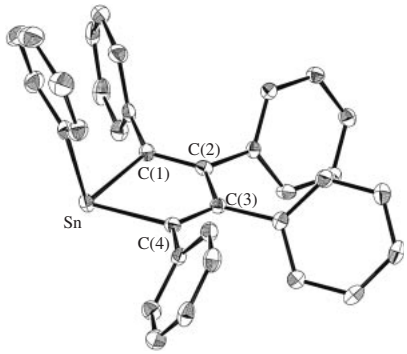


Figure 1. ORTEP drawing of $Ph_5C_4Sn^-\cdot[Li^+(12\text{-crown-}4)_2]$ (**4**) with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms and $Li^+(12\text{-crown-}4)_2$ moiety were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn–C(1), 2.2198(17); Sn–C(4), 2.1926(17); C(1)–C(2), 1.363(2); C(2)–C(3), 1.493(3); C(3)–C(4), 1.364(2); C(1)–Sn–C(4), 78.79(7).

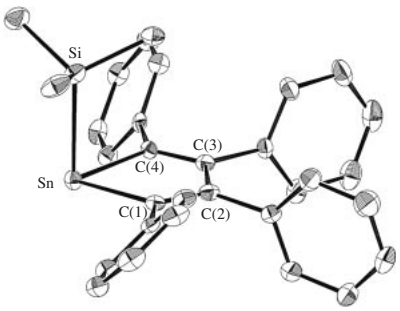


Figure 2. ORTEP drawing of $Ph_4(Me_3Si)C_4Sn^-\cdot[Li^+(12\text{-crown-}4)_2]$ (**6**) with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms and $Li^+(12\text{-crown-}4)_2$ moiety were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn–C(1), 2.197(4); Sn–C(4), 2.198(4); C(1)–C(2), 1.360(6); C(2)–C(3), 1.478(5); C(3)–C(4), 1.350(6); Sn–Si, 2.6154(14); C(1)–Sn–C(4), 78.56(15).

density functional theory at the B3LYP[15] level using the LANL2DZ basis set augmented by a *d* polarization function ($\eta = 0.186$ (Sn) and 0.246 (Ge)) for Sn and Ge,[16,17] and 6-31G(d) for C,[18,19] H,[18] and Si.[20] In the optimized geometry, the C(α)–Sn–Si angle is about 91°, which is consistent with the X-ray measured value. The HOMO consists of mainly a lone pair on the tin atom, while the HOMO−1 consists of a π-orbital of the butadiene moiety (Figure 3). These suggest that there is no significant interaction between the σ(Sn–Si) bond and the π-orbitals of the butadiene moiety, preventing six-electron aromatic delocalization due to σ–π conjugation, even though the Sn–Si bond is oriented perpendicularly to the stannole ring. To compare the C(α)–Sn–X angle (X = H, CH_3, SiH_3, GeH_3, and Ph), geometric optimizations of $C_4H_4SnX^-$ were also carried out. The C(α)–Sn–Si angle is calculated to be the smallest among those of these species (Table 1). According to the natural population analysis (Table 1), as the tin atom is less positively charged, the C(α)–Sn–X angle tends to become smaller except for $C_4H_4SnH^-$, though the reason for this exception remains unresolved. Although the σ(Sn–Si)–π(butadiene) or σ^*(Sn–Si)–π(butadiene) interactions could affect the angles, such interactions were not found in the $C_4H_4Sn(SiH_3)^-$. In addition, no significant σ(Sn–Si)–π^*(butadiene) interaction was found.[21] According to the natural bond orbital (NBO) analysis, s-character of the lone pair in $C_4H_4Sn(SiH_3)^-$ (69%) is larger than that in $C_4H_4Sn(CH_3)^-$ (67%), and therefore it seems that electron-donating substituents enhance s-character of the lone pair on the tin atom, and decrease s-character of the tin atom in the Sn–X bonds, leading to smaller C(α)–Sn–X angles.

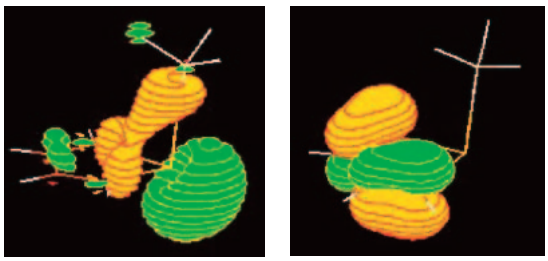


Figure 3. HOMO and HOMO−1 of $C_4H_4Sn(SiH_3)^-$.

Table 1. The C(α)–Sn–X Angle and Natural Population of Sn in $C_4H_4SnX^-$

X	Angle/°	Natural population
H	98.0	0.52
CH_3	97.8	0.75
SiH_3	90.9	0.53
GeH_3	92.5	0.54
Ph	98.4	0.79

In summary, lithiostannoles **2** and **5** were isolated and the molecular structures of their lithium salts **4** and **6** were established by X-ray diffraction analysis. The stannole rings have 1,3-butadiene character, indicating their non-aromatic nature. The remarkable pyramidalization around the tin atom of **6** was found and the angles around the tin atoms of several lithiostannoles were calculated and compared. Isolation of lithiostannoles will enable us to prepare novel transition metals complexes bearing a stannole ligand, leading to discovery of new structures and new catalytic reactivity.

Experimental

General Procedure. All reactions were carried out under argon. THF, diethyl ether, dimethoxyethane (DME), and C_6D_6 used in the synthesis or NMR analyses were distilled from sodium benzophenone ketyl under argon atmosphere followed by a potassium mirror using trap-to-trap technique. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{7}Li NMR (156 MHz), and ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker DPX-400 or a DRX-400 spectrometer. Data for the X-ray crystallographic analyses were collected on a Bruker SMART APEX diffractometer equipped with a CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at −175 °C and the structures were solved by direct methods.

Isolation of Lithiostannole 2. In a glovebox, a mixture of 1,1,2,3,4,5-hexaphenylstannole (**1**)[9] (792.0 mg, 1.26 mmol) and lithium (21.4 mg, 3.08 mmol) was stirred in THF (3 mL) at room temperature for 2 h. After removal of insoluble materials by filtration, the filtrate was concentrated. To the resulting residue

was added DME (3 mL) and then the solution was stirred at room temperature for 1 h. After removal of volatile substances, the residue was washed with hexane and 1-dilithio-1,2,3,4,5-pentaphenylstannole (**2**) was obtained (644.9 mg, 91%).[8]

Isolation of Lithiostannole 5. To a THF (6 mL) solution of 1,1-dilithio-2,3,4,5-tetraphenylstannole (**3**)[10] (763.6 mg, 1.56 mmol) was added a THF (2.3 mL) solution of chlorotrimethylsilane (0.58 M, 1.33 mmol) at −80 °C. The mixture was stirred at the same temperature and then gradually warmed to room temperature. After removal of volatile substances, the residue was degassed by freeze–pump–thaw cycles and sealed. In a glovebox, materials insoluble in toluene were removed by filtration and the filtrate was concentrated to provide a crude product, which was washed with hexane, and the resulting material was 1-lithio-2,3,4,5-tetraphenyl-1-trimethylsilylstannole (**5**) (774.6 mg, 89%). **5**: ^{1}H NMR (THF–C_6D_6): δ 0.44 (s, J(Sn–H) = 16 Hz, 9H), 6.75–6.79 (m, 4H), 6.84–6.88 (m, 4H), 6.95–7.00 (m, 12H); ^{13}C NMR (THF–C_6D_6): δ 3.25 (q, J(Sn–C) = 14 Hz), 122.00 (d), 123.89 (d), 127.01 (d), 127.13 (d), 129.60 (d, J(Sn–C) = 18 Hz), 131.91 (d), 146.23 (s), 150.44 (s), 150.61 (s), 178.18 (s, J(Sn–C) = 170 Hz); ^{7}Li NMR (THF–C_6D_6): δ −0.76; ^{119}Sn NMR (THF–C_6D_6): δ −183.4 (J(Sn–Si) = 156 Hz).

X-ray Crystallographic Analysis of 4 and 6. For **4**: Formula: $C_{50}H_{57}LiO_8Sn$, FW: 911.61, crystal dimension: 0.45 × 0.40 × 0.40 mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.599(3)$ Å, $b = 15.468(3)$ Å, $c = 21.131(4)$ Å, $\beta = 93.712(4)°$, $V = 4435.6(16)$ Å^3, $D_{calcd} = 1.365$ g cm^{-3}, $R_1 = 0.032$ ($I > 2\sigma(I)$, 8375 reflections), $_wR_2 = 0.086$ (for all reflections) for 10620 reflections and 541 parameters, GOF = 1.035. For **6**: Formula: $C_{47}H_{61}LiO_8SiSn$, FW: 907.70, crystal dimension: 0.25 × 0.20 × 0.15 mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.751(3)$ Å, $b = 13.297(3)$ Å, $c = 14.490(3)$ Å, $\alpha = 90.328(6)°$, $\beta = 91.518(6)°$, $\gamma = 94.667(5)°$, $V = 2255.8(9)$ Å^3, $D_{calcd} = 1.336$ g cm^{-3}, $R_1 = 0.058$ ($I > 2\sigma(I)$, 8264 reflections), $_wR_2 = 0.158$ (for all reflections) for 10364 reflections and 526 parameters, GOF = 1.076. CCDC-763873 and -763874 contain the supplementary crystallographic data for **4** and **6**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: (internat.) +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

This work was partially supported by Grant-in-Aids for Scientific Research (No. 20038010 for M.S. and No. 18066017 for S.N.) in Priority Areas "Molecular Theory for Real Systems" and by the Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science and Technology of Japan. M. Saito acknowledges a research grant from Toray Science Foundation.

Supporting Information

Orbital diagrams of $C_4H_4Sn(SiH_3)^-$. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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21 Details, see Supporting Information.