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Synthesis and Structure of Pentaorganostannate Having Five Carbon Substituents

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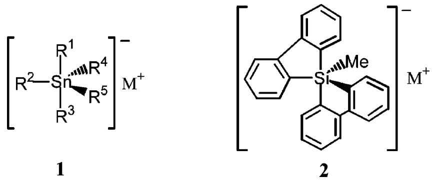
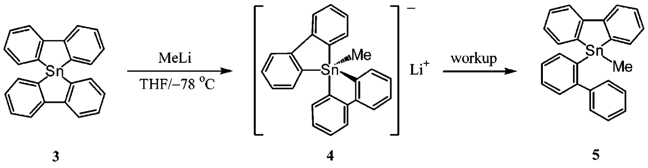
The transmetalation reaction is one of the most important methods for the creation of a metal−carbon bond.[1] Among various types of transmetalation reactions, since the first report on the reaction of tetravinylstannane with phenyllithium to give vinyllithium,[2] the tin-lithium exchange[3] reaction has been of great importance for the synthesis of particular organolithium reagents that are difficult or ineffective to prepare by the lithium-halogen exchange reaction.[4] Consequently, the tin-lithium exchange reaction is now widely applied for the synthesis of organolithium compounds which play important roles in organic chemistry. Although the intermediates of the transmetallation reactions on the tin atom were believed to be lithium pentaorganostannates bearing five carbon substituents, as evidenced by low-temperature NMR spectroscopy (Chart 1),[5] and mechanistic features such as stereochemistry at the tin atom have been well demonstrated,[6] no structural detail of a stable lithium pentaorganostannate bearing five carbon substituents on the tin atom has so far appeared. On the other hand, many pentacoordinated organotin compounds containing electronegative ligands have been already synthesized and characterized by X-ray crystallographic analysis.[7] Very recently, stable pentaorganosilicates bearing five carbon substituents on the silicon atom have been characterized by X-ray crystallographic analysis[8] and the unique electronic structure contrary to the three-centered four-electron model has been discussed (Chart 1).[9] We report herein the synthesis of the first stable lithium pentaorganostannate bearing five carbon substituents on the tin atom, a genuine intermediate of the tin−lithium exchange reaction, by the reaction of spirostannabifluorene with methyllithium and its X-ray structural characterization. The unique structure of the lithium pentaorganostannate is also discussed by the aid of theoretical calculations.

Chart 1. Pentaorganostannates **1** and -Silicates **2** Having Five Carbon Substituents



Reaction of spirostannabifluorene **3**[10] with methyllithium in THF at −78 °C gave a yellow solution, suggesting the formation of anionic species. The ^{119}Sn NMR spectrum of the solution with C_6D_6 for NMR lock revealed only one signal at −253.0 ppm at 213 K, remarkably shifted upfield compared to that of the starting material, **3** (−67.4 ppm in $CDCl_3$). This upfield resonance of the ^{119}Sn nucleus could be reasonably interpreted in terms of the formation of a pentacoordinated organotin species, that is, lithium pentaorganostannate **4** (Scheme 1),[11] as was observed in the ^{119}Sn NMR spectra of the reported intermediary lithium pentaorganostannate bearing five carbon substituents on the tin atom at low temperature (−300 to −270 ppm).[6] In the ^{13}C NMR spectrum, a signal assignable to the Sn−Me carbon was observed at −2.98 ppm with a characteristic ^1J(Sn−C) coupling constant (394 Hz) due to a Sn−C bond. A single resonance due to the α-carbon on the aromatic ring was observed at 156.82 ppm with a large coupling constant of 369 Hz, suggesting a rapid pseudorotation of **4** even at 213 K.[12] The ^1J(Sn−C(Ar)) coupling constant (369 Hz) is larger than the ^1J(Sn−C) found in Me_4Sn (340 Hz)[13] and smaller than the ^1J(Sn−C(Ar)) of Ph_3SnMe (511 Hz),[14] appearing as the average of ^1J(Sn−C(apical)) and ^1J(Sn−C(equatorial)). Thus, the apical bond is concluded to have a considerable s character.

Scheme 1 . Reaction of Spirobistannafluorene **3** with Methyllithium



Remarkably, lithium stannate **4** was stable even at room temperature in an argon atmosphere, as evidenced by the remaining upfield resonance as the sole signal in the ^{119}Sn NMR spectrum, and could be isolated by recrystallization from DME in 63% yield,[15] although an attempt to isolate stannate **4** as an ammonium salt in air failed to give **5** in 88% yield, as was observed in the normal transmetallation reactions on the tin atom.[16] The structure of **4** was finally established by X-ray crystallographic analysis (Figure 1).[17] The lithium cation is coordinated with three DME molecules and is completely separated from the anionic moiety with the distance of about 6.8 Å. The stannate moiety has a distorted trigonal bipyramidal structure, as do other pentacoordinated organotin compounds.[3c,18] The methyl group of **4** is situated in an equatorial position, while the other carbon atoms bonded to the tin atom are situated in equatorial and apical positions, similar to the structures of the reported silicon analogues.[8a,b] The bond angle around the tin atom along the apical axis is 168.4(3)°, deviating from 180° of the ideal trigonal bipyramidal structure and smaller than that in **2** (174.93(9)[8b] and 177.41(9)°).[8a] The sum of the bond angles around the tin atom is 360° and hence the tin atom has an sp^2 geometry. The apical bond length is 2.268(7) Å, longer than those of the equatorial bonds (2.186(1) and 2.196(5) Å) which are slightly longer than the normal tin−carbon bonds (2.14 Å),[7] reflecting the hypervalent state of the central tin atom. The equatorial Si−C bonds that are shorter than the apical Si−C bonds in **2** are also longer than the corresponding standard single bonds.[8a,b]

To get more insight into the structure of **4**, theoretical calculations were carried out. Geometrical optimization was carried out with density functional theory at the B3LYP level[19] using the Gaussian 03 program.[20] The LANL2DZ basis set augmented by a d polarization function (d exponent 0.186) was used for Sn,[21] while the 6-31G(d) basis set was used for C and H.[22] The anion moiety

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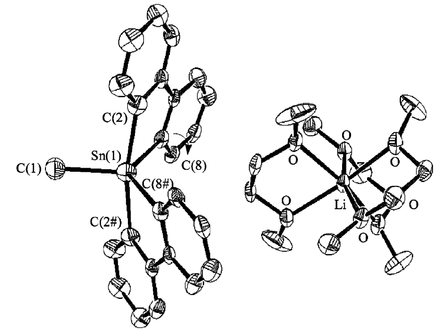
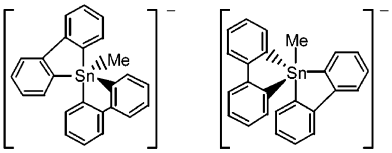


Figure 1. ORTEP drawing of **4**-**3**DME with thermal ellipsoids plots (30% probability for non-hydrogen atoms). The minor part of the disordered moieties and all hydrogen atoms were omitted for clarity.

Scheme 2. Relative Engergy of Pseudorotomers



4 (0.0) **6** (12.2)

Table 1. Calculated and Observed Bond Lengths (Å) and Angles (deg) of **4**

Sn−C(Me)	2.188	2.186(1)	C(Me)-Sn−C(eq)	118.6	119.15(13)
Sn−C(ax)	2.274	2.268(7)	C(eq)-Sn−C(eq)	122.0	121.7(3)
Sn−C(eq)	2.192	2.196(5)	C(ax)-Sn−C(ax)	171.6	168.4(3)

of lithium stannate **4** was fully optimized and the calculated structure was consistent with that found in the X-ray structural analysis (Scheme 2 and Table 1). The calculated length of the apical tin−carbon bond is 2.274 Å, longer than those of the equatorial bonds (2.188 and 2.192 Å). Contrary to the apical bond in the three-centered four-electron model, the apical bond of **4** has a considerable s character at the Sn atom, as was reported in the theoretical calculations of **2**.[9] The pseudorotamer **6** whose methyl group is located in an apical position was also optimized and calculated to be less stable than **4** by 12.2 kcal/mol. The energy difference suggests that pseudorotation between **4** and **6** is unlikely at 213 K, as also evidenced by a normal ^1J(Sn−Me) coupling constant of 394 Hz, although rapid pseudorotation between the two enantiomers having a methyl group at the equatorial position takes place.[23]

In summary, the first stable pentaorganostannate **4** bearing five carbon substituents, an intermediate of tin−lithium exchange reaction, was synthesized and characterized. The crystal structure of **4** has a distorted trigonal bipyramid whose methyl group is located in an equatorial position, while **4** undergoes rapid pseudorotation in solution. The apical tin-carbon bond has a considerable s character at the Sn atom, in contrast to the three-centered four-electron model.

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Supporting Information Available: Complete ref 20, experimental details from **3** to **5**, refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, CIF for **4**−**3**DME, and Cartesian coordinates of the optimized structure of **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In an NMR tube, to a THF (0.2 mL) solution of spirostannabifluorene **3** (46 mg, 0.11 mmol) was added methyllithium (0.11 mL; 0.98 N in diethyl ether, 0.11 mmol) and benzene-d_6 (0.2 mL) for NMR lock at −78 °C. **4**: ^{1}H NMR(400 MHz, THF-C_6D_6, 213 K) δ 0.03 (br s, 3H), 6.84−7.14 (m, 8H), 7.67−8.04 (m, 8H). ^{13}C NMR(101 MHz, THF-C_6D_6, 213 K) δ −2.98 (q, J(Sn−C) = 394 Hz), 120.46 (d), 125.08 (d), 126.14 (d), 136.86 (d), 145.80 (s, J(Sn−C) = 74 Hz), 156.82 (s, J(Sn-C) = 369 Hz). ^{119}Sn NMR-(149 MHz, THF-C_6D_6, 213 K) δ −252.95. ^{7}Li NMR(156 MHz, THF-C_6D_6, 213 K) δ −0.27.

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(15) In a glovebox, to a THF (2 mL) solution of spirostannabifluorene **3** (48 mg, 0.11 mmol) was added methyllithium powder (10 mg, 0.11 mmol as MeLi-Et_2O). To the resulting solution was added dimethoxyethane (DME) (1 mL) to give yellow crystals of lithium stannate **4**−**3**DME (51 mg, 63%).

(16) For the experimental details, see Supporting Information.

(17) Crystals suitable for X-ray diffraction were obtained by recrystallization of a THF/DME solution of **4** at −33 °C in a glovebox. The crystal was mounted in a glass capillary. The intensity data were collected at −180 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. Crystal data of **4**−**3**DME: formula, $C_{37}H_{33}LiO_6Sn$; fw = 699.26; crystal dimension, 0.50 × 0.20 × 0.20; monoclinic, $C2/c$; a = 11.5850(10), b = 20.8836(17), c = 15.2368(12) Å, β = 102.415(2)°, V = 3600.1(5) Å^3, $Z = 4$, D_{calcd} = 1.290 g cm^{-3}. $R_1 = 0.067$ ($I > 2\sigma(I)$, 2760 reflections), $wR_2 = 0.147$ (for all reflections) for 3206 reflections and 251 parameters. GOF = 1.115. Disorders around the DME molecules were found. Although disordered carbon and oxygen atoms of the DME molecules could be refined, some hydrogen atoms could not be placed.

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