

Formation of Pentaorganostannates from Bis(2-bromo-2'-biphenyl)stannanes and *tert*-Butyllithium upon Substitution of Alkyl and Aryl Groups on Tin Atoms

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Dedicated to Professor Takayuki Kawashima on the occasion of his retirement from the University of Tokyo

Keywords: Stannanes / Nucleophilic substitution / Hypervalent compounds

The reaction of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium in the presence of diaryl- and dialkyldichlorostannanes leads to the extrusion of aryl and alkyl groups on the tin atom, affording 9-stannafluorene derivatives bearing biphenyl groups. The intermediates of the reactions were assigned to the corresponding pentaorganostannates, which

were characterized by NMR spectroscopy. Unexpectedly, the dissociation of the aryl and alkyl groups from the tin atoms in intramolecular nucleophilic substitution reactions was preferable to that of chloride ions in intermolecular nucleophilic substitution reactions.

Introduction

Bimolecular nucleophilic substitution reactions at carbon atoms, denoted as S_N2 reactions, are one of the most important reactions in organic chemistry, and the pentacoordinate transition state is well established.^[1] The leaving group stability of the functional groups on the carbon atom affects the reaction pathways. For instance, a halogen atom, except for a fluorine atom, on carbon is easily dissociated as a halide anion, whereas an alkyl or an aryl group would rarely be dissociated as an alkyl or an aryl anion, respectively. Nucleophilic substitution reactions of heavier group 14 elements, however, sometimes do demonstrate the dissociation of alkyl groups as alkyl anions, probably via penta-valent organometallate complexes as key intermediates.^[2] Among such species, pentaorganostannates are of great importance as intermediates of the tin–lithium exchange reaction, which is widely applied for the synthesis of organolithium compounds,^[3] and we have recently reported the synthesis of the first stable pentaorganostannate and its molecular structures.^[4,5] In the course of our studies on the synthesis of the 9,10-distannaanthracene dianion,^[6] we already reported the synthesis of 9,10-dihydro-9,10-distannaanthracenes from bis(2-bromophenyl)stannanes.^[7] Bis(2-bromophenyl)stannanes were synthesized from *o*-lithiobromobenzene, prepared by the reaction of *o*-dibromobenzene

with butyllithium below –110 °C, whereas treatment of *o*-dibromobenzene with butyllithium at –90 °C led to the formation of biphenyllithium via benzyne.^[8] We became interested in the application of biphenyllithium to the synthesis of other π -extended ring compounds besides 9,10-dihydro-9,10-distannaanthracenes. We report herein that the reactions of bis(2-bromo-2'-biphenyl)stannanes with *tert*-butyllithium undergo unexpected substitution reactions on the tin atom via pentaorganostannates with the extrusion of aryl or alkyl groups.

Results and Discussion

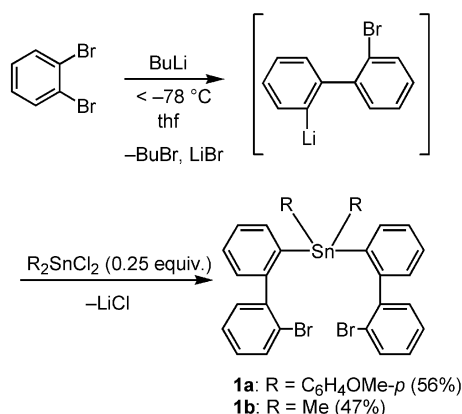
Synthesis of Bis(2-bromo-2'-biphenyl)stannanes **1**

After treatment of *o*-dibromobenzene with butyllithium at –78 °C,^[8] the reaction mixture was treated with dichlorodimethylstannane and dichloro[bis(*p*-methoxyphenyl)]stannane to give the corresponding bis(2-bromo-2'-biphenyl)stannanes **1a** and **1b**, respectively, in moderate yields (Scheme 1).

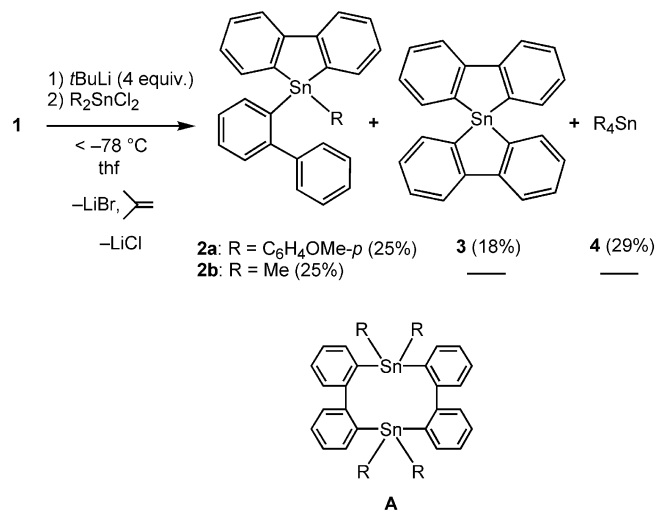
Reaction of Bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-Butyllithium: Quenched by Dichlorostannanes

We expected that the dilithio compounds derived from the reaction of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium could react with dichlorostannanes to give the corresponding 10-membered ring compounds **A**, similar to the synthesis of 9,10-dihydro-9,10-distannaanthracenes.^[7] However, treatment of bis(2-bromo-2'-bi-

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Scheme 1. Preparation of bis(2-bromo-2'-biphenyl)stannanes **1**.

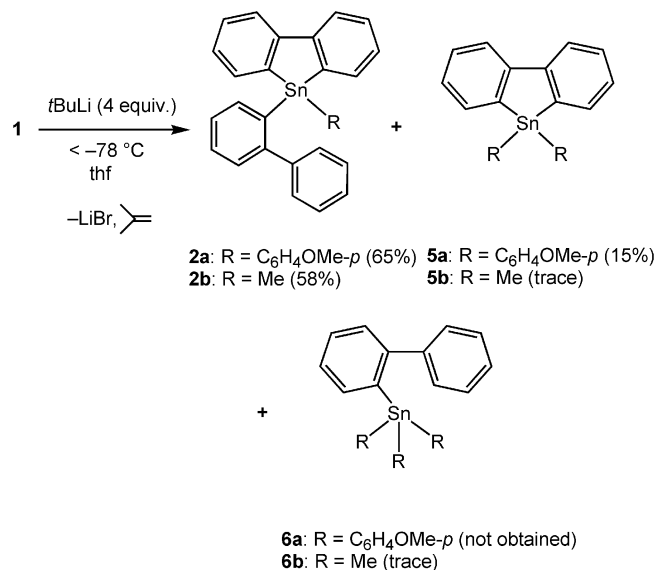
phenyl)stannane **1a** with *tert*-butyllithium followed by dichloro[bis(*p*-methoxyphenyl)]stannane^[9] afforded biphenylstannafluorene **2a** (25%), spirobistannafluorene **3**^[10] (18%), and tetrakis(*p*-methoxyphenyl)stannane^[9] **4** (29%; Scheme 2). Compounds **2a** and **3** are clearly formed by the dissociation of one and two *p*-methoxyphenyl groups, respectively, from the tin atom. In the reaction of **1b** with *tert*-butyllithium and dichlorodimethylstannane, the corresponding biphenylstannafluorene **2b** was obtained in 25% yield, whereas spirobistannafluorene **3** was not obtained. The formation of **2b** suggests that one methyl group on the tin atom was replaced by a biphenyl moiety. It is somewhat inconceivable that nucleophilic substitution with the extrusion of aryl and alkyl groups was preferable to that with the extrusion of chloride ions.

Scheme 2. Reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium, quenched by dichlorostannanes.

Reactions of Bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-Butyllithium

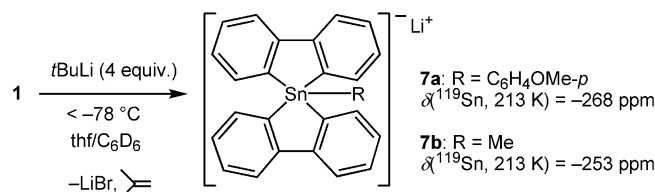
To understand the effects of the additional dichlorostannanes, reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium were also examined. Treat-

ment of **1a** with *tert*-butyllithium provided **2a** (65%) and 9-stannafluorene **5a**^[11] (15%), whereas spirobistannafluorene **3** was not obtained (Scheme 3). In the reaction of **1b** with *tert*-butyllithium, **2b** (58%), **5b**^[12,13] (trace), and **6b**^[13,14] (trace) were obtained.

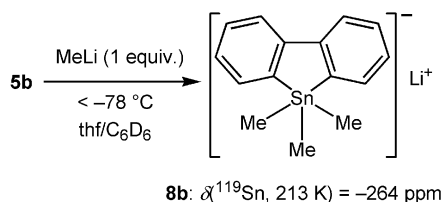
Scheme 3. Reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium.

Intermediates in the Reaction of Bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-Butyllithium

To elucidate the mechanism of these reactions, the reactions of **1** with *tert*-butyllithium were monitored. After treatment of **1b** with *tert*-butyllithium, the ¹¹⁹Sn NMR spectrum of the reaction mixture in THF with C₆D₆ for NMR lock at 213 K revealed complete disappearance of the signal for **1b** (−59, −57 ppm at 378 K)^[15] and only one signal at −253 ppm, which was identified as methylstannate **7b** (Scheme 4). We have already reported the characterization of **7b**, synthesized by the reaction of **3** with methyl lithium, by X-ray crystallographic analysis.^[4] In the reaction of **1a** with *tert*-butyllithium, the ¹¹⁹Sn NMR spectrum of the reaction mixture at 213 K revealed only one signal at δ = −268 ppm, which was in the same region as that of **7b**, suggesting the formation of the intermediary (*p*-methoxyphenyl)stannate **7a** (Scheme 4). Monitoring the reaction of 9-stannafluorene **5b** with methyl lithium at 213 K by ¹¹⁹Sn NMR spectroscopy revealed a signal at −264 ppm,

Scheme 4. Intermediates of the reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium.

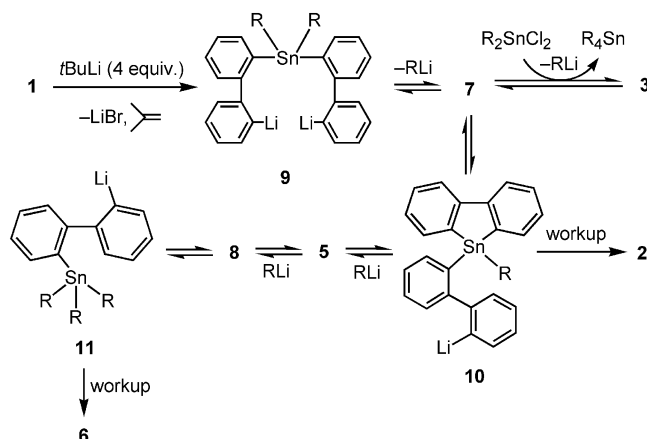
which was in the same region as that of **7b**, and hence, the intermediate was assigned to trimethylstannate **8b** (Scheme 5).



Scheme 5. Intermediate of the reaction of 9,9-dimethyl-9-stannafluorene (**5b**) with methyl lithium.

Mechanism for the Reactions of Bis(2-bromo-2'-biphenyl)-stannanes **1** with *tert*-Butyllithium

A plausible mechanism is shown in Scheme 6. First, the dilithiation of **1** occurs to provide dilithio compound **9**, which undergoes intramolecular nucleophilic substitution to afford pentaorganostannate **7** with the extrusion of RLi. Although stannate **7** and spirobistannafluorene **3** exist in equilibrium with RLi, in the presence of dichlorostannane as a trapping reagent, dissociated RLi is trapped by dichlorostannane, so that the equilibrium shifts toward spirobistannafluorene **3**. Stannate **7** is also in equilibrium with lithiobiphenylstannafluorene **10**, which is converted into **2** after usual workup. In contrast, in the absence of the trapping reagent, this equilibrium does not favor spirobistannafluorene **3**, because the RLi is not consumed. Therefore, in an equilibrium mixture, stannafluorene **5** exists, resulting from nucleophilic attack of the remaining RLi on the tin atom of **10**, although the yield of **5** is not very high. Stannafluorene **5** reacts with RLi to afford lithiostannylbiphenyl **11** via stannate **8b**. Although the reason why spirobistannafluorene **3** was not obtained in the reaction of **1b** with *tert*-butyllithium in the presence of dichlorodimethylstannane is still unclear, the unfavorable generation of the less-



Scheme 6. Mechanism for the reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium.

stable methyllithium compared with *p*-methoxyphenyllithium pushes the equilibrium between **7b** and **3** toward **7b**, which is in equilibrium with **10b**.

Conclusions

Reactions of bis(2-bromo-2'-biphenyl)stannanes **1** with *tert*-butyllithium in the presence of diaryl- and dialkyldichlorostannane did not afford the expected 10-membered compounds, but the corresponding biphenyl derivatives and spirobistannafluorene, which were derived from somewhat unexpected substitution of aryl and alkyl groups on the tin atoms. In the absence of diaryldichlorostannane, the formation of spirobistannafluorene **3** was suppressed, even though reaction of **1b** with *tert*-butyllithium in the presence of dichlorodimethylstannane did not provide spirobistannafluorene **3** because dissociation of two methyl groups on the tin atom was unfavorable. The intermediates of the reactions were assigned to the corresponding pentaorganostannates, which could be characterized by NMR spectroscopy. The dissociation of aryl and alkyl groups in intramolecular nucleophilic substitution reactions from the tin atoms was surprisingly preferable to that of chloride ions in intermolecular nucleophilic substitution reactions. The possibility of dissociating aryl and alkyl groups from the tin atom should be considered in future syntheses of organotin compounds.

Experimental Section

General Procedures: All experiments were performed under an argon atmosphere by using usual glass apparatus. THF, diethyl ether, and [D₆]benzene were distilled from sodium/benzophenone followed from potassium mirror. ¹H NMR (400 MHz), ¹³C NMR (101 MHz), ¹¹⁹Sn NMR (149 MHz), and ⁷Li NMR (156 MHz) spectra were recorded with a Bruker DRX-400 or a Bruker DPX-400 spectrometer. Wet column chromatography (WCC) and preparative thin-layer chromatography (PTLC) were carried out with Kanto silica gel 60N and Merck silica gel 60 PF₂₅₄, respectively. High-resolution mass spectra were recorded with a JEOL JMX-700AM mass spectrometer. All melting points were determined with a Mitamura Riken Kogyo MEL-TEMP apparatus. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Bis(2-bromo-2'-biphenyl)bis(*p*-methoxyphenyl)stannane (1a**):** To a THF (15 mL) solution of 1,2-dibromobenzene (0.80 mL, 6.63 mmol) was added butyllithium (2.67 M in hexane, 2.5 mL, 6.68 mmol) at -78°C , and the resulting mixture was stirred at the same temperature for 1 h. To the mixture was added a THF (3 mL) solution of dichloro[bis(*p*-methoxyphenyl)]stannane^[9] (674.6 mg, 1.67 mmol), and the reaction mixture was warmed to room temperature. After removal of the volatile substances, the residue was subjected to WCC (hexane/ethyl acetate, 5:1) to afford **1a** (739.2 mg, 56%). M.p. $145\text{--}149^{\circ}\text{C}$ (dichloromethane/methanol). ¹H NMR ([D₈]toluene, 373 K): $\delta = 3.42$ (s, 6 H), 6.56–6.60 (m, 2 H), 6.65–6.74 (m, 6 H), 6.92–7.01 (m, 4 H), 7.11–7.17 (m, 4 H), 7.18–7.27 (m, 4 H), 7.62–7.89 (m, 4 H) ppm. ¹³C NMR ([D₈]tolu-

ene, 373 K): δ = 55.55 (q), 115.47 (d, $J_{\text{Sn,C}}$ = 60 Hz), 125.42 (s), 127.93 (d, $J_{\text{Sn,C}}$ = 24 Hz), 128.05 (d, $J_{\text{Sn,C}}$ = 60 Hz), 129.24 (d, $J_{\text{Sn,C}}$ = 11 Hz), 129.69 (d), 131.96 (d, $J_{\text{Sn,C}}$ = 41 Hz), 132.81 (d), 133.95 (d), 138.37 (s), 139.21 (d, $J_{\text{Sn,C}}$ = 47 Hz), 139.45 (d, $J_{\text{Sn,C}}$ = 156 Hz), 141.91 (s), 146.03 (s, $J_{\text{Sn,C}}$ = 18 Hz), 150.62 (s, $J_{\text{Sn,C}}$ = 33 Hz), 161.65 (s) ppm. ^{119}Sn NMR ($[\text{D}_8]\text{toluene}$, 373 K): δ = -122.37 ppm. $\text{C}_{38}\text{H}_{30}\text{Br}_2\text{O}_2\text{Sn}$ (797.18): calcd. C 57.25, H 3.79; found C 57.33, H 3.65.

Bis(2-bromo-2'-biphenyl)stannane (1b): To a THF (15 mL) solution of 1,2-dibromobenzene (0.66 mL, 5.47 mmol) was added butyllithium (1.60 M in hexane, 3.6 mL, 5.76 mmol) at -78°C , and the resulting mixture was stirred at the same temperature for 1 h. To the mixture was added a THF (2 mL) solution of dichlorodimethylstannane (303.9 mg, 1.38 mmol), and the reaction mixture was warmed to room temperature. After removal of the volatile substances, materials insoluble in dichloromethane were filtered off. After concentration of the filtrate, the residue was recrystallized from dichloromethane and ethanol to afford **1b** (390.1 mg, 47%). M.p. 112–113 $^\circ\text{C}$ (dichloromethane/methanol). ^1H NMR ($[\text{D}_8]\text{toluene}$, 373 K): δ = -0.34–0.16 (m, 6 H), 6.76–6.80 (m, 2 H), 6.87–6.91 (m, 2 H), 6.98–6.99 (m, 2 H), 7.10–7.17 (m, 6 H), 7.27–7.45 (m, 4 H) ppm. ^{13}C NMR ($[\text{D}_8]\text{toluene}$, 373 K): δ = -7.18 (q), 125.39 (s), 127.84 (d), 127.96 (d, $J_{\text{Sn,C}}$ = 34, 37 Hz), 128.92 (d, $J_{\text{Sn,C}}$ = 11 Hz), 129.62 (d), 130.74 (d, $J_{\text{Sn,C}}$ = 37 Hz), 132.77 (d, $J_{\text{Sn,C}}$ = 137 Hz), 133.74 (d, $J_{\text{Sn,C}}$ = 17 Hz), 137.91 (d), 142.92 (s), 146.37 (s, $J_{\text{Sn,C}}$ = 20 Hz), 150.20 (s, $J_{\text{Sn,C}}$ = 29 Hz) ppm. ^{119}Sn NMR ($[\text{D}_8]\text{toluene}$, 373 K): δ = -58.81, -57.04 ppm. $\text{C}_{26}\text{H}_{22}\text{Br}_2\text{Sn}$ (612.98): calcd. C 50.95, H 3.62; found C 50.90, H 3.46.

Reaction of 1a with *tert*-Butyllithium Quenched by Dichloro[bis(*p*-methoxyphenyl)]stannane: To a THF (10 mL) solution of **1a** (506.4 mg, 0.64 mmol) was added *tert*-butyllithium (1.42 M in pentane, 1.80 mL, 2.55 mmol) at -78°C , and the resulting mixture was stirred for 15 min at the same temperature. To the mixture was added a THF (2 mL) solution of dichloro[bis(*p*-methoxyphenyl)]stannane^[9] (276.1 mg, 0.68 mmol), and the reaction mixture was warmed to room temperature. After removal of the volatile substances, the residue was subjected to WCC (hexane/ethyl acetate, 5:1) to afford 9-(2-biphenyl)-9-*p*-methoxyphenyl-9-stannafluorene (**2a**; 86.8 mg, 25%), spirostannafluorene^[10] **3** (48.2 mg, 18%), and tetrakis(*p*-methoxyphenyl)stannane^[9] (**4**; 100.2 mg, 29%). Data for **2a**: M.p. 112 $^\circ\text{C}$ (dichloromethane/methanol). ^1H NMR (CDCl_3): δ = 3.73 (s, 3 H), 6.71–6.77 (m, 2 H), 7.03–7.18 (m, 2 H), 7.24–7.28 (m, 2 H), 7.30–7.47 (m, 12 H), 7.18–7.27 (m, 4 H), 7.62–7.89 (m, 4 H) ppm. ^{13}C NMR (CDCl_3): δ = 54.96 (q), 114.26 (d, $J_{\text{Sn,C}}$ = 63 Hz), 122.72 (d, $J_{\text{Sn,C}}$ = 42 Hz), 127.03 (d, $J_{\text{Sn,C}}$ = 55 Hz), 127.50 (d), 127.67 (d, $J_{\text{Sn,C}}$ = 43 Hz), 128.67 (d), 128.68 (d), 128.79 (d), 129.31 (d, $J_{\text{Sn,C}}$ = 45 Hz), 129.34 (s), 129.38 (s, $J_{\text{Sn,C}}$ = 8 Hz), 136.28 (d, $J_{\text{Sn,C}}$ = 40 Hz), 137.45 (d, $J_{\text{Sn,C}}$ = 48 Hz), 137.61 (s), 139.09 (s), 139.64 (s), 145.56 (s, $J_{\text{Sn,C}}$ = 20 Hz), 147.85 (s, $J_{\text{Sn,C}}$ = 74 Hz), 150.08 (s), 160.31 (s) ppm. ^{119}Sn NMR (CDCl_3): δ = -65.99 ppm. $\text{C}_{31}\text{H}_{24}\text{O}_2\text{Sn}$ (531.25): calcd. C 70.09, H 4.55; found C 69.95, H 4.40. Data for **3**: M.p. 216–218 $^\circ\text{C}$ (dichloromethane/methanol). ^1H NMR (CDCl_3): δ = 7.26–7.34 (m, 4 H), 7.47–7.51 (m, 4 H), 7.53–7.66 (m, 4 H), 8.06–8.11 (m, 4 H) ppm. ^{13}C NMR (CDCl_3): δ = 122.85 (d, $J_{\text{Sn,C}}$ = 47 Hz), 128.29 (d, $J_{\text{Sn,C}}$ = 49 Hz), 130.16 (d, $J_{\text{Sn,C}}$ = 9 Hz), 135.96 (s, $J_{\text{Sn,C}}$ = 501, 524 Hz), 137.03 (d, $J_{\text{Sn,C}}$ = 48 Hz), 148.10 (s, $J_{\text{Sn,C}}$ = 80 Hz) ppm. ^{119}Sn NMR (CDCl_3): δ = -67.43 ppm. $\text{C}_{24}\text{H}_{16}\text{Sn}$ (423.1): calcd. C 68.13, H 3.81; found C 67.99, H 3.72.

Reaction of 1b with *tert*-Butyllithium Quenched by Dichlorodimethylstannane: To a THF (10 mL) solution of **1b** (121.3 mg, 0.20 mmol) was added *tert*-butyllithium (1.42 M in pentane,

0.57 mL, 0.81 mmol) at -78°C , and the resulting mixture was stirred for 15 min at the same temperature. To the mixture was added a THF (1 mL) solution of dichlorodimethylstannane (45.5 mg, 0.21 mmol), and the reaction mixture was warmed to room temperature. After concentration of the filtrate, the residue was recrystallized from dichloromethane and ethanol to afford 9-(2-biphenyl)-9-methyl-9-stannafluorene (**2b**; 21.3 mg, 25%). M.p. 131–132 $^\circ\text{C}$ (dichloromethane/methanol). ^1H NMR (CDCl_3): δ = 0.11 (s, $J_{\text{Sn,H}}$ = 61, 63 Hz, 3 H), 7.26–7.33 (m, 3 H), 7.37–7.46 (m, 6 H), 7.46–7.62 (m, 6 H), 7.93–7.98 (m, 2 H) ppm. ^{13}C NMR (CDCl_3): δ = -8.03 (q, $J_{\text{Sn,C}}$ = 397 Hz), 122.64 (d, $J_{\text{Sn,C}}$ = 40 Hz), 126.95 (d, $J_{\text{Sn,C}}$ = 53 Hz), 127.59 (d, $J_{\text{Sn,C}}$ = 43 Hz), 127.61 (d), 128.63 (d), 128.65 (d), 128.74 (d), 128.81 (d), 129.09 (d, $J_{\text{Sn,C}}$ = 11 Hz), 129.28 (d, $J_{\text{Sn,C}}$ = 9 Hz), 136.15 (d, $J_{\text{Sn,C}}$ = 41 Hz), 137.19 (d, $J_{\text{Sn,C}}$ = 40 Hz), 138.29 (d), 140.54 (s), 145.79 (s, $J_{\text{Sn,C}}$ = 21 Hz), 148.26 (s), 149.91 (s) ppm. ^{119}Sn NMR (CDCl_3): δ = -105.93 ppm. $\text{C}_{25}\text{H}_{30}\text{Sn}$ (449.25): calcd. C 68.38, H 4.59; found C 68.10, H 4.43.

Reaction of 1a with *tert*-Butyllithium: To a THF (4 mL) solution of **1a** (113.6 mg, 0.14 mmol) was added *tert*-butyllithium (1.42 M in pentane, 0.40 mL, 0.57 mmol) at -78°C , and the reaction mixture was warmed to room temperature. After removal of the volatile substances, the residue was subjected to WCC (hexane/ethyl acetate, 5:1) to afford **2a** (49.5 mg, 65%) and 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene^[11] (**5a**; 10.3 mg, 15%).

Reaction of 1b with *tert*-Butyllithium: To a THF (5 mL) solution of **1b** (117.8 mg, 0.19 mmol) was added *tert*-butyllithium (1.76 M in pentane, 0.50 mL, 0.88 mmol) at -78°C , and the reaction mixture was warmed to room temperature. After removal of the volatile substances, materials insoluble in dichloromethane were removed by filtration. The residue was subjected to PTLC (hexane) to afford **2b** (49.6 mg, 58%).

Monitoring the Reaction of 1a with *tert*-Butyllithium by ^{119}Sn NMR Spectroscopy: In an NMR tube, to a THF (0.4 mL) solution of **1a** (49.7 mg, 0.062 mmol) was added *tert*-butyllithium (1.46 M in pentane, 0.17 mL, 0.25 mmol) at -78°C and C_6D_6 (0.20 mL). The ^{119}Sn NMR spectrum of the reaction mixture at 213 K revealed the formation of pentaorganostannate **7a**. ^{119}Sn NMR ($\text{THF}/\text{C}_6\text{D}_6$, 213 K): δ = -268.28 ppm.

Monitoring the Reaction of 1b with *tert*-Butyllithium by ^{119}Sn NMR Spectroscopy: In an NMR tube, to a THF (0.4 mL) solution of **1b** (35.8 mg, 0.058 mmol) was added *tert*-butyllithium (1.46 M in pentane, 0.16 mL, 0.23 mmol) at -78°C and C_6D_6 (0.20 mL). The ^{119}Sn NMR spectrum of the reaction mixture at 213 K revealed the formation of pentaorganostannate **7b**.^[4] ^{119}Sn NMR ($\text{THF}/\text{C}_6\text{D}_6$, 213 K): δ = -252.88 ppm.

Monitoring the Reaction of 9-Stannafluorene 5b with Methylolithium by ^{119}Sn NMR Spectroscopy: In an NMR tube, to a THF (0.3 mL) solution of **5b** (94.5 mg, 0.31 mmol) was added methylolithium (0.98 M in ethyl ether, 0.32 mL, 0.31 mmol) at -78°C and C_6D_6 (0.20 mL). The ^{119}Sn NMR spectrum of the reaction mixture at 213 K revealed the formation of pentaorganostannate **8b**. ^1H NMR (THF , $\text{Et}_2\text{O}/\text{C}_6\text{D}_6$, 213 K): δ = 0.01 (s, $J_{\text{Sn,H}}$ = 40 Hz, 9 H), 6.93–7.10 (m, 4 H), 7.70–7.86 (m, 4 H) ppm. ^{13}C NMR (THF , $\text{Et}_2\text{O}/\text{C}_6\text{D}_6$, 213 K): δ = 0.55 (q, $J_{\text{Sn,C}}$ = 295, 303 Hz), 119.09 (d, $J_{\text{Sn,C}}$ = 31 Hz), 124.92 (d), 125.20 (d), 136.17 (d, $J_{\text{Sn,C}}$ = 42 Hz), 144.68 (s, $J_{\text{Sn,C}}$ = 68 Hz), 165.01 (s, $J_{\text{Sn,C}}$ = 308, 323 Hz) ppm. ^{119}Sn NMR (THF , $\text{Et}_2\text{O}/\text{C}_6\text{D}_6$, 213 K): δ = -263.77 ppm. ^7Li NMR (THF , $\text{Et}_2\text{O}/\text{C}_6\text{D}_6$, 213 K): δ = -0.20 ppm.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Young Scientists (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 17750032 to M.S.). M.S. acknowledges a research grant from Toray Science Foundation.

- [1] For examples, see: a) M. B. Smith, J. March in *March's Advanced Organic Chemistry*, John Wiley & Sons, Hoboken, **2007**; b) J. E. McMurry in *Organic Chemistry*, Brooks/Cole Pub., California, **2007**; c) K. P. C. Volhardt, N. E. Schore in *Organic Chemistry*, W. H. Freeman & Co., New York, **2007**.
- [2] For examples, see: a) M. Ishikawa, T. Tabohashi, H. Sugisawa, K. Nishimura, M. Kumada, *J. Organomet. Chem.* **1983**, 250, 109; b) Z. Wang, H. Fang, Z. Xi, *Tetrahedron Lett.* **2005**, 46, 499; c) C. Wang, Q. Luo, H. Sun, X. Guo, Z. Xi, *J. Am. Chem. Soc.* **2007**, 129, 3094.
- [3] a) H. J. Reich, N. H. Phillips, *Pure Appl. Chem.* **1987**, 59, 1021; b) J. Clayden in *Organolithiums: Selectivity for Synthesis*, Elsevier, Oxford, **2002**, p. 136; c) A. G. Davis in *Comprehensive Organometallic Chemistry II* (Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Exeter, **1995**, p. 217.
- [4] M. Saito, S. Imaizumi, T. Tajima, K. Ishimura, S. Nagase, *J. Am. Chem. Soc.* **2007**, 129, 10974.
- [5] Before ref.^[4] was published, some derivatives stable at low temperature had been observed by ¹¹⁹Sn NMR spectroscopy, see: a) H. J. Reich, N. H. Phillips, *J. Am. Chem. Soc.* **1986**, 108, 2102; b) A. J. Ashe III, L. L. Lohr, S. M. Al-Taweel, *Organometallics* **1991**, 10, 2424.
- [6] M. Saito, N. Henzan, M. Yoshioka, *Chem. Lett.* **2005**, 34, 1018.
- [7] a) M. Saito, M. Nitta, M. Yoshioka, *Organometallics* **2001**, 20, 749; b) M. Saito, N. Henzan, M. Nitta, M. Yoshioka, *Eur. J. Inorg. Chem.* **2004**, 743.
- [8] a) L. S. Chen, G. J. Chen, C. Tamborski, *J. Organomet. Chem.* **1980**, 193, 283; b) F. Leroux, M. Schlosser, *Angew. Chem. Int. Ed.* **2002**, 41, 4272.
- [9] B. N. Biddle, J. S. Gray, A. J. Crowe, *Appl. Organomet. Chem.* **1987**, 1, 261.
- [10] R. Gelius, *Chem. Ber.* **1960**, 93, 1759.
- [11] M. Saito, M. Shimosawa, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2006**, 35, 940.
- [12] J. P. M. Van Klink, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt, A. L. Spek, *Organometallics* **2002**, 21, 2119.
- [13] The formation of trace amounts of **5b** and **6b** was evidenced by ¹H NMR spectroscopic analysis of the crude product.
- [14] Compound **6b** was alternatively synthesized by the reaction of **5b** with methyllithium. Data for **6b**: ¹H NMR (CDCl₃): δ = 0.02 (s, J_{Sn,H} = 53 Hz, 9 H), 7.33–7.45 (m, 7 H), 7.54–7.68 (m, 1 H) ppm. ¹³C NMR (CDCl₃): δ = –7.96 (q, J_{Sn,C} = 338, 354 Hz), 126.43 (d, J_{Sn,C} = 45 Hz), 128.20 (d), 128.27 (d), 128.57 (d, J_{Sn,C} = 35 Hz), 128.86 (d), 136.28 (d, J_{Sn,C} = 36 Hz), 142.27 (s, J_{Sn,C} = 447, 468 Hz), 145.37 (s, J_{Sn,C} = 17 Hz), 150.29 (s, J_{Sn,C} = 29 Hz) ppm. HRMS: calcd. for C₁₄H₁₅Sn [M – Me] 303.0198; found 303.0202.
- [15] The NMR spectra of **1** were quite complicated, probably due to involvement of conformational isomers related to the biphenyl moieties.

Received: January 29, 2010
Published Online: April 9, 2010