



Synthesis and structure of the dithienostannole anion

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ABSTRACT

Novel dithienostannoles were synthesized by the reactions of the corresponding dilithiobithiophenes with dichlorodiphenylstannane. A unique byproduct, 10-membered ring compound was also obtained. Reduction of type A dithienostannole with lithium afforded 2,2'-dilithio-3,3'-bithiophene, while reduction of type B dithienostannole with lithium afforded the corresponding dithienostannole anion. The structure and aromaticity of the dithienostannole anion are also discussed.

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1. Introduction

For a decade, there has been considerable interest in the anions and dianions of Group 14 elements, which are heavier congeners of the cyclopentadienyl anion [1]. After considerable works on the synthesis of non-annulated Group metallole anions and dianions, attention was next paid to the effect of benzannulation of the metallole anions and dianions on their aromaticity [2–4]. The benzannulated metallole anions are non-aromatic, while the metallole rings of the corresponding dianions have considerable aromatic characters. On the other hand, thiophene has long played important roles as a building block of π -conjugated compounds and has been applied to the synthesis of useful materials [5]. In the course of the studies on the expansion of π -conjugated compounds, quite recently, thiophene-annulated siloles have been synthesized and been found to exhibit luminescent and semiconducting properties [6]. Therefore, thiophene-annulation of Group 14 metallole anions and dianions is worth considering as a new annulation mode. We report herein the synthesis of two types of thiophene-annulated stannoles (the annulation modes are denoted as Types A and B, hereafter; Chart 1) and their reduction, which is dependent on the annulation mode. Theoretical calculations are also carried out to investigate on the structure of the resulting new thiophene-annulated stannole anion.

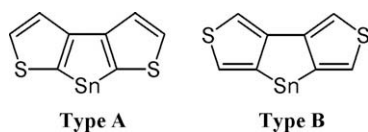
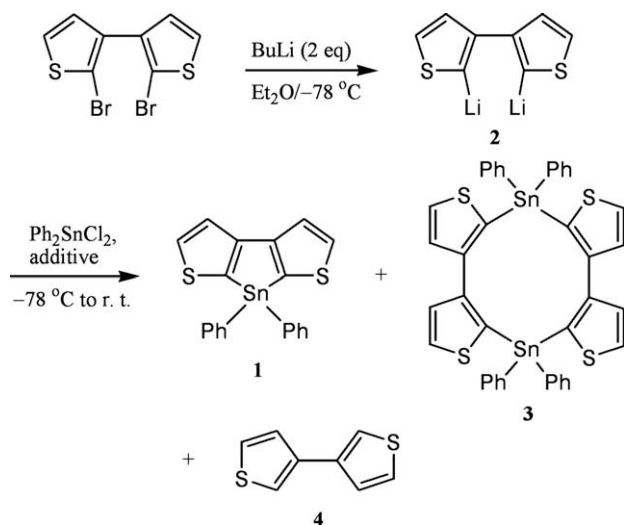
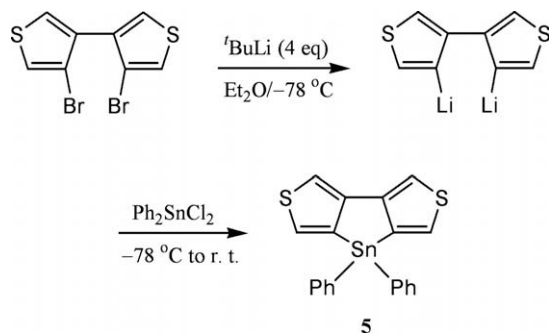
2. Results and discussion

2.1. Synthesis of two thiophene-annulated stannoles

Since we have already succeeded in the synthesis of stannole dianions by the reduction of the corresponding diphenyl derivatives [4,7], we chose dithienostannoles having two phenyl groups on the tin atom as precursors of the corresponding anions and dianions. Firstly, we tried the synthesis of type A dithienostannole **1** by the reaction of 2,2'-dilithio-3,3'-bithiophene (**2**), prepared from 2,2'-dibromo-3,3'-bithiophene [8] and butyllithium, with dichlorodiphenylstannane. However, reaction of 2,2'-dilithio-3,3'-bithiophene (**2**) with an equimolar amount of dichlorodiphenylstannane afforded 10-membered ring compound **3** (12%), which arose from two bithiophene and diphenylstannylene units, and 3,3'-bithiophene (**4**) (41%) (Scheme 1). The structure of 10-membered ring compound **3** was finally confirmed by X-ray crystallographic analysis. In contrast, reaction of 2,2'-dilithio-3,3'-bithiophene with an equimolar amount of dichlorodiphenylstannane in the presence of two equivalents of copper(I) iodide [9] provided diphenyldithienostannole **1** in 13% yield together with **3** (5%). Diphenyldithienostannole **1** was so unexpectedly extremely unstable under atmosphere that we could not purify it at an elemental analysis level, even through the NMR signals of **1** could be completely assigned.

Secondly, the synthesis of a type B dithienostannole was investigated. In contrast to the synthesis of **1**, the corresponding dilithiobithiophene prepared from 4,4'-dibromo-3,3'-bithiophene [10] reacted with dichlorodiphenylstannane without copper(I) iodide to afford the synthesis of type B diphenyldithienostannole **5** in

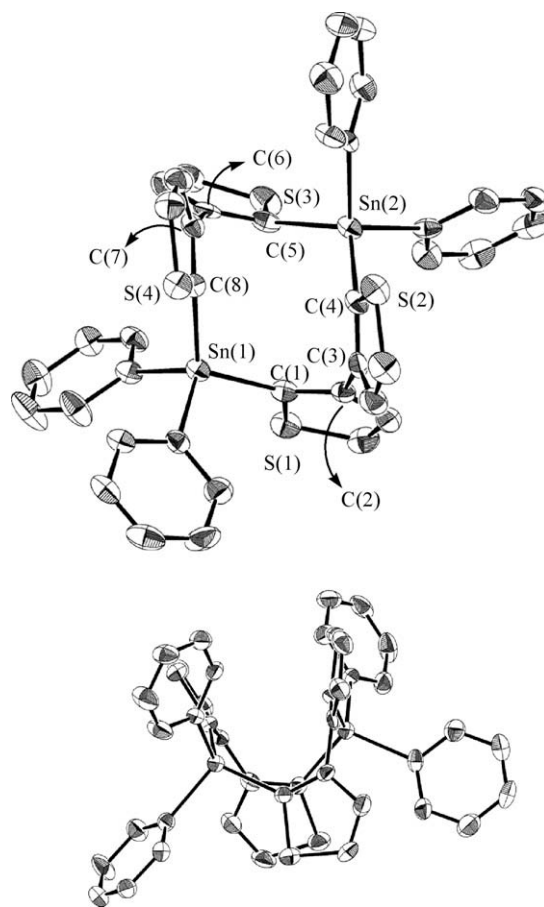
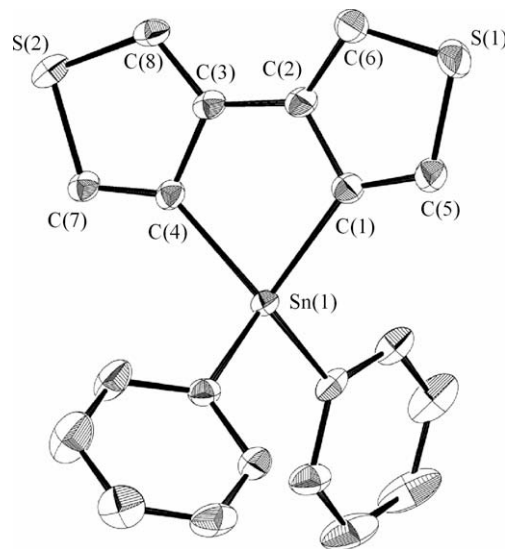
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**Chart 1.** Annulation modes of thiophene-annulated stannoles.**Scheme 1.** Reactions of 2,2'-dilithio-3,3'-bithiophene **2** with dichlorodiphenylstannane.**Scheme 2.** Preparation of type B dithienostannole **5**.

61% yield (Scheme 2). The structure of diphenyldithienostannole **5** was finally confirmed by X-ray crystallographic analysis.

2.2. Molecular structures of 10-membered ring compound **3** and type B dithienostannole **5**

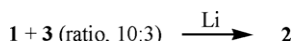
There have appeared only a few reports on the molecular structures of monocyclic 10-membered ring compounds containing two heavier Group 14 atoms and eight carbon atoms [11,12]. With regards to the distannacyclodecane, the sole example of the X-ray structural determination has been reported [12]. Therefore, the structure of **3** is worthy of discussion. The 10-membered ring of **3** has a boat-like conformation (Fig. 1), completely different from that of the previous example having a zigzag conformation where two boat-like moieties are connected with each other from the opposite directions [12]. The tin–carbon distances in **3** (2.117(6)–2.139(6) Å) are in the normal range (2.14 Å) [13].

**Fig. 1.** ORTEP drawings of **3** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–C(1), 2.123(6); Sn(1)–C(8), 2.117(6); Sn(2)–C(4), 2.124(6); Sn(2)–C(5), 2.134(6); C(1)–Sn(1)–C(8), 116.7(2); C(4)–Sn(2)–C(5), 117.1(2).**Fig. 2.** ORTEP drawing of **5** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–C(1), 2.139(5); Sn(1)–C(4), 2.142(4); C(1)–C(2), 1.428(6); C(2)–C(3), 1.468(7); C(3)–C(4), 1.445(6); C(1)–C(5), 1.352(7); C(2)–C(6), 1.374(7); C(3)–C(8), 1.364(6); C(4)–C(7), 1.367(6); C(1)–Sn(1)–C(4), 83.25(18).

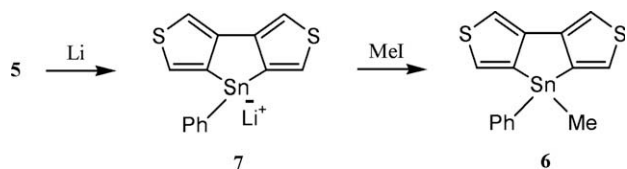
The structure of type B dithienostannole **5** is shown in Fig. 2. Since no structural reports on the molecular structures of Type A or B Group 14 metalloles have appeared to date, type B dithienostannole **5** is the first example of these categories. The tricyclic framework is almost planar and the tin–carbon bond distances in **5** (2.128(5)–2.142(4) Å) are in the normal range (2.14 Å) [13]. The carbon–carbon distances in the central five-membered ring are 1.428(6), 1.445(6) and 1.468(7) Å, which are expected from the resonance form in the annulation mode of **5**.

2.3. Reduction of type A dithienostannole 1

Since type A dithienostannole **1** was very unstable and it could not be purified by either gel permeation chromatography or column chromatography, reduction of a crude product (ratio, **1**:**3** = ca. 10:3) was carried out. Monitoring the reduction by NMR spectroscopy revealed the formation of 2,2'-dilithio-3,3'-bithiophene (**2**) (Scheme 3). The formation of 2,2'-dilithio-3,3'-bithiophene (**2**) was confirmed by its alternative synthesis from 2,2'-dibromo-3,3'-bithiophene [8] and *t*-butyllithium. The formation of **2** clearly shows that reductive cleavage of the tin–thiophene carbon bonds



Scheme 3. Reduction of type A dithienostannole **1**.



Scheme 4. Reduction of type B dithienostannole **5**: formation of dithienostannole anion **7**.

occurred, in contrast to the reduction of hexaphenylstannole with lithium, leading to reductive cleavage of the tin–phenyl bonds to afford the stannole dianion [7]. However, a fate of the tin moiety could not be discussed. Although the ^{119}Sn NMR signals were observed at –127, –120 and –106 ppm, we could assign only the signal at –106 ppm to Ph_3SnLi [14]. According to the ^1H NMR spectrum, 2,2'-dilithio-3,3'-bithiophene (**2**) was found to be a major product and signals in the aromatic region were complicated [15].

2.4. Reduction of type B dithienostannole 5

Reduction of type B dithienostannole **5** with lithium in ether and THF provided complex mixtures. However, when the reduction was carried out in DME, the ^{119}Sn NMR spectrum of the resulting mixture showed only a signal at –211 ppm. After removal of insoluble materials in DME and concentration of the filtrate in a glovebox, the ^{119}Sn NMR spectrum of the residue still showed a signal at –210 ppm. Treatment of the residue with iodomethane then afforded methylphenyldithienostannole **6** in 23% yield [16], revealing the formation of intermediary dithienostannole anion **7** (Scheme 4). After reduction of dithienostannole **5** with lithium in DME followed by removal of insoluble materials in DME and concentration of the filtrate in a glovebox, the residue was washed by hexane to afford dithienostannole anion **7** in 75% yield. Although the effect of solvents on the reduction of type B dithienostannole **5** is still difficult to explain, it results probably from stabilization of the lithium atom by coordination with DME molecules [17].

2.5. NMR spectra of dithienostannole anion 7

The ^1H NMR signals assignable to the thiophene protons of dithienostannole anion **7** (6.57 and 6.80 ppm) shift to upfield, compared with those of the starting stannole **5** (7.21 and 7.50 ppm), suggesting very slight loss of aromaticity of the thiophene moieties of **7**, even though a simple solvent effect cannot be ruled out. In the ^{13}C NMR spectrum, a signal assignable to the α -carbon of the

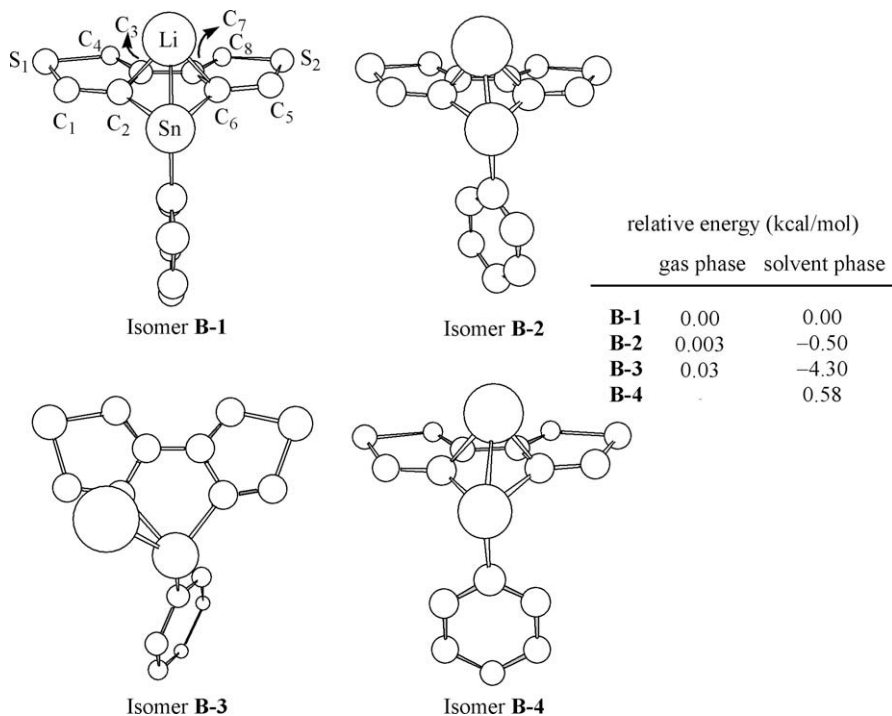


Fig. 3. Geometric optimization of dithienostannole anion **7**.

Table 1
Selected bond length (Å) in isomer B.

C1–C2	1.367	Sn–C2	2.326
C2–C3	1.456	Sn–C6	2.326
C3–C4	1.376	Sn–Li	2.612
C3–C7	1.474		

stannole ring was observed in a low field (171.00 ppm), similar to those of the stannole anions [18]. The ^{119}Sn NMR signal of **7** was observed at -211 ppm, which is in the upfield compared with that of **5** (-168 ppm). Similar upfield shift was also observed from a diphenylstannaindene and the corresponding anion [4a]. The ^7Li NMR signal of **7** was observed at -2.2 ppm, which is located between those of the aromatic stannole dianion (-4.4 ppm) [7] and the non-aromatic stannole anion (-0.64 ppm) [18]. Therefore, the structure and aromaticity of **7** is of considerable interest, even though the X-ray crystallographic analysis could not be achieved.

2.6. Theoretical calculations of dithienostannole anion **7**

To gain insight into the structure and aromaticity of **7**, the geometry of **7** was optimized with hybrid density functional theory at the B3LYP [19] level using the GAUSSIAN 03 program [20]. As indicated in Fig. 3, three different lithiodithienostannoles (**B-1**, **2** and **3**) were found to be minima in the gas phase and one more isomer (**B-4**) was also found in the solvent phase (diethylether) with polarized continuum model (PCM) [21]. In the structure **B-1**, the most stable in the gas phase, the lithium atom is located in the center of the stannole ring and the phenyl ring is perpendicular to the tricyclic framework. The tin–lithium bond distance (Table 1) is calculated to be 2.612 Å, which is slightly shorter than that of the stannole dianion (2.758 and 2.769 Å) [7]. The carbon–carbon distances in the central five-membered ring (1.456 and 1.474 Å) are almost the same as those found in **5** ($1.428(6)$ and $1.468(7)$ Å), while the tin–carbon bonds (2.326 Å) are about 0.2 Å longer than those of **5**. The distances of C1–C2 and C3–C4 bonds (1.367 and 1.376 Å, respectively) in the thiophene moieties suggest that the thiophene rings have still considerable aromatic character. The other three structures have almost the same energies as that of **B-1** in the gas phase with the differences less than 0.03 kcal/mol. Among these structures, the structure **B-3** is worth mentioning. The lithium atom is located nearly above the thiophene ring with the distances between the tin and lithium atoms of 2.623 and 2.884 Å, in the gas phase and the solvent phase, respectively, which are comparable with the corresponding bond distances of **B-1**, and the structure **B-3** is the most stable in the solvent phase. Therefore, the relatively upfield resonance in the ^7Li NMR is probably caused by the equilibrated structure **B-3** in solution, where the lithium atom is shielded by aromatic ring current of the thiophene ring. To gain more insight into the aromaticity of dithienostannole anion **7**, NICS values of the free dithienostannole anion were calculated [22]. NICS(1) and NICS(–1) [23] values of the thiophene rings range from -10.0 to -9.4 ppm, suggesting that they have still considerable aromatic character, while those of the central five-membered ring are -0.21 and 0.55 ppm, respectively, suggesting that the stannole ring is non-aromatic.

3. Conclusions

Reduction of the type A dithienostannole **1** with lithium afforded 2,2'-dilithio-3,3'-bithiophene **2**. In contrast, reduction of the type B dithienostannole **5** with lithium afforded dithienostannole anion **7**, as evidenced by NMR spectroscopy and a trapping experiment. Annulation mode of the dithienostannoles therefore affected reactivity of the dithienostannoles. Theoretical calculations

of dithienostannole anion **7** suggest that the central stannole ring has non-aromatic character, while the thiophene rings are still aromatic. The optimized structure of dithienostannole anion **7**, having a lithium atom in the center of the stannole ring, suggests that dithienostannole anion **7** would be a potential ligand for a transition metal. Further investigation on the synthesis of transition metal complexes using dithienostannole anion **7** and the synthesis of dithienostannole dianions is currently in progress.

4. Experimental

4.1. General procedures

All experiments were performed under an argon atmosphere using usual glass apparatus or a glovebox. THF, diethyl ether, DME and benzene- d_6 were distilled over sodium/benzophenone followed from potassium mirror. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker DPX-400 or a Bruker DRX-400 spectrometer. ^{119}Sn NMR (149 MHz) and ^7Li NMR (156 MHz) spectra were recorded on a Bruker DPX-400 spectrometer. The $J(\text{C}, \text{Sn})$ couplings were observed in the ^{13}C NMR spectra as satellite signals. When the $J(\text{C}, ^{117}\text{Sn}/^{119}\text{Sn})$ coupling constants were observed separately, each of them were calculated. FAB mass spectra were recorded on a JEOL JMS-700AM. Wet column chromatography (WCC) was carried out with Kanto silica gel 60N. Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns with chloroform as the eluant. All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

4.2. Reaction of 2,2'-dilithio-3,3'-bithiophene (**2**) with dichlorodiphenylstannane

To a diethylether (10 mL) solution of 2,2'-dilithio-3,3'-bithiophene (**2**), prepared from 2,2'-dibromo-3,3'-bithiophene [8] (131.1 mg, 0.40 mmol) and butyllithium (0.3 mL, 0.88 mmol; 2.66 M in hexane), was added a THF (4 mL) solution of dichlorodiphenylstannane (157.4 mg, 0.46 mmol) at room temperature and the resulting mixture was heated under reflux. After removal of precipitates, the filtrate was concentrated and the residue was subjected to WCC (hexane:ethyl acetate = 20:1) to afford 7,7,14,14-tetraphenyl-7,14-dihydro[1,6]distannecino[2,3-*b*:5,4-*b'*:7,8-*b''*:10, 9-*b'''*]tetrathiophene (**3**) (21.7 mg, 13%) and 3,3'-bithiophene (**4**) (27.3 mg, 41%). **3**: mp 147 – 148 °C (dichloromethane + hexane). ^1H NMR(CDCl_3): δ = 6.91(d, $J(\text{H}, \text{H}) = 5$ Hz, 4H, C_β), 7.27–7.34(m, 20H), 7.43(d, $J(\text{H}, \text{H}) = 5$ Hz, 4H, C_α); ^{13}C NMR(CDCl_3): δ = 128.28(d, $J(\text{C}, \text{Sn}) = 57$ Hz), 129.03(d, $J(\text{C}, \text{Sn}) = 12$ Hz), 130.19(d, $J(\text{C}, \text{Sn}) = 49$ Hz), 131.90(d, $J(\text{C}, \text{Sn}) = 28$ Hz), 132.85(s), 136.52(d, $J(\text{C}, \text{Sn}) = 80$ Hz), 137.88(s), 148.10(s, $J(\text{C}, \text{Sn}) = 28$ Hz); ^{119}Sn NMR(CDCl_3): δ = -161.4 . Anal. Calc. for $\text{C}_{40}\text{H}_{28}\text{S}_4\text{Sn}_2$ (874.36): C, 54.94; H, 3.22. Found: C, 54.45; H, 3.14%.

4.3. Preparation of type A dithienostannole **1**

To a diethylether (20 mL) solution of 2,2'-dilithio-3,3'-bithiophene (**2**), prepared from 2,2'-dibromo-3,3'-bithiophene [8] (703.4 mg, 2.17 mmol) and *t*-butyllithium (5.5 mL, 8.64 mmol; 1.57 M in pentane), was added copper(I) iodide (872.2 mg, 4.56 mmol) at -78 °C and the resulting mixture was stirred for 1.5 h at the same temperature. To the suspension was added a diethylether (5 mL) solution of dichlorodiphenylstannane (749.6 mg, 2.80 mmol) at -78 °C and the resulting mixture was

stirred overnight, warming to room temperature. After removal of insoluble materials in dichloromethane, the resulting mixture was subjected to GPC to afford 7,7-diphenyl-7*H*-stannolo[2,3-*b*:5,4-*b'*]dithiophene (**1**) (120.3 mg, 13%) and **3** (45.0 mg, 5%). Although the NMR signals of **1** could be completely assigned, the elemental analysis could not be carried out because of its unexpected instability. The compound **1** gradually decomposed to complex mixtures during its purification. **1**: ^1H NMR(CDCl_3): δ = 7.34–7.43(m, 6H), 7.48(d, $J(\text{H}, \text{H})$ = 5 Hz, 2H, C_{α}), 7.60–7.63(m, 4H), 7.66(d, $J(\text{H}, \text{H})$ = 5 Hz, 2H); ^{13}C NMR(CDCl_3): δ = 123.38(d, $J(\text{C}, \text{Sn})$ = 47 Hz), 129.03(d, $J(\text{C}, \text{Sn})$ = 12 Hz), 130.07(d, $J(\text{C}, \text{Sn})$ = 14 Hz), 132.17(s), 134.71(d, $J(\text{C}, \text{Sn})$ = 18 Hz), 135.80(s), 136.89(d, $J(\text{C}, \text{Sn})$ = 47 Hz), 152.51(s, $J(\text{C}, \text{Sn})$ = 55 Hz); ^{119}Sn NMR(CDCl_3): δ = –126.0. FAB MS [$\text{M}+\text{H}$]: 439.

4.4. Preparation of type B dithienostannole 5

To a diethylether (25 mL) solution of 4,4'-dilithio-3,3'-bithiophene, prepared from 4,4'-dibromo-3,3'-bithiophene [**10**] (1008.8 mg, 3.11 mmol) and *t*-butyllithium (8.0 mL, 12.6 mmol; 1.57 M in pentane), was added a diethylether (10 mL) solution of dichlorodiphenylstannane (1166.0 mg, 3.39 mmol) at –78 °C and the resulting mixture was stirred overnight, warming to room temperature. After removal of insoluble materials in dichloromethane, the resulting mixture was subjected to WCC (hexane:ethyl acetate = 20:1) to afford 4,4-diphenyl-4*H*-stannolo[2,3-*c*:4,5-*c'*]dithiophene (**5**) (829.4 mg, 61%). **5**: mp 182 °C (dichloromethane + ethanol)(decomp). ^1H NMR(CDCl_3): δ = 7.37–7.41(m, 6H), 7.51(d, $J(\text{H}, \text{H})$ = 2 Hz, 2H), 7.55(d, $J(\text{H}, \text{H})$ = 2 Hz, 2H), 7.60–7.63(m, 4H); ^{13}C NMR(CDCl_3): δ = 116.55(d, $J(\text{C}, \text{Sn})$ = 48 Hz), 129.14(d, $J(\text{C}, \text{Sn})$ = 59 Hz), 129.83(d, $J(\text{C}, \text{Sn})$ = 13 Hz), 132.07(d, $J(\text{C}, \text{Sn})$ = 60 Hz), 136.74(s, $J(\text{C}, ^{117}\text{Sn}/^{119}\text{Sn})$ = 567/593 Hz), 137.26(s, $J(\text{C}, \text{Sn})$ = 45 Hz), 142.56(s, $J(\text{C}, ^{117}\text{Sn}/^{119}\text{Sn})$ = 463/484 Hz), 147.90(s, $J(\text{C}, ^{117}\text{Sn}/^{119}\text{Sn})$ = 66/69 Hz); ^{119}Sn NMR(CDCl_3): δ = –153.5. Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{S}_2\text{Sn}$ (437.18): C, 54.95; H, 3.23. Found: C, 54.92; H, 3.09%.

4.5. X-ray crystallographic analysis of **3** and **5**

Crystals suitable for X-ray diffraction were obtained by recrystallization in dichloromethane and hexane solution of **3** and in dichloromethane and ethanol solution of **5**. The intensity data were collected at –170 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) and graphite monochromator. **3**: Formula $\text{C}_{40}\text{H}_{28}\text{S}_4\text{Sn}_2$, FW = 874.36, crystal dimension 0.15 × 0.10 × 0.10 mm, monoclinic, space group $P2_1/c$, Z = 8, a = 11.997(2) Å, b = 35.517(7) Å, c = 17.429(3) Å, β = 107.901(5)°, V = 7067(2) Å³, D_{calcd} = 1.643 g cm^{–3}, R_1 = 0.056 ($I > 2\sigma(I)$, 8488 reflections), wR_2 = 0.087 (for all reflections) for 12 812 reflections and 829 parameters, GOF = 1.008. **5**: Formula $\text{C}_{20}\text{H}_{14}\text{S}_2\text{Sn}$, FW = 437.18, crystal dimension 0.10 × 0.10 × 0.08 mm, monoclinic, space group $P2_1/c$, Z = 8, a = 8.3266(4) Å, b = 17.7263(8) Å, c = 23.7621(11) Å, β = 98.094(1)°, V = 3472.3(3) Å³, D_{calcd} = 1.673 g cm^{–3}, R_1 = 0.042 ($I > 2\sigma(I)$, 5278 reflections), wR_2 = 0.092 (for all reflections) for 6276 reflections and 461 parameters, GOF = 1.067.

4.6. Reduction of type A dithienostannole 1

To a diethylether (36 mL) solution of 2,2'-dilithio-3,3'-bithiophene (**2**), prepared from 2,2'-dibromo-3,3'-bithiophene [**8**] (439.4 mg, 1.36 mmol) and *t*-butyllithium (3.5 mL, 5.49 mmol; 1.57 M in pentane), was added copper(I) iodide (529.2 mg, 2.57 mmol) at –78 °C and the resulting mixture was stirred for 1.5 h at the same temperature. To the suspension was added a diethylether (5 mL) solution of dichlorodiphenylstannane

(475.7 mg, 1.38 mmol) at –78 °C and the resulting mixture was stirred overnight, warming to room temperature. In a glovebox, after removal of insoluble materials, the filtrate was concentrated to give a mixture of **1** and **3** in the ratio of 10:3, estimated by ^{119}Sn NMR spectroscopy. Since the ^1H NMR spectrum of the crude product revealed that other compounds besides **1** and **3** were also formed and purification by recrystallization in a glovebox was difficult, the yield of **1** in the mixture could not be estimated. To a diethylether (1 mL) solution of the mixture was added lithium (120.1 mg, 17.3 mmol) and the mixture was stirred for 2 h. After removal of insoluble materials, the residue was dissolved in benzene- d_6 and the formation of 2,2'-dilithio-3,3'-bithiophene (**2**) was confirmed by NMR spectroscopy. The ^{119}Sn NMR spectrum revealed signals at –127, –120 and –106 ppm and the signal at –106 ppm was assigned to Ph_3SnLi [**14**].

4.7. Alternative synthesis of 2,2'-dilithio-3,3'-bithiophene (**2**) from 2,2'-dibromo-3,3'-bithiophene

To a diethylether (15 mL) solution of 2,2'-dibromo-3,3'-bithiophene [**8**] (234.9 mg, 0.72 mmol) was added *t*-butyllithium (1.85 mL, 2.90 mmol; 1.57 M in pentane) at –78 °C and the resulting mixture was stirred for 1 h, warming to room temperature. After removal of volatile substances, the residue was dissolved in benzene- d_6 . **2**: ^1H NMR(C_6D_6): δ = 7.99(d, $J(\text{H}, \text{H})$ = 4 Hz, 2H), 8.05(d, $J(\text{H}, \text{H})$ = 4 Hz, 2H); ^{13}C NMR(CDCl_3): δ = 127.90(d), 136.02(d), 153.93(s), 159.68(s).

4.8. Reduction of type B dithienostannole 5 in diethylether

In a glovebox, to a diethylether (1 mL) solution of type B dithienostannole **5** (90.5 mg, 0.21 mmol) was added lithium (16.2 mg, 2.33 mmol) at room temperature and the resulting mixture was stirred for 9 h. After removal of insoluble materials, monitoring the residue by NMR spectroscopy revealed the formation of a complex mixture.

4.9. Reduction of type B dithienostannole 5 in THF

In a glovebox, to a THF (2 mL) solution of type B dithienostannole **5** (104.2 mg, 0.24 mmol) was added lithium (22.2 mg, 3.20 mmol) at room temperature and the resulting mixture was stirred for 3 h. After removal of insoluble materials, the filtrate was treated with iodomethane (0.19 mL, 3.08 mmol). Although the resulting mixture was complicated, purification of the residue by GPC afforded 4-methyl-4-phenyl-4*H*-stannolo[2,3-*c*:4,5-*c'*]dithiophene (**6**) (0.3 mg, 0.3%). **6**: ^1H NMR(CDCl_3): δ = 0.80(s, $J(\text{H}, \text{Sn})$ = 61, 64 Hz, 3H), 7.33–7.38(m, 2H), 7.43(d, $J(\text{H}, \text{H})$ = 5 Hz, 4H), 7.48–7.50(m, 3H); ^{13}C NMR(CDCl_3): δ = –8.82(q), 115.77(d), 128.62(d), 129.40(d), 131.39(d), 136.30(d), 138.51(s), 143.43(s), 147.49(s); ^{119}Sn NMR(CDCl_3): δ = –114.5. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{S}_2\text{Sn}$ (375.11): C, 48.03; H, 3.23. Found: C, 48.24; H, 3.17%.

4.10. Reduction of type B dithienostannole 5 in DME

In a glovebox, to a DME (1 mL) solution of type B dithienostannole **5** (31.7 mg, 0.07 mmol) was added lithium (5.7 mg, 0.82 mmol) at room temperature and the reaction mixture was stirred overnight. After removal of insoluble materials, the filtrate was treated with iodomethane (0.17 mL, 2.75 mmol). The reaction mixture was purified by GPC to afford **6** (6.2 mg, 23%).

4.11. Isolation of dithienostannole anion 7

In a glovebox, to a DME (1 mL) solution of type B dithienostannole **5** (34.9 mg, 0.08 mmol) was added lithium (6.3 mg,

0.91 mmol) at room temperature and the reaction mixture was stirred overnight. After removal of insoluble materials, the filtrate was concentrated and the residue was washed with hexane to afford 4-lithio-4-phenyl-4*H*-stannolo[2,3-*c*:4,5-*c'*]dithiophene (**7**) (38.2 mg, 75%). **7**: ^1H NMR(DME with $(\text{CD}_3)_2\text{C}=\text{O}$ in a sealed tube for NMR lock): $\delta = 6.36(\text{t}, J(\text{H}, \text{H}) = 2, 7 \text{ Hz}, 1\text{H}), 6.45(\text{dd}, J(\text{H}, \text{H}) = 7, 7 \text{ Hz}, 2\text{H}), 6.57(\text{d}, J(\text{H}, \text{H}) = 2 \text{ Hz}, 2\text{H}), 6.80(\text{d}, J(\text{H}, \text{H}) = 2 \text{ Hz}, 2\text{H}), 7.06(\text{dd}, J(\text{H}, \text{H}) = 2, 7 \text{ Hz}, 2\text{H})$; ^{13}C NMR(DME with $(\text{CD}_3)_2\text{C}=\text{O}$ in a sealed tube for NMR lock): $\delta = 111.56(\text{d}, J(\text{C}, \text{Sn}) = 17 \text{ Hz}), 123.44(\text{d}), 124.27(\text{d}, J(\text{C}, \text{Sn}) = 18 \text{ Hz}), 126.17(\text{d}, J(\text{C}, \text{Sn}) = 41 \text{ Hz}), 137.47(\text{d}, J(\text{C}, \text{Sn}) = 52 \text{ Hz}), 153.09(\text{s}), 166.34(\text{s}), 171.01(\text{s})$; ^{119}Sn NMR(DME with $(\text{CD}_3)_2\text{C}=\text{O}$ in a sealed tube for NMR lock): $\delta = -210.6$; ^7Li NMR(DME with $(\text{CD}_3)_2\text{C}=\text{O}$ in a sealed tube for NMR lock): $\delta = -2.2$.

4.12. Computational details

Geometry optimization was carried out with density functional theory (DFT) at the B3LYP level using the GAUSSIAN 03 program [20]. The basis set employed was [4333111/433111/43] augmented by two *d* polarization functions (*d* exponents 0.253 and 0.078) for Sn [7,24] and 6-311G** for C, H, Li and S. To estimate the solvation energy, the geometry of dithienostannole anion **7** was reoptimized at the same level in the presence of the solvent (dithylether) with polarized continuum model (PCM) [21].

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Appendix A. Supplementary material

CCDC 728387 and 728422 contain the supplementary crystallographic data for compounds **3** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.026.

References

- [1] (a) For examples of reviews, see: E. Colomer, R.J.P. Corriu, M. Lheureux, *Chem. Rev.* 90 (1990) 265; (b) J. Dubac, C. Guérin, P. Meunier, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, John Wiley and Sons, Chichester, 1998, p. 1961; (c) M. Saito, M. Yoshioka, *Coord. Chem. Rev.* 249 (2005) 765.
- [2] (a) For Si: H. Gilman, R.D. Gorsich, *J. Am. Chem. Soc.* 80 (1958) 3243; (b) J.-H. Hong, P. Boudjouk, I. Stoenescu, *Organometallics* 15 (1996) 2179; (c) S.-B. Choi, P. Boudjouk, P. Wei, *J. Am. Chem. Soc.* 120 (1998) 5814; (d) S.-B. Choi, P. Boudjouk, *J. Chem. Soc., Dalton Trans.* (2000) 841; (e) Y. Liu, T.C. Stringfellow, D. Ballweg, I.A. Guzei, R. West, *J. Am. Chem. Soc.* 124 (2002) 49.
- [3] (a) For Ge: S.-B. Choi, P. Boudjouk, K. Qin, *Organometallics* 19 (2000) 1806; (b) Y. Liu, D. Ballweg, T. Müller, I.A. Guzei, R.W. Clark, R. West, *J. Am. Chem. Soc.* 124 (2002) 12174.
- [4] (a) For Sn: M. Saito, M. Shimosawa, M. Yoshioka, K. Ishimura, S. Nagase, *Organometallics* 25 (2006) 2967; (b) M. Saito, M. Shimosawa, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* 35 (2006) 940.
- [5] (a) For very recent examples, see: M.R. Harpham, O. Süzer, C.-Q. Ma, P. Bäuerle, T. Goodson III, *J. Am. Chem. Soc.* 131 (2009) 973; (b) J.-C. Li, H.-Y. Lee, S.-H. Lee, K. Zong, S.-H. Jin, Y.-S. Lee, *Synth. Met.* 159 (2009) 201.
- [6] J. Ohshita, Y. Kurushima, K.-H. Lee, A. Kunai, Y. Ooyama, Y. Harima, *Organometallics* 26 (2007) 6591.
- [7] M. Saito, R. Haga, M. Yoshioka, K. Ishimura, S. Nagase, *Angew. Chem., Int. Ed.* 44 (2005) 6553.
- [8] M.J. Marsella, K. Yoon, F.S. Tham, *Org. Lett.* 3 (2001) 2129.
- [9] Even though the mechanism for the formation of type A dithienostannole **1** using copper(I) iodide is still unclear, the expected 1,4-dicopper-1,3-butadiene would function as a key intermediate, see: C. Wang, J. Yuan, G. Li, Z. Wang, S. Zhang, Z. Xi, *J. Am. Chem. Soc.* 128 (2006) 4564.
- [10] A. Rajca, M. Miyasaka, M. Pink, H. Wang, S. Rajca, *J. Am. Chem. Soc.* 126 (2004) 15211.
- [11] Y. Miyake, M. Wu, M.J. Rahman, Y. Kuwatani, M. Iyoda, *J. Org. Chem.* 71 (2006) 6110.
- [12] (a) A.G. Davies, M.-W. Tse, J.D. Kennedy, W. McFarlane, G.S. Pyne, M.F.C. Ladd, D.C. Povey, *J. Chem. Soc., Chem. Commun.* (1978) 791; (b) A.G. Davies, M.-W. Tse, J.D. Kennedy, W. McFarlane, G.S. Pyne, M.F.C. Ladd, D.C. Povey, *J. Chem. Soc., Perkin Trans. 2* (1981) 369.
- [13] K.M. Mackay, in: S. Patai (Ed.), *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Wiley, Chichester, 1995 (Chapter 2).
- [14] M. Saito, Y. Okamoto, M. Yoshioka, *Appl. Organomet. Chem.* 19 (2005) 894.
- [15] According to our experiences, diphenyl-substituted stannoles are more stable than the corresponding methyl-substituted stannoles and type A dithienostannole **1** was very unstable. Therefore, type A methyl-substituted stannoles are thought to be more unstable than **1** and trapping experiments with electrophiles such as iodomethane were not carried out. Even 2,2'-dibromo-3,3'-bithiophene[8] is very unstable and should be used as soon as possible after the preparation.
- [16] Although the yield of **6** was not high, the ^{119}Sn NMR spectrum of the crude product revealed two signals at -114 and -92 ppm, the former of which was a main signal, assigned to methylphenyldithienostannole **6**. Therefore, the moderate yield of **6** was probably caused by loss of mass during the workup process.
- [17] The lithium atom is known to be coordinated with DME molecules, for example, see: M. Saito, S. Imaizumi, T. Tajima, K. Ishimura, S. Nagase, *J. Am. Chem. Soc.* 129 (2007) 10974.
- [18] R. Haga, M. Saito, M. Yoshioka, *Eur. J. Inorg. Chem.* (2007) 1297.
- [19] (a) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648; (b) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN 03*, Revision E. 01, Gaussian Inc., Wallingford, CT, 2004.
- [21] (a) B. Mennucci, J. Tomasi, *J. Chem. Phys.* 106 (1997) 5151; (b) M.T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* 107 (1997) 3032; (c) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* 286 (1998) 253; (d) M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* 117 (2002) 43.
- [22] (a) P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R.v.E. Hommes, *J. Am. Chem. Soc.* 118 (1996) 6317; (b) P.v.R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N.J.R.v.E. Hommes, *Org. Lett.* 3 (2001) 2465.
- [23] The side where the phenyl ring is located is defined to be a minus Z region.
- [24] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzerm, Y. Sakai, H. Tatewaki, *GAUSSIAN Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, 1984.