Synthesis, Structures and Reactions of Novel 9,10-Dihydro-9,10-distannaanthracenes

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A method for the synthesis of 9,10-dihydro-9,10-distannaanthracenes has been improved and applied to the synthesis of novel unsymmetrical 9,10-dihydro-9,10-distannaanthracenes. The first 9,9,10,10-tetrahalo-9,10-dihydro-9,10-distannaanthracenes were successfully synthesized by halogenation of 9,9,10,10-tetrakis(*p*-methoxyphenyl)-9,10-dihydro-9,10-distannaanthracene. The structures of the newly obtained 9,10-dihydro-9,10-distannaanthracenes were determined by X-ray analysis.

Introduction

Since the first synthesis of 9,9,10,10-tetraphenyl-9,10-dihydro-9,10-disilaanthracene,[1] studies of the synthesis, structures, and reactions of 9,10-dihydro-9,10-disilaanthracene have been developed.[2] The corresponding germanium analogs, 9,10-dihydro-9,10-digermaanthracenes, have also been synthesized and characterized.[3] One of the interesting features of 9,10-dihydro-9,10-dimetallaanthracenes is the conformations of their central six-membered rings which are dependent on substituents on the metal.[4−7] Although a few 9,10-dihydroanthracenes having a tin atom at the 10-position have been reported,[4,8] only one report on the 9,10-dihydro-9,10-distannaanthracene has appeared, but without synthetic or structural details.[9] During the course of our studies on tin-containing compounds with unique structures, we have already reported the first syntheses and structures of 9,9,10,10-tetramethyl- and 9,9,10,10-tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracenes.[7,10] The tetramethyl derivative has a butterfly conformation, while the tetra-*tert*-butyl derivative has a planar structure. The dependence of conformation on substituents prompted us to investigate some other 9,10-dihydro-9,10-distannaanthracenes having aryl groups and those with unsymmetrical structures. The utility of 9,10-dihydro-9,10-dimetallaanthracene derivatives as potential precursors for metal-containing reactive species is also of interest. Recently, fascinating silicon-containing reactive species such as a bis(silyl anion)[11] and a relatively stable silyl radical[6] have been reported to be derived from 9,10-dihydro-9,10-disilaanthracenes. 9,9,10,10-Tetrahalogenated 9,10-dihydro-9,10-distannaanthracenes are expected to be good precursors for reactive tin-containing species having a 9,10-distannaanthracene skeleton. However, no report on such halogenated derivatives has appeared.

We report herein an improved method for the synthesis of aryl-substituted and unsymmetrical substituted 9,10-dihydro-9,10-distannaanthracenes. Halogenation of 9,9,10,10-tetrakis(*p*-methoxyphenyl)-9,10-dihydro-9,10-distannaanthracene to give the first 9,9,10,10-tetrahalo-9,10-dihydro-9,10-distannaanthracenes is also reported. The structures of the newly obtained 9,10-dihydro-9,10-distannaanthracenes are discussed.

Results and Discussion

Improved Method for the Synthesis of 9,10-Dihydro-9,10-distannaanthracenes

A previous publication reported the synthesis of 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**1**) from the reaction of bis(*o*-bromophenyl)dimethylstannane (**2**) and dichlorodimethylstannane with magnesium in the presence of a catalytic amount of copper(I) cyanide in 25% yield.[7] By using *tert*-butyllithium for the lithiation of **2** in THF at −78 °C, the yield of **1** was increased to 51% (Scheme 1).

Introduction of *p*-methoxyphenyl groups on the tin was examined using *tert*-butyllithium. Bis(*o*-bromophenyl)bis(*p*-methoxylphenyl)stannane (**3**) was synthesized by the reaction of (2-bromophenyl)lithium with bis(*p*-methoxyphenyl)dichlorostannane[12] in 48% yield. Lithiation of **3** using *tert*-butyllithium and subsequent reaction with bis(*p*-methoxyphenyl)dichlorostannane gave the 9,9,10,10-tetrakis(*p*-methoxyphenyl)-substituted compound **4** in 46% yield (Scheme 1).

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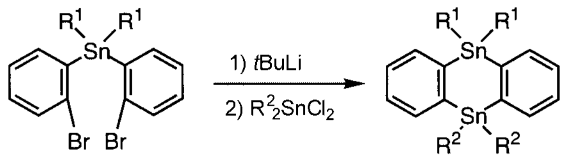
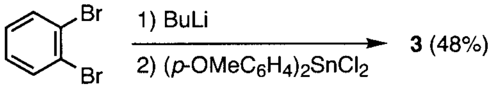


2 (R^1 = Me)
3 (R^1 = p-OMeC$_6$H$_4$)

1 ($R^1 = R^2$ = Me: 51%)
4 ($R^1 = R^2$ = p-OMeC$_6$H$_4$: 46%)
5 (R^1 = Me, R^2 = tBu: 19%)
6 (R^1 = p-OMeC$_6$H$_4$, R^2 = Me: 14%)

	1	**4**	**5**	**6**	**9**	**10**
R^1	Me	p-OMeC$_6$H$_4$	Me	p-OMeC$_6$H$_4$	Cl	I
R^2	Me	p-OMeC$_6$H$_4$	tBu	Me	Cl	I



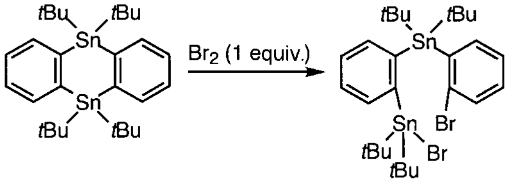
Scheme 1

Synthesis of Unsymmetrically-Substituted 9,10-Dihydro-9,10-distannaanthracenes

This improved method can be applied to the synthesis of unsymmetrically-substituted 9,10-dihydro-9,10-distannaanthracenes. Thus, lithiation of **2** and **3** with *tert*-butyllithium in THF at −78 °C and subsequent treatment with di-*tert*-butyldichlorostannane and dichlorodimethylstannane gave the 9,9-di-*tert*-butyl-10,10-dimethyl-substituted and 9,9-bis(*p*-methoxyphenyl)-10,10-dimethyl-substituted compounds **5** and **6** in yields of 19 and 14%, respectively (Scheme 1). The structures of **5** and **6** were determined using ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

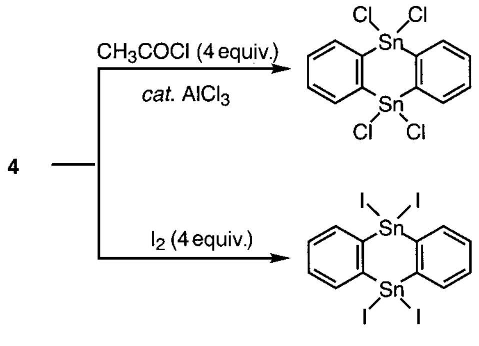
Halogenation of 9,10-Dihydro-9,10-distannaanthracenes

In order to prepare further functionalized 9,10-dihydro-9,10-distannaanthracenes, the halogenations of the tetra-*tert*-butyl-substituted 9,10-dihydro-9,10-distannaanthracene **7**[7] and the 9,9,10,10-tetrakis(*p*-methoxyphenyl)-substituted 9,10-dihydro-9,10-distannaanthracene **4** were investigated. Reaction of **7** with bromine (1 equiv.) gave the dibromide **8** (77%) through the cleavage of a tin−phenyl bond because the ease of cleavage of the Sn−C bond is in the order of Sn−aromatic > −vinyl > −alkyl (Scheme 2).[13] Conversely, chlorination of **4** using acetyl chloride and aluminum chloride[14] gave 9,9,10,10-tetrachloro-9,10-dihydro-9,10-distannaanthracene (**9**), reflecting the ease of cleavage of an Sn−*p*-methoxyphenyl bond (Scheme 3). The *p*-methoxyphenyl group on tin is easily substituted by a halogen.[14] Reaction of **4** with iodine gave the tetraiodide **10** (Scheme 3). These haloganated 9,10-dihydro-9,10-distannaanthracenes, the first examples of a 9,9,10,10-tetrahalo-9,10-dihydro-9,10-distannaanthracene, are expected to be good precursors for reactive tin-containing species such as 9,10-distannaanthracene.



7 **8** (77%)

Scheme 2



9 (18%)

10 (51%)

Scheme 3

X-ray Crystallographic Structures of the Newly Obtained 9,10-Dihydro-9,10-distannaanthracenes 4, 6, and 10

The X-ray crystallographic analyses were carried out at room temperature. The molecular structures of **4**, **6**, and **10** with selected bond lengths and angles are shown in Figures 1, 2, and 3, respectively. The central six-membered ring of

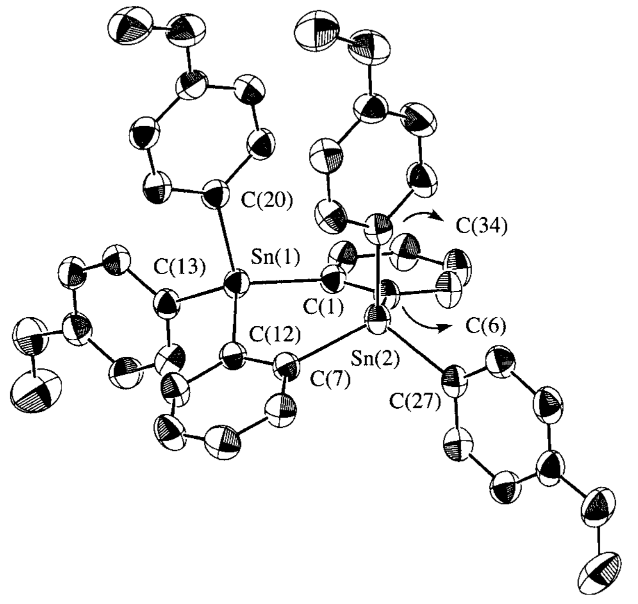


Figure 1. ORTEP drawing of **4** with thermal ellipsoids plots (40% probability for non-hydrogen atoms); selected bond lengths [Å] and angles (deg): Sn(1)−C(13) 2.127(3), Sn(1)−C(20) 2.127(3), Sn(2)−C(27) 2.135(3), Sn(2)−C(34) 2.130(3); C(1)−Sn(1)−C(12) 108.90(12), C(6)−Sn(2)−C(7) 109.07(12), C(13)−Sn(1)−C(20) 111.22(13), C(7)−Sn(2)−C(34) 109.00(13)

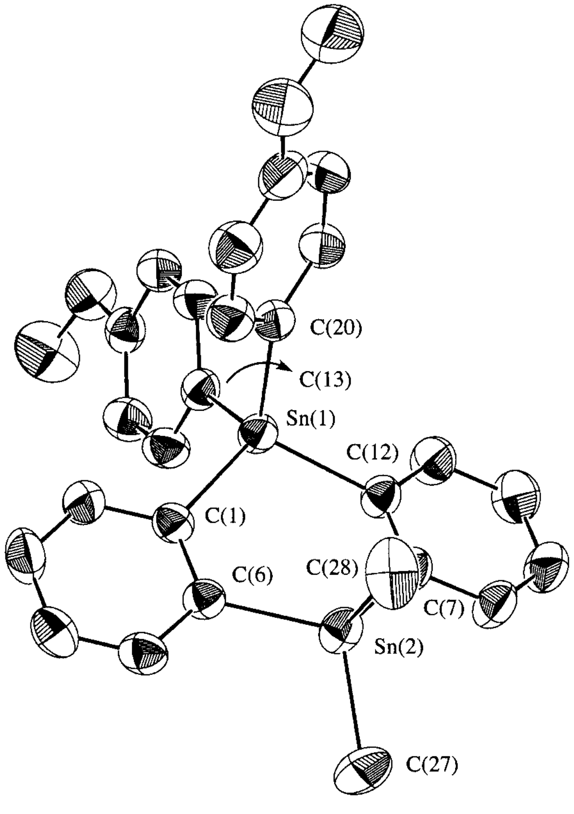


Figure 2. ORTEP drawing of **6** with thermal ellipsoids plots (40% probability for non-hydrogen atoms); selected bond lengths [Å] and angles (deg): Sn(1)−C(13) 2.137(3), Sn(1)−C(20) 2.146(4), Sn(2)−C(27) 2.145(5), Sn(2)−C(28) 2.128(5); C(1)−Sn(1)−C(12) 110.18(13), C(6)−Sn(2)−C(7) 108.63(13), C(13)−Sn(1)−C(20) 108.19(13), C(7)−Sn(2)−C(27) 112.3(2)

6 adopts a boat conformation and hence the tricyclic framework has a butterfly conformation with a dihedral angle of 156° as observed in the 9,9,10,10-tetramethyl derivative (143°).[7] Although 9,9,10,10-tetraphenyl-9,10-dihydro-9,10-disilaanthracene has a planar structure,[15] the central six-membered ring of **4** has a boat conformation with a dihedral angle of 149° due to the $Sn-C_6H_4OMe$-*p* bonds being longer than the Si−Ph bonds in the tetraphenyl compound so that the *p*-methoxyphenyl group can be orientated in a pseudoaxial position. The tetra-iodo derivative **10** has a planar structure, as observed in the 9,9,10,10-tetra-*tert*-butyl derivative,[7] probably due to the steric bulk of the iodine atom.

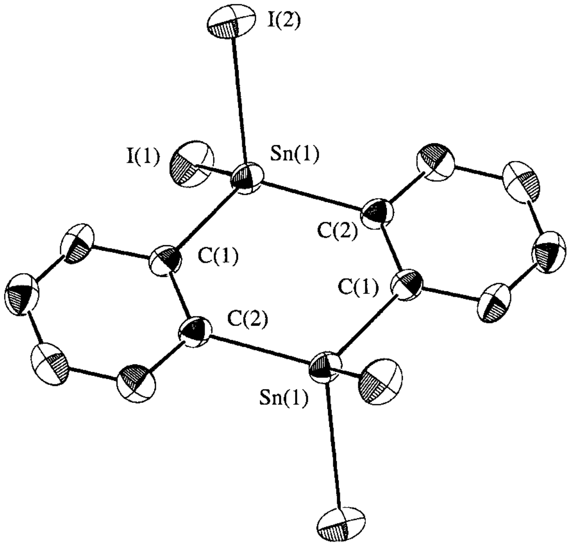


Figure 3. ORTEP drawing of **10** with thermal ellipsoids plots (40% probability for non-hydrogen atoms); selected bond lengths [Å] and angles (deg): Sn(1)−I(1) 2.6812(8), Sn(1)−I(2) 2.6795(8), Sn(1)−C(1) 2.129(7), Sn(1)−C(2) 2.124(8); C(1)−Sn(1)−C(2) 114.8(3), I(1)−Sn(1)−I(2) 104.76(3)

Conclusion

A novel method for the synthesis of 9,10-dihydro-9,10-distannanthracenes has been developed and novel 9,10-dihydro-9,10-distannanthracenes having unsymmetrical structures have been synthesized. Halogenation of 9,9,10,10-tetrakis(*p*-methoxyphenyl)-9,10-dihydro-9,10-distanna-anthracene gave the first 9,9,10,10-tetrahalo-9,10-dihydro-9,10-distannaanthracenes. Although the 9,10-dihydro-9,10-distannanthracenes having *p*-methoxyphenyl groups on the tin have a butterfly conformation, the 9,9,10,10-tetraiodo derivative has a planar structure for steric reasons. Further investigations on the synthesis of reactive tin-containing species having a 9,10-distannaanthracene skeleton from 9,9,10,10-tetrahalo derivatives are currently in progress.

Experimental Section

General Procedure: All reactions were carried out under argon. THF and diethyl ether used in the syntheses were distilled from sodium benzophenone ketyl under an argon atmosphere before use. Magnesium (turnings) was purchased from Wako Pure Chemical Industries, Ltd. ^{1}H (400 MHz), ^{13}C NMR (101 MHz) and ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Although $^{n}J(\text{Sn}-{}^{13}\text{C})$ couplings were observed in the ^{13}C NMR spectra as satellite signals, most of the $^{n}J({}^{119}\text{Sn}-{}^{13}\text{C})$ and $^{n}J({}^{117}\text{Sn}-{}^{13}\text{C})$ values could not be separately estimated because of broadening. The multiplicities of signals in the ^{13}C NMR spectra given in parentheses were deduced from DEPT spectra. Wet column chromatography (WCC) was carried out by using Merck Kieselgel 60 (SiO_2). All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Chemical Analysis Center, Saitama University. Data for the X-ray crystallographic analyses were collected on Mac Science Xdip or MXC18 K diffractometers with Mo-K_α radiation ($\lambda = 0.71073$ Å) and the structures were solved by direct methods.

Improved Synthesis of 9,9,10,10-Tetramethyl-9,10-dihydro-9,10-distannaanthracene (1): To a THF (10 mL) solution of bis(*o*-bromophenyl)dimethylstannnane[7] (**2**) (232 mg, 0.50 mmol) was added *t*BuLi (1.60 M in pentane; 1.25 mL, 2.00 mmol) at −78 °C and the resultant solution was stirred at this temperature for 1 h. After addition of a THF (5 mL) solution of dichlorodimethylstannane (110 mg, 0.50 mmol) at the same temperature, the reaction mixture was allowed to warm to room temperature. The resultant mixture was extracted with diethyl ether and the organic layer was washed with aqueous NH_4Cl. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane/ethyl acetate, 20:1) to afford 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene[7] (**1**) (116 mg, 51%).

Preparation of Bis(*o*-bromophenyl)bis(*p*-methoxylphenyl)stannane (3): To a solution of butyllithium (1.56 M in hexane; 6.24 mL, 4.00 mmol) in a mixture of THF (10 mL) and diethyl ether (10 mL) was added 1,2-dibromobenzene (0.72 mL, 5.97 mmol) at −110 °C and the resultant solution was stirred at this temperature for 1.5 h. Subsequently, bis(*p*-methoxyphenyl)dichlorostannane[12] (1.304 g, 3.23 mmol) in THF (5 mL) and diethyl ether (5 mL) was added at −110 °C. The reaction mixture was allowed to warm to room temperature. The resultant mixture was extracted with diethyl ether and the organic layer was washed with aqueous NH_4Cl. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane/dichloromethane, 1:3) followed by recrystallization from dichloromethane and methanol to give bis(*o*-bromophenyl)bis(*p*-methoxylphenyl)stannane (**3**) (0.926 g, 48%). **3**: M.p. 142−145 °C (recrystallization from dichloromethane/methanol). ^{1}H NMR: $\delta = 3.82$ (s, 6 H), 6.94−6.99 (m, 4 H), 7.25−7.27 (m, 4 H), 7.38−7.40 (m, 2 H), 7.52−7.68 (m, 6 H). ^{13}C NMR: $\delta = 55.0$ (q), 114.4 [d, $J(\text{Sn}-\text{C}) = 61$ Hz), 126.9 [d, $J(\text{Sn}-\text{C}) = 47$ Hz), 128.4 (s), 130.9 (d), 132.1 [d, $J(\text{Sn}-\text{C}) = 31$ Hz), 132.5 [s, $J(\text{Sn}-\text{C}) = 14$ Hz], 138.6 [d, $J(\text{Sn}-\text{C}) = 46$ Hz], 139.3 [d, $J(\text{Sn}-\text{C}) = 36$ Hz), 144.5 (s), 160.4 (s). ^{119}Sn NMR: $\delta = -116.5$ ppm. $C_{26}H_{22}Br_2O_2Sn$ (644.98): calcd. C 48.42, H 3.44; found C 48.54, H 3.35.

Preparation of 9,9,10,10-Tetrakis(*p*-methoxyphenyl)-9,10-dihydro-9,10-distannaanthracene (4): To a THF (10 mL) solution of **3** (1.006 g, 1.56 mmol) was added *t*BuLi (1.6 M in pentane; 3.0 mL, 4.8 mmol) at −78 °C and the resultant solution was stirred at this temperature for 20 min. After addition of a THF (5 mL) solution of bis(*p*-methoxyphenyl)dichlorostannane[12] (0.684 g, 1.69 mmol) at the same temperature, the reaction mixture was allowed to warm to room temperature. The resultant mixture was extracted with diethyl ether and the organic layer was washed with aqueous NH_4Cl. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane/dichloromethane, 1:4) followed by recrystallization from hexane and dichloromethane to give 9,9,10,10-tetrakis(*p*-methoxyphenyl)-9,10-dihydro-9,10-distannaanthracene (**4**) (0.584 g, 46%). **4**: M.p. 221−222 °C (recrystallization from hexane/dichloromethane). ^{1}H NMR: $\delta = 3.77$ (s, 12 H), 6.79−6.83 (m, 8 H), 7.28−7.29 (m, 4 H), 7.34−7.36 (m, 8 H), 7.57−7.60 (m, 4 H). ^{13}C NMR: $\delta = 54.9$ (q), 114.3 (d), 128.6 [s, $^{1}J(\text{Sn}-\text{C}) = 522$, 546 Hz], 128.8 [d, $J(\text{Sn}-\text{C}) = 49$ Hz], 137.3 [d, $J(\text{Sn}-\text{C}) = 45$, 55 Hz], 138.4 [d, $J(\text{Sn}-\text{C}) = 44$ Hz], 150.8 [s, $^{1}J(\text{Sn}-\text{C}) = 520$, 544, $^{2}J(\text{Sn}-\text{C}) = 52$ Hz], 160.3 (s). ^{119}Sn NMR: $\delta = -173.6$ [$^{3}J(\text{Sn}-\text{Sn}) = 761$ Hz] ppm. $C_{40}H_{36}O_4Sn_2$ (818.16): calcd. C 58.72, H 4.44; found C 58.63, H 4.29.

Preparation of 9,9-Di-*tert*-butyl-10,10-dimethyl-9,10-dihydro-9,10-distannaanthracene (5): To a THF (10 mL) solution of **2** (240 mg, 0.52 mmol) was added *t*BuLi (1.60 M in pentane; 1.30 mL, 2.08 mmol) at −78 °C and the resultant solution was stirred at this temperature for 30 min. To the reaction mixture was added a THF (5 mL) solution of di-*tert*-butyldichlorostannane (160 mg, 0.50 mmol) at the same temperature. After stirring for 2 h at −78 °C, the reaction mixture was gradually allowed to warm to room temperature. The resultant mixture was extracted with diethyl ether and the organic layer was washed with aqueous NH_4Cl. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane/ethyl acetate, 100:1) to afford 9,9-di-*tert*-butyl-10,10-dimethyl-9,10-dihydro-9,10-distannaanthracene (**5**) (52 mg, 19%). **5**: M.p. 77−79 °C (recrystallization from hexane/methanol). ^{1}H NMR: $\delta = 0.36$ [s, 6 H, $^{2}J(\text{Sn}-\text{H}) = 52$, 55 Hz], 1.30 [s, 18 H, $^{3}J(\text{Sn}-\text{H}) = 63$, 65 Hz], 7.27−7.30 (m, 4 H), 7.54−7.56 (m, 4 H). ^{13}C NMR: $\delta = -7.7$ [q, $^{1}J(\text{Sn}-\text{C}) = 329$, 345 Hz], 29.9 [s, $^{1}J(\text{Sn}-\text{C}) = 365$, 382 Hz], 31.5 (q), 127.6 (d), 128.1 (d), 136.3 [d, $J(\text{Sn}-\text{C}) = 42$, 48 Hz], 137.4 [d, $J(\text{Sn}-\text{C}) = 42$, 54 Hz], 152.0 [s, $^{1}J(\text{Sn}-\text{C}) = 362$, 379, $^{2}J(\text{Sn}-\text{C}) = 53$ Hz], 153.4 [s, $^{1}J(\text{Sn}-\text{C}) = 500$, 523, $^{2}J(\text{Sn}-\text{C}) = 35$ Hz]. ^{119}Sn NMR: $\delta = -156.3$ [$^{3}J(\text{Sn}-\text{Sn}) = 497$, 546 Hz], −121.1 [$^{3}J(\text{Sn}-\text{Sn}) = 497$, 546 Hz] ppm. $C_{22}H_{32}Sn_2$ (533.94): calcd. C 49.49, H 6.04; found C 49.96, H 6.06.

Preparation of 9,9-Bis(*p*-methoxyphenyl)-10,10-dimethyl-9,10-dihydro-9,10-distannaanthracene (6): To a THF (5 mL) solution of **3** (196 mg, 0.30 mmol) was added *t*BuLi (1.60 M in pentane; 0.75 mL, 1.20 mmol) at −78 °C and the resultant solution was stirred at this temperature for 1 h. To the reaction mixture was added a THF (5 mL) solution of dichlorodimethylstannane (74 mg, 0.30 mmol) at the same temperature. After stirring for 1 h at −78 °C, the reaction mixture was gradually allowed to warm to room temperature. The resultant mixture was extracted with diethyl ether and the organic layer was washed with aqueous NH_4Cl. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane/ethyl acetate, 6:1) to afford 9,9-bis(*p*-methoxyphenyl)-10,10-dimethyl-9,10-dihydro-9,10-distannaanthracene (**6**) (27 mg, 14%). **6**: M.p. 115−118 °C (recrystallization from hexane/dichloromethane). ^{1}H NMR: $\delta = 0.32$ [s, 6 H, $^{2}J(\text{Sn}-\text{H}) = 54$, 56 Hz], 3.80 (s, 6 H), 6.93 (d, $J = 9$ Hz, 4 H), 7.24−7.28 (m, 2 H), 7.30−7.34 (m, 2 H), 7.38−7.50 (m, 4 H), 7.53−7.65 (m, 4 H). ^{13}C NMR: $\delta = -8.5$ [q, $^{1}J(\text{Sn}-\text{C}) = 344$ Hz], 55.0 (q), 114.5 [d, $J(\text{Sn}-\text{C}) = 55$ Hz], 128.3 (d), 128.6 (d), 128.9 (s), 136.1 [d, $J(\text{Sn}-\text{C}) = 46$, 56 Hz], 136.9 [d, $J(\text{Sn}-\text{C}) = 55$ Hz], 138.4 [d, $J(\text{Sn}-\text{C}) = 44$ Hz], 150.0 (s), 152.7 (s), 160.5 (s). ^{119}Sn NMR: $\delta = -171.6$ [$^{3}J(\text{Sn}-\text{Sn}) = 727$, 796 Hz], −116.5 [$^{3}J(\text{Sn}-\text{Sn}) = 727$, 796 Hz] ppm. $C_{28}H_{28}O_2Sn_2$ (633.96): calcd. C 53.05, H 4.45; found C 53.32, H 4.38.

Reaction of 9,9,10,10-Tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracene (7) with Bromine: To a carbon tetrachloride (15 mL) solution of **7** (162 mg, 0.26 mmol) was added a carbon tetrachloride (5 mL) solution of bromine (42 mg, 0.26 mmol) at room temperature. After removal of the solvent, the residue was recrystallized from dichloromethane and methanol to give [2- (bromodi-*tert*-butylstannyl)](2-bromophenyl)di-*tert*-butylstannane (**8**) (133 mg, 77%). **8**: M.p. 182−184 °C (recrystallization from dichloromethane/methanol). ^{1}H NMR: δ = 1.26 [s, 18 H, ^3J(Sn−H) = 81, 84 Hz], 1.36 [br. s, 18 H, ^3J(Sn−H) = 68 Hz], 7.04−7.17 (m, 3 H), 7.20−7.24 (m, 1 H), 7.31−7.35 (m, 1 H), 7.50−7.55 (m, 1 H), 7.73−7.75 (m, 1 H). ^{13}C NMR: δ = 30.8 (q), 31.6 (br. q), 35.9 [s, ^1J(Sn−C) = 360, 377 Hz], 125.8 [d, J(Sn−C) = 34 Hz], 126.4 [d, J(Sn−C) = 11, 62 Hz], 127.5 [d, J(Sn−C) = 15, 40 Hz], 129.0 (d), 131.7 (s), 131.8 (d), 136.8 [d, J(Sn−C) = 48, 83 Hz], 139.2 [d, J(Sn−C) = 23 Hz], 141.0 [d, J(Sn−C) = 38, 61 Hz], 151.4 [s, J(Sn−C) = 43 Hz], 151.9 (s), 153.3 [s, J(Sn−C) = 50 Hz]. ^{119}Sn NMR: δ = −78.5 (br.), 3.9 ppm. $C_{28}H_{44}Br_2Sn_2$ (777.92): calcd. C 43.23, H 5.70; found C 43.45, H 5.72.

Preparation of 9,9,10,10-Tetrachloro-9,10-dihydro-9,10-distannaanthracene (9): To a toluene (5 mL) solution of **4** (183 mg, 0.22 mmol) was added acetyl chloride (0.063 mL, 0.84 mmol) in the presence of a catalytic amount of aluminum trichloride at 0 °C. After separation of insoluble materials in dichloromethane by filtration, the residue was crystallized from chloroform and dichloromethane to afford 9,9,10,10-tetrachloro-9,10-dihydro-9,10-distannaanthracene (**9**) (24 mg, 18%). **6**: M.p. 285−288 °C (decomp.) (recrystallization from dichloromethane/chloroform). ^{1}H NMR: δ = 7.63−7.69 (m, 4 H), 7.74−7.94 (m, 4 H). ^{13}C NMR: δ = 133.1 [d, J(Sn−C) = 92 Hz, C_β], 137.1 [d, J(Sn−C) = 84, 103 Hz, C_α], 152.4 (s, C_{ipso}) ppm. $C_{12}H_8Cl_4Sn_2$ (531.4): calcd. C 27.12, H 1.52; found C 27.28, H 1.42.

Preparation of 9,9,10,10-Tetraiodo-9,10-dihydro-9,10-distannaanthracene (10): A dichloromethane (50 mL) solution of iodine (700 mg, 2.76 mmol) was added to a dichloromethane (10 mL) solution of **4** (566 mg, 0.69 mmol). The mixture was heated to reflux for 1 day. After separation of insoluble materials in diethyl ether by filtration, the residue was crystallized from dichloromethane to afford 9,9,10,10-tetraiodo-9,10-dihydro-9,10-distannaanthracene (**10**) (316 mg, 51%). **10**: M.p. 278−280 °C (recrystallization from dichloromethane). ^{1}H NMR: δ = 7.52−7.55 (m, 4 H), 7.63−7.83 (m, 4 H). ^{13}C NMR: δ = 132.2 [d, J(Sn−C) = 14, 66 Hz, C_β], 136.9 [d, J(Sn−C) = 46, 76 Hz, C_α], 148.3 (s, C_{ipso}). ^{119}Sn NMR: δ = 189.1 ppm. $C_{12}H_8I_4Sn_2$ (897.2): calcd. C 16.06, H 0.90; found C 16.16, H 0.77.

Crystal and Experimental Data at 298 K for 4: $C_{40}H_{36}O_4Sn_2$, M = 818.104, crystal size 0.30 × 0.30 × 0.20 mm, monoclinic, a = 18.191(5), b = 11.400(2), c = 19.522(10) Å, β = 118.23(6) °, V = 3572(2) Å^3, D = 1.521 Mg·m^{-3}, μ(Mo-K_α) = 1.437 mm^{-1}, Z = 4, space group $P2_1/c$. Data were collected on a Mac Science MXC18 K diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR[16] and refined by full-matrix least-squares procedures (SHELXL-97)[17] on F^2 for all reflections (7777 reflections) for 416 variable parameters. $R_1(wR_2)$ = 0.037 (0.091) for all data, GOF = 1.158.

Crystal and Experimental Data at 298 K for 6: $C_{28}H_{28}O_2Sn_2$, M = 633.91, crystal size 0.30 × 0.30 × 0.10 mm, monoclinic, a = 17.2610(5), b = 9.4070(3), c = 28.0101(6) Å, β = 144.904(1)°, V = 2615.0(1) Å^3, D = 1.610 Mg·m^{-3}, μ(Mo-K_α) = 1.931 mm^{-1}, Z = 4, space group $P2_1/c$. Data were collected on a Mac Science DIP3000 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR[16] and refined by full-matrix least-squares procedures (SHELXL-97)[17] on F^2 for all reflections (5432 reflections) for 290 variable parameters. $R_1(wR_2)$ = 0.039 (0.090) for all data, GOF = 1.060.

Crystal and Experimental Data at 298 K for 10: $C_6H_4I_2Sn$, M = 448.596, crystal size 0.40 × 0.40 × 0.20 mm, triclinic, a = 7.407(5), b = 8.042(4), c = 9.203(7) Å, α = 102.42(5), β = 108.29(5), γ = 104.52(6)°, V = 477.4(5) Å^3, D = 3.121 Mg·m^{-3}, μ(Mo-K_α) = 9.066 mm^{-1}, Z = 2, space group $P\bar{1}$. Data were collected on a Mac Science MXC18 K diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR[16] and refined by full-matrix least-squares procedures (SHELXL-97)[17] on F^2 for all reflections (2175 reflections) for 83 variable parameters. $R_1(wR_2)$ = 0.052 (0.145) for all data, GOF = 1.041.

CCDC-212959 (**4**), -212958 (**6**) -213182 (**10**) contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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