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Synthesis and Structures of Two 9,10-Dihydro-9,10-distannaanthracenes

Masaichi Saito,* Minehiko Nitta, and Michikazu Yoshioka

Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Urawa, Saitama, 338-8570 Japan

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The 9,9,10,10-tetramethyl- and 9,9,10,10-tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracenes have been synthesized and characterized. The X-ray crystallographic analysis of 9,10-dihydro-9,10-distannaanthracenes showed that the central tricyclic framework of the tetramethyl derivative has a butterfly conformation with a dihedral angle of 143°, while the central six-membered ring of the tetra-*tert*-butyl derivative has a planar structure. The synthesis and structure of a novel tribenzostannepin are also described.

Introduction

Since the synthesis of 9,9,10,10-tetraphenyl-9,10-dihydro-9,10-disilaanthracene,[1] studies on the synthesis, structures, and reactions of 9,10-dihydro-9,10-disilaanthracene have been developed.[2] The corresponding germanium analogues, 9,10-dihydro-9,10-digermaanthracenes, were also synthesized and characterized.[3] One of the most interesting features of 9,10-dihydro-9,10-dimetallaanthracene derivatives is their utility as potential precursors for metal-containing reactive species. Also of interest is the conformation of their central six-membered ring. Very recently, fascinating silicon-containing reactive species such as a bis(silyl anion)[4] and a relatively stable silyl radical[5] have been reported to be derived from 9,10-dihydro-9,10-disilaanthracenes. The conformation of the central ring of a 9,10-dihydro-9,10-dimetallaanthracene is dependent on substituents on the metal.[5−7] The syntheses of 9,10-dihydro-9,10-dimetallaanthracenes thus far reported are limited to those having methyl or phenyl substituents on the metal. Recently, 9,10-di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracene has been synthesized.[5] However, a 9,10-dihydro-9,10-dimetallaanthracene having two bulky substituents on both of the two central metal atoms has not yet been reported. As for tin analogues, although a few 9,10-dihydroanthracenes having a tin atom at the 10-position have been reported,[6,8] only one report on the 9,10-dihydro-9,10-distannaanthracene is available, but without synthetic and structural details.[9,10] We report herein the first synthesis and structures of 9,9,10,10-tetramethyl- and 9,9,10,10-tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracenes. The conformation of the central six-membered ring is found to be remarkably dependent on substituents on each tin atom. The synthesis and structure of the novel tribenzostannepin is also described.

Results and Discussion

Synthesis of 9,9,10,10-Tetramethyl-9,10-dihydro-9,10-distannaanthracene (1). First we attempted to synthesize 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**1**) by the direct coupling of 1,2-dilithiobenzene, prepared from 1,2-bis(trimethylstannyl)benzene,[11] with an equimolar quantity of dimethyldichlorostannane. However, this reaction was unsuccessful. Next, the direct coupling of 1,2-dibromobenzene with dimethyldichlorostannane was attempted. Treatment of an equimolar mixture of 1,2-dibromobenzene and dimethyldichlorostannane with magnesium activated by 1,2-dibromoethane gave 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**1**) in 5% yield. The yield of **1** was improved by the following stepwise method (Scheme 1). (2-Bromophenyl)lithium (2 equiv) prepared by the reaction of 1,2-dibromobenzene with *n*-butyllithium at −110 °C was treated with dimethyldichlorostannane to give bis(2-bromophenyl)dimethylstannane (**2**), the structure of which was determined by spectral data and finally confirmed by X-ray structural analysis. When a THF solution of **2** was treated with magnesium in the presence of a catalytic amount of copper(I) cyanide[12] under reflux for 1.5 h, the solution turned dark brown. Addition of dimethyldichlorostannane to this solution, followed by heating at reflux for

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* Corresponding author. E-mail: masaichi@chem.saitama-u.ac.jp.

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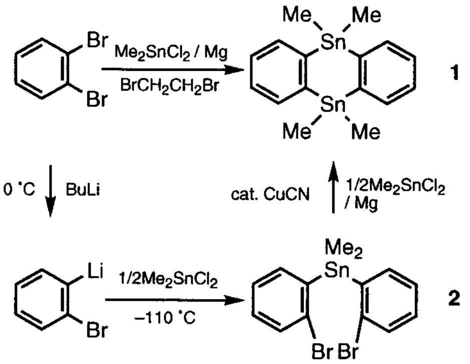
Scheme 1



2 h, gave a dark green solution. After hydrolytic workup and subsequent column chromatography (silica gel elution with hexane), 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**1**) was obtained in 25% yield.

Structure of 1. The X-ray crystallographic analysis of **1** was carried out at 203 K. An ORTEP drawing of **1** is shown in Figure 1 with selected bond lengths and angles. There are two molecules in the unit cell. The central six-membered ring has a boat comformation, and hence the tricyclic framework has a butterfly conformation with a dihedral angle of 143 °, which is the smallest among those of 9,10-dihydro-9,10-dimetallaanthracenes of group 14 metals.[3,13] The dihedral angle becomes smaller as the atomic number of the group 14 elements increases (Table 1) in the series of 9,10-dihydro-9,10-dimetallaanthracene derivatives of group 14 elements. Although the dependence of the dihedral angle on the metal is not well understood, it probably results from a balance of axial−axial interaction and equatorial peri-protons interaction. Interestingly, one of the aromatic moieties of each of the two molecules in the unit cell is face to face with the other like a π-dimer[14] with a distance of about 4 Å. Since the ORTEP drawing of **1** shows that each tin has pseudoaxial and pseudoequatorial methyl substituents, its ^{1}H NMR spectrum is anticipated to show two signals for these nonequivalent methyl groups. However, there appeared only a singlet assignable to methyl hydrogens at δ 0.47, which did not change significantly in the temperature range from 20 to −70 °C. It is reasonably assumed that a rapid boat-to-boat inversion occurs in solution as in the case of other tetramethyl derivatives.[7]

Introduction of *tert*-Butyl Groups on the Tin: Formation of the Novel Tribenzostannepin. The synthesis of the 9,10-dihydro-9,10-distannaanthracene having two *tert*-butyl groups on both of the two tin atoms was also investigated. First, we have attempted to synthesize bis(2-bromophenyl)di-*tert*-butylstannane by the reaction of di-*tert*-butyldichlorostannane with (2-bromophenyl)lithium using the method applied in the preparation of the methyl derivative; that is, (2-bromophenyl)lithium (2 equiv) was treated with di-*tert*-butyldichlorostannane, and then the mixture was warmed to room temperature. However, an unanticipated product, tribenzostannepin **3**, was obtained together with stannafluorene **4**[15] (Scheme 2). The structure of **3** was established by X-ray crystallographic analysis. An ORTEP drawing of **3** is shown in Figure 2 with selected bond lengths and angles. The central seven-membered ring has a boat conformation. To the best of our knowledge, tribenzostannepin **3** is the first example of a tribenzo-fused stannepin, although several stannepins have been synthesized.[16] In the ^{1}H NMR spectrum of **3**, there appeared two signals assignable to the hydrogens of *tert*-butyl groups, and these signals did not coalesce at 60 °C, suggesting the rigid comformation of **3**, as in the case of tribenzosilepin.[17] Although the mechanism for the formation of **3** is still unclear, the tribenzo skeleton of **3** was reasonably assumed to be formed by successive couplings of benzyne generated from 2-bromophenyllithium with 1,2-dibromobenzene.[18]

Synthesis and Structure of 9,9,10,10-Tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracene (5). Since the reaction of (2-bromophenyl)lithium with di-*tert*-butyldichlorostannane under the conditions described above gave **3**, to suppress the generation of benzyne from (2-bromophenyl)lithium, the reaction of (2-bromophenyl)lithium with di-*tert*-butyldichlorostannane was conducted at low temperature. After treatment of (2-bromophenyl)lithium with an equimolar amount of di-*tert*-butyldichlorostannane at −110 °C, the reaction was quenched with aqueuos NH_4Cl at the same temperature. After hydrolytic workup, di-*tert*-butyl(2-bromophenyl)chlorostannane (**6**) was obtained in 39% yield (Scheme 2), the structure of which was determined by spectral data and elemental analysis. The formation of **6** prompted us to examine its self-coupling. Reaction of **6** with *tert*-butyllithium (2.2 equiv) afforded the self-coupling product, 9,9,10,10-tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracene (**5**), in 70% yield. The structure of the latter was determined from its ^{1}H and ^{13}C NMR spectra and elemental analysis (Scheme 3). The formation of **5** is worthy of note from the standpoint of the first 9,10-dihydro-9,10-dimetallaanthracene having two bulky groups on both of the central metals. The X-ray crystallographic analysis of **5** showed that the central six-membered ring had a planar structure, preventing a pseudoaxial orientation of the *tert*-butyl groups, in sharp contrast to the dimethyl derivative, which has a butterfly conformation (Figure 3).

Conclusion

The synthesis and structures of the 9,10-dihydro-9,10-distannaanthracenes were reported. The conformation of the central six-membered ring is remarkably dependent on the substituents on the tin. The central tricyclic framework of the tetramethyl derivative has a butterfly conformation with a dihedral angle of 143°, while that of the tetra-*tert*-butyl derivative has a planar structure, probably due to steric reasons.

The generation of tin-containing reactive species from these newly obtained 9,10-dihydro-9,10-distannaanthracenes is currently in progress.

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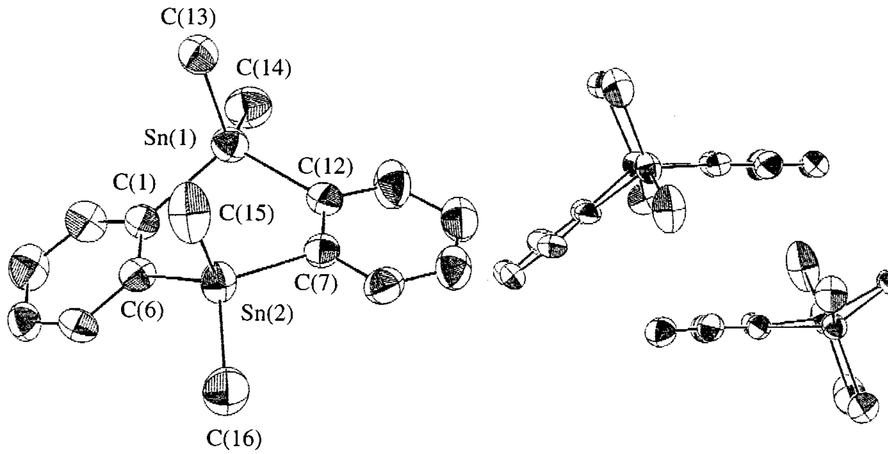
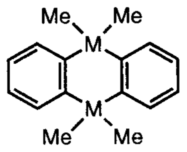


Figure 1. ORTEP drawing of **1** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). One of these molecules in the unit cell (left) and the side view of the unit cell (right). Selected bond lengths (Å) and angles (deg): Sn(1)–C(1), 2.120(8); Sn(1)–C(12), 2.122(9); Sn(2)–C(6), 2.138(6); Sn(2)–C(7), 2.155(8); C(1)–Sn(1)–C(12), 107.2(4); C(6)–Sn(2)–C(7), 107.1(3); Sn(1)–C(1)–C(6), 121.9(6); Sn(1)–C(12)–C(7), 122.9(6); Sn(2)–C(6)–C(1), 121.6(6); Sn(2)–C(7)–C(12), 120.8(6).

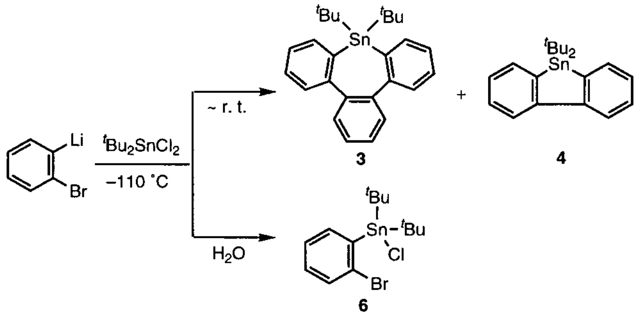
Table 1. Dihedral Angles of 9,10-Dihydro-9,10-dimetallaanthracenes



M	dihedral angle (deg)
Si	156[a]
Ge	152[b]
Sn	143[c]

[a] Ref 13. [b] Ref 3. [c] This work.

Scheme 2



Experimental Section

General Procedure. All reactions were carried out under argon. THF and diethyl ether used in the synthesis were distilled from sodium benzophenone ketyl under argon atmosphere before use. Magnesium (turnings) was purchased from Wako Pure Chemical Industries, Ltd. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Flash column chromatography (FCC) and wet column chromatography (WCC) were carried out with Wako gel C-300 and Merck Kieselgel 60 (SiO_2) or Merck aluminum oxide 90 (Al_2O_3). 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 Chemical Analytical Center, Saitama University. Data for the X-ray crystallographic analyses were collected on Mac Science Xdip or MXC18K diffractometers with Mo Kα radiation (λ = 0.71073 Å), and the structures were solved by direct methods.

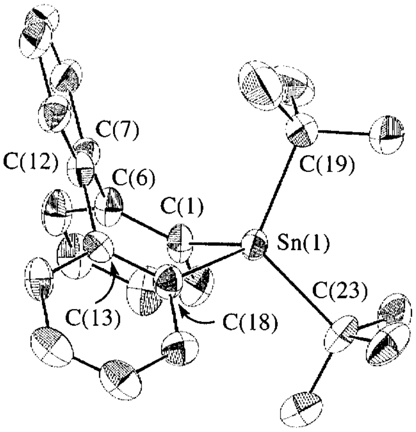
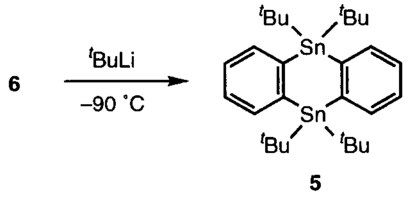


Figure 2. ORTEP drawing of **3** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Sn(1)–C(1), 2.147(4), Sn(1)–C(18), 2.177(4); C(1)–C(6), 1.406(5); C(6)–C(7), 1.505(6); C(7)–C(12), 1.397(5); C(12)–C(13), 1.534(5); C(13)–C(18), 1.367(5); C(1)–Sn(1)–C(18), 95.7(2); C(19)–Sn(1)–C(23), 113.5(2).

Scheme 3



Direct Synthesis of 9,9,10,10-Tetramethyl-9,10-dihydro-9,10-distannaanthracene (1). A THF (7 mL) solution of 1,2-dibromoethane (1.6 mL, 18.6 mmol) with magnesium (559 mg, 23.0 mmol) was heated at reflux for 15 min. To this mixture then was added in succession, with stirring, a THF (2 mL) solution of 1,2-dibromobenzene (0.36 mL, 2.98 mmol) and a THF (3 mL) solution of dimethyldichlorostannane (663 mg, 3.02 mmol). After the mixture had been stirred and heated at reflux for 1.5 h, aqueous NH_4Cl was added, and the resulting mixture was extracted with diethyl ether. After removal of ether, the residue was subjected to FCC (hexane) to afford 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**1**) (32 mg, 5%). **1**: mp 101 °C (recrystallization from methanol). ^{1}H NMR: δ 0.47(s, 12H), 7.27–7.30(m, 4H), 7.54–

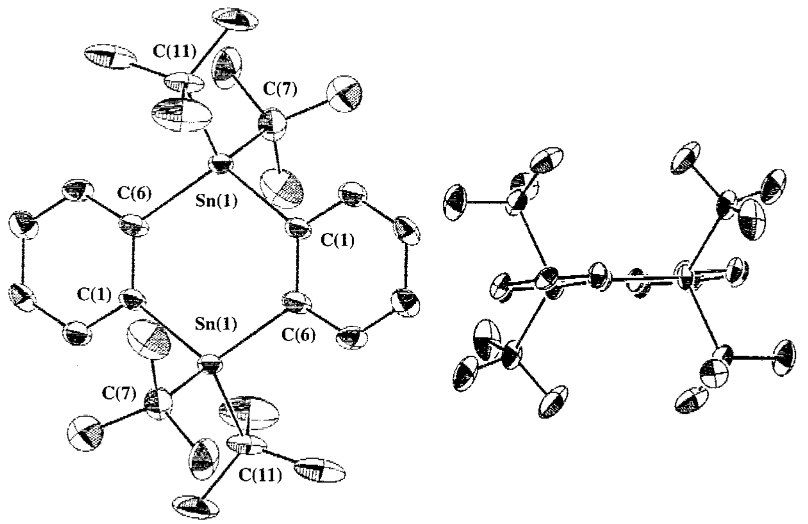


Figure 3. ORTEP drawing of **5** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). One of these molecules in the unit cell (left) and the side view (right). Selected bond lengths (Å) and angles (deg): Sn(1)−C(1), 2.149(2); Sn(1)−C(6), 2.145(3); Sn(1)−C(7), 2.197(4); Sn(1)−C(11), 2.187(3); C(1)−Sn(1)−C(6), 111.4(1), C(7)−Sn(1)−C(11), 116.4(2).

7.56(m, 4H); ^{13}C NMR: δ −8.34(q), 128.19(d), 135.79(d), 152.07(s). Anal. Calcd for $C_{16}H_{20}Sn_2$: C, 42.73; H, 4.48. Found: C, 43.32; H, 4.44.

Stepwise Synthesis of 9,9,10,10-Tetramethyl-9,10-dihydro-9,10-distannaanthracene (1). (1) Preparation of Bis(2-bromophenyl)dimethylstannane (2). To a solution of *n*-butyllithium (1.53 M in hexane; 3.92 mL, 6.00 mmol) in a mixture of THF (15 mL) and diethyl ether (15 mL) was added 1,2-dibromobenzene (0.71 mL, 5.89 mmol) at −110 °C, and the resulting solution was stirred at this temperature for 2.5 h. Subsequently, dimethyldichlorostannane (661 mg, 3.01 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 overnight. Then aqueous NH_4Cl (saturated, 15 mL) was added, and the mixture was extracted with diethyl ether. After removal of volatile components, the residue was subjected to WCC (SiO_2, hexane) to give bis(2-bromophenyl)dimethylstannane (**2**) (1127 mg, 83%). **2**: mp 46−47 °C (recrystallization from hexane−methanol, 10:1). ^{1}H NMR: δ 0.71(s, 6H), 7.18−7.29(m, 4H), 7.32−7.35(m, 2H), 7.52−7.55(m, 2H). ^{13}C NMR: δ −6.06(q), 126.63(d), 130.61(d), 131.80(d), 132.75(s), 138.31(d), 145.10(s). Anal. Calcd for $C_{14}H_{14}Br_2Sn$: C, 36.49; H, 3.06. Found: C, 36.76; H, 3.01.

(2) Preparation of 1 from 2. Compound **2** (1843 mg, 4.00 mmol), magnesium (195 mg, 8.02 mmol), and a catalytic amount of copper(I) cyanide (31 mg) in 20 mL of THF were stirred and heated at reflux for 1.5 h. Subsequently, a THF (10 mL) solution of dimethyldichlorostannane (967 mg, 4.40 mmol) was added. After the mixture had been heated at reflux for 2 h, aqueous NH_4Cl was added. The resulting mixture was extracted with diethyl ether. After removal of ether, the residue was subjected to WCC (SiO_2, hexane) to afford **1** (454 mg, 25%). The compound **1** obtained by this method is identical to that prepared by the direct synthesis, as evidenced by ^{1}H NMR.

Reaction of (2-Bromophenyl)lithium with Di-*tert*-butyldichlorostannane. A solution of 1,2-dibromobenzene (1.19 mL, 10.0 mmol) in THF (7 mL) and diethyl ether (7 mL) was allowed to react with *n*-butyllithium (1.50 M in hexane, 6.73 mL, 10.1 mmol) at −110 °C. The resulting mixture was stirred for 1 h at this temperature. Addition of di-*tert*-butyldichlorostannane (1.550 g, 5.10 mmol) in THF (3 mL) and ether (3 mL) at −110 °C followed. After the mixture had warmed to room temperature, solvents were removed under reduced pressure. The residue was subjected to WCC (Al_2O_3, hexane) to afford 9,9-di-*tert*-butyl-9*H*-tribenzo[*b*,*d*,*f*]stannepin (**3**) (248 mg, 16%) and 9,9-di-*tert*-butyl-9-stannafluorene (**4**) (79 mg, 4%). **3**: mp 216−217 °C (recrystallization from methylene chloride). ^{1}H NMR: δ 0.81(s, 9H), 1.59(s, 9H), 7.18−7.39(m, 10H), 7.61−7.74(m, 2H). ^{13}C NMR: δ 29.43(s), 31.67(q), 32.02(q), 125.51(d), 127.05(d), 128.35(d), 131.21(d), 133.68(d), 134.69(d), 143.32(s), 146.65(s), 149.48(s). Anal. Calcd for $C_{26}H_{30}Sn$: C, 67.71; H, 6.66. Found: C, 67.70; H, 6.59. **4**: mp 40.5−41.5 °C (recrystallization from hexane). ^{1}H NMR: δ 1.30(s, 18H), 7.23−7.26(m, 2H), 7.34−7.40(m, 2H), 7.56−7.58(m, 2H), 7.92 (d, J = 8 Hz, 2H). ^{13}C NMR: δ 31.25(s), 31.47(q), 122.56(d), 127.15(d), 128.77(d), 136.42(d), 141.49(s), 149.46(s). Anal. Calcd for $C_{20}H_{26}Sn$: C, 62.37; H, 6.81. Found: C, 62.60; H, 6.85.

Preparation of (2-Bromophenyl)di-*tert*-butylchlorostannane (6). To 1,2-dibromobenzene (1.08 mL, 8.95 mmol) in THF (10 mL) and diethyl ether (10 mL) was added *n*-butyllithium (1.50 M in hexane, 6.07 mL, 9.11 mmol) at −110 °C. The resulting mixture was stirred for 2 h at this temperature. Addition of di-*tert*-butyldichlorostannane (2.765 g, 9.10 mmol) in THF (5 mL) and diethyl ether (5 mL) at −110 °C followed. The reaction mixture was stirred for 2 h at −110 °C, and subsequently the reaction was quenched with aqueous NH_4Cl at the same temperature. The organic layer was extracted with ether. After removal of volatile components under reduced pressure and removal of unreacted di-*tert*-butyldichlorostannane by recrystallization from hexane, the residue was purified by recrystallization from methanol to afford (2-bromophenyl)di-*tert*-butylchlorostannane (**6**) (1.495 g, 39%). **6**: mp 57−59 °C (recrystallization from hexane). ^{1}H NMR: δ 1.43(s, 18H), 7.22−7.27(m, 1H), 7.34−7.38(m, 1H), 7.47−7.53(m, 1H), 7.80−7.91(m, 1H). ^{13}C NMR: δ 30.68(q), 30.96(q), 37.84(s), 127.23(d), 129.74(s), 131.08(d), 131.10(d), 139.20(d), 147.06(s). Anal. Calcd for $C_{14}H_{22}BrClSn$: C, 39.62; H, 5.23. Found: C, 39.69; H, 5.17.

Preparation of 9,9,10,10-Tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracene (5). To a THF (5 mL) solution of (2-bromophenyl)di-*tert*-butylchlorostannane (**6**) (170 mg, 0.40 mmol) was added *t*-BuLi (1.48 M in pentane, 0.54 mL, 0.80 mmol) at −90 °C. After gradual warming to room temperarure, aqueous NH_4Cl was added to the reaction mixture. The resulting mixture was extracted with diethyl ether. After removal of ether, the residue was subjected to WCC (SiO_2, hexane) to afford 9,9,10,10-tetra-*tert*-butyl-9,10-dihydro-9,10-distannaanthracene (**5**) (87 mg, 70%). **5**: mp 254−255 °C (recrystallization from methylene chloride−ethanol, 10:1). ^{1}H NMR: δ 1.26(s, 36H), 7.24−7.28(m, 4H), 7.52−7.56(m, 4H); ^{13}C NMR: δ 29.75(s), 31.50(q), 127.22(d), 137.75(d), 152.99-

(s). Anal. Calcd for $C_{28}H_{44}Sn_2$: C, 54.41; H, 7.18. Found: C, 54.51; H, 7.24.

Crystal and Experimental Data at 298 K for 2. $C_{14}H_{14}Br_2Sn_2$, $M = 460.78$, monoclinic, $a = 11.689(1)$, $b = 11.0470(9)$, $c = 12.3370(8)$ Å, $\beta = 104.681(5)°$, $V = 1541.1(2)$ Å^3, $D = 1.986$ Mg m^{-3}, $Z = 4$, space group $P2_1/n$. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed at calculated positions (d(C−H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 3121 observed reflections [$I > 2.00\sigma(I)$] and 168 variable parameters with $R(R_w) = 0.066$ (0.087).

Crystal and Experimental Data at 203 K for 1. $C_{16}H_{20}Sn_2$, $M = 449.76$, orthorhombic, $a = 8.8260(6)$, $b = 15.7350(9)$, $c = 24.503(1)$ Å, $V = 3402.9(3)$ Å^3, $D = 1.756$ Mg m^{-3}, $Z = 8$, space group $P2_12_12_1$. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed at calculated positions (d(C−H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 4269 observed reflections [$I > 2.00\sigma(I)$] and 325 variable parameters with $R(R_w) = 0.050$ (0.066).

Crystal and Experimental Data at 298 K for 3. $C_{26}H_{30}Sn$, $M = 461.26$, orthorhombic, $a = 9.995(2)$, $b = 23.150(3)$, $c = 9.607(1)$ Å, $V = 2223.0(5)$ Å^3, $D = 1.378$ Mg m^{-3}, $Z = 4$, space group $P2_12_12_1$. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed at calculated positions (d(C−H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 2778 observed reflections [$I > 2.00\sigma(I)$] and 274 variable parameters with $R(R_w) = 0.043$ (0.071).

Crystal and Experimental Data at 123 K for 5. $C_{28}H_{44}Sn_2$, $M = 618.04$, triclinic, $a = 10.0710(4)$, $b = 10.4310(5)$, $c = 14.1980(8)$ Å, $\alpha = 105.766(2)$, $\beta = 92.805(2)$, $\gamma = 90.788(2)°$, $V = 1433.2(1)$ Å^3, $D = 1.432$ Mg m^{-3}, $Z = 2$, space group $P\bar{1}$. In the unit cell, there are two independent halves of each molecule. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed at calculated positions (d(C−H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 5146 observed reflections [$I > 0.00\sigma(I)$] and 266 variable parameters with $R(R_w) = 0.047$ (0.103).

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1**, **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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