Extending Distannoxane Double Ladders Using Rigid Spacers: A Double Ladder with Eight Chiral Tin Atoms—and a Twist!

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The new bulky silicon-containing ditin precursor *p*-$(RCl_2SnCH_2SiMe_2)_2C_6H_4$ (R = CH_2SiMe_3 (**4**)) has been synthesized and further reacted to form a unique double ladder {[*p*-$(R(Cl)SnCH_2SiMe_2)_2C_6H_4$]O}$_4$ (**6**). The two layers within **6** are twisted with respect to one another, resulting in a helical motif and a total absence of molecular symmetry so that there are eight chiral tin atoms within the system. The structure is compared to the double ladder {[*m*-$(R(Cl)SnCH_2CH_2)_2C_6H_4$]O}$_4$ (**11**), which was prepared from the less sterically demanding ditin precursor *m*-$(RCl_2SnCH_2CH_2)_2C_6H_4$ (**10**). The two layers within **11** are parallel, and the molecule contains only two kinds of tin atom.

Introduction

Among the many and varied applications of organotin compounds, their use in catalysis continues to attract considerable attention.[1] In this context we have recently reported examples of double and triple ladders (**A**, R = alkyl, X = Cl, OAc; **B**, X = Cl, R = CH_2SiMe_3).[2−4] Their structures are related to the well-known single ladders (distannoxanes) **C** (R = alkyl, aryl, X = range of anions), which are useful as mild Lewis acid catalysts in a variety of organic reactions.[5−18] Interestingly, distannoxanes have not yet found utility in synthesis requiring chiral transformations, probably because no suitable chiral distannoxanes have yet been reported. Furthermore, distannoxanes undergo extensive dissociation in solution, a property that also reduces their potential as chiral information transfer reagents.[19−23] By contrast, double and triple ladders undergo fewer dissociation reactions in solution, but, significantly, in these cases chiral information is retained at the tin centers.[4] A key motivation for our investigations has been the synthesis of new double ladders that have little or no symmetry as well as to increase the size of the interlayer region.[24] Such new molecular tin-oxo species hold considerable potential both for chiral catalysis and for genuine host−guest chemistry.

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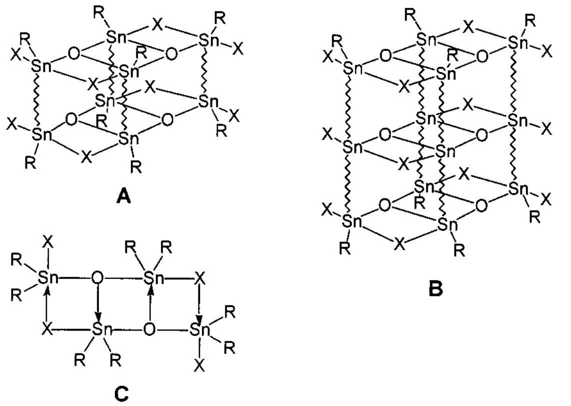


Double ladders are obtained by the controlled hydrolysis or oxygenolysis of precursors containing two tin atoms linked by appropriate organic spacers. Recently, we found that incorporation of a Me_2Si group at a β position to tin in ditin precursors gives rise to novel structures, probably as a consequence of the steric requirements of the silicon-bound Me groups.[3,4,24] With this in mind we designed and synthesized new spacers including one containing a rigid phenylene group linked to two tin atoms via Me_2Si units. This modification leads to the first example of a double ladder containing eight different *chiral* tin centers. Particularly interesting is that the new spacer group confers a novel helical motif on the overall molecular geometry. The results of this study are reported herein.

Results and Discussion

Reaction of the chloromethyldimethylsilylated benzene, **1**, with $NaSnPh_3$ affords the triphenyltin-substituted derivative **2** as colorless crystals (eq 1).

$$\underset{\mathbf{1}}{p\text{-}(ClCH_2SiMe_2)_2C_6H_4} + 2\,Ph_3SnNa \xrightarrow[-2\,NaCl]{liq.\ NH_3} \underset{\mathbf{2}}{p\text{-}(Ph_3SnCH_2SiMe_2)_2C_6H_4} \quad (1)$$

Reaction of compound **2** with iodine gives p-($Ph_2ISnCH_2SiMe_2)_2C_6H_4$, which was further reacted with ClMgR (R = CH_2SiMe_3) to yield p-($Ph_2RSnCH_2SiMe_2)_2C_6H_4$, **3**. The phenyl groups in the tetraorganotin derivative **3** were replaced by chlorine upon treatment with $HgCl_2$ to yield the tetrachloro-substituted ditin derivative p-($RCl_2SnCH_2SiMe_2)_2C_6H_4$, **4**, which in turn was reacted with sodium hydroxide. The product of the latter reaction was formulated as the tetrahydroxy-substituted organotin compound p-[$R(OH)_2SnCH_2SiMe_2]_2C_6H_4$, **5**.

Reaction of the organotin chloride **4** with the spacer-bridged bis-diorganotin dihydroxide **5** provided, after the workup procedure, a colorless solid, hereafter referred to as compound **6′**, the elemental analysis of which is in agreement with the empirical formula $C_{80}H_{169}Cl_7O_5Si_{16}Sn_8$. The IR spectrum of **6′**shows a ν(OH) at 3652 cm^{-1}, and the ^{119}Sn NMR (C_6D_6/CD_2Cl_2, 5:1) spectrum showed at least 26 clearly defined resonances in the region usually associated with tetraorganodistannoxanes adopting ladder-type structures (δ −55 to −160 ppm). The number of signals suggests the existence in solution of a statistical mixture of tetraorganodistannoxanes likely to adopt double ladder structures (and/or other oligomers) in which chloride is partially replaced by hydroxide. There was no significant change in spectral appearance of the ^{119}Sn NMR spectrum measured in toluene at 80 °C. Attempts to obtain a solid state ^{119}Sn NMR spectrum for **6′** were not successful. From this material a single crystal, **6**, suitable for X-ray diffraction was obtained.

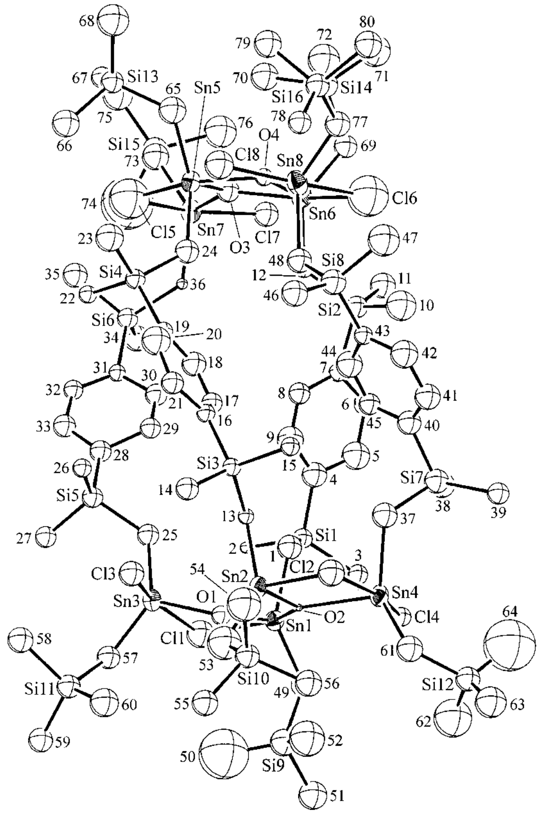
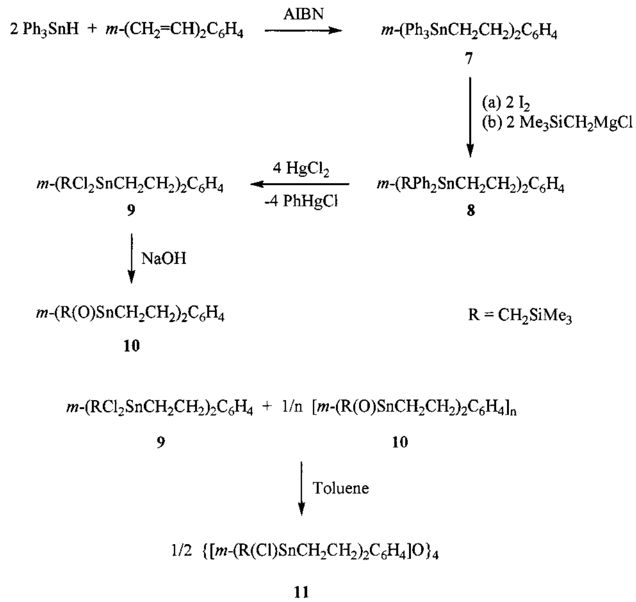


Figure 1. Molecular structure and atomic numbering scheme for **6**; hydrogen atoms have been omitted for clarity. Carbon atoms are indicated by number only.

The X-ray structure analysis of **6** (Figure 1) was modeled as the chloride species (see below) and establishes the double ladder motif as seen in previous examples, but contrary to previous structures of this type, there is *no* center of inversion. Solutions of **6′** in CH_2Cl_2 show no optical rotation, and it appears that isolation of **6** is an example of fortuitous spontaneous crystallization of one enantiomer. The structure may be described as being a construction of two ladders, of the type shown in **C**, linked by $-CH_2SiMe_2C_6H_4SiMe_2CH_2-$ spacers and with the remaining tin-bound groups being CH_2SiMe_3. Each of the two $Sn_4O_2Cl_4$ planes are nearly planar (mean deviations 0.13 and 0.14 Å, respectively) and approximately parallel, forming a dihedral angle of 7.7°. The tin atoms exist in distorted trigonal bipyramidal geometries with trigonal C_2O and axial O, Cl donor sets for Sn(1), Sn(2), Sn(5), and Sn(6) and trigonal C_2O and axial Cl, Cl donor sets for the remaining tin atoms. The geometric parameters for **6** are largely as expected and are not discussed in detail.

A close inspection of the Sn−Cl separations in the X-ray structure of **6** supports the interpretation, as given above, for the large number of ^{119}Sn NMR resonances measured for the bulk material. The Sn−Cl distances of the Sn(5)−Sn(8) distannoxane are system-

Scheme 1



atically shorter than those within the other distannoxane, indicating the possibility of (partial) substitution of chloride for hydroxide. Attempts at refinement with partial occupancy did not result in a significantly better model, but it is noted that the structure analysis is less than optimal (see Experimental Section) and such small changes in a large structure of this type and quality would not be readily detectable.

Of particular interest in the structure of **6** is the chirality adopted by the overall molecule. This is manifested in the twist between the top and bottom distannoxane "faces" that results in an overall helical arrangement for the molecule.

Crystals of another distannoxane, **11**, containing the *meta* $-(CH_2)_2C_6H_4(CH_2)_2-$ spacer, were also obtained (Scheme 1), and its crystal structure was determined.

The crystallographically determined structure of **11**, characterized as the toluene solvate, is shown in Figure 2; the crystallographic unit cell comprises two double ladders, each disposed about a center of inversion, and four disordered toluene molecules (see Experimental Section). The structure of **11** resembles closely that found for related species, including that of **6**. To a first approximation the $Sn_4Cl_4O_2$ face of the molecule is planar with the range of deviations from their least-squares plane being 0.0143(3) Å for Sn(1) to −0.174(3) Å for O(1). The average separation between the two faces (from symmetry the dihedral angle is 0°) is calculated to be 10.6 Å. The tin atoms exist in distorted trigonal bipyramidal geometries with trigonal C_2O and axial O, Cl donor sets for Sn(1) and Sn(2), and trigonal C_2O and axial Cl, Cl donor sets for the Sn(3) and Sn(4). As for **6**, a detailed discussion of the derived interatomic parameters is not warranted. The structure, including its centrosymmetricity, resembles that observed previously for related systems[2−4] but clearly contrasts the chiral distannoxane observed for **6**. In the following discussion, an argument based on steric reasons is proposed to account for the unique helical motif found in **6**.

As can be seen from Figure 1, the tin atoms in **6** lie on opposite sides of each spacer, as for **11**, and the

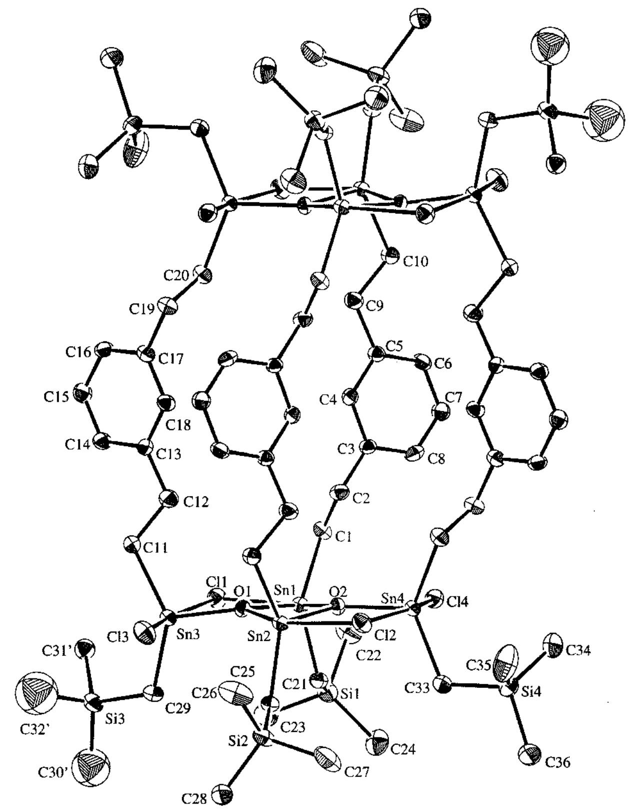
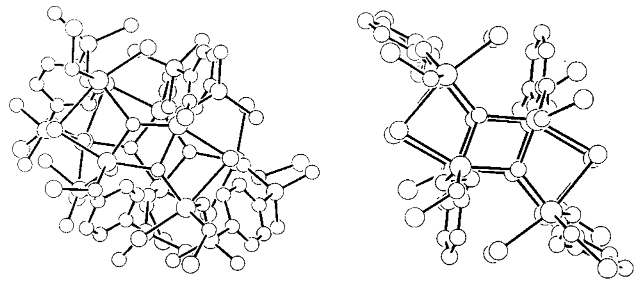


Figure 2. Molecular structure and atomic numbering scheme for the double ladder in **11**·toluene; hydrogen atoms have been omitted for clarity.

silicon-bound methyl groups are directed outside of the cavity. In turn, this arrangement forces a preferred orientation of the spacers in order to minimize repulsions between the silicon-bound methyl substituents. So, rather than having the spacers spanning two approximately superimposable Sn_4O_2 units in an extended conformation resulting in the formation of a molecular box, as in **11**, the spacers in **6** are forced into an arrangement linking two Sn_4O_2 units of differing orientations. Thus, the result of the conformational requirements of the spacer ligands is to introduce a twist in the molecule as a whole, leading to molecular chirality, i.e., one face of the molecular box in **11** is rotated relative to the other in **6**. The magnitude of this twist can be estimated by calculating the relative orientation of the central Sn_4O_2 cores, which in **6** approximates 31°. Views highlighting the relative distribution of the spacer groups and central cores for each of **6** and **11** are shown in Figure 3. From this diagram it is evident that the distribution of the spacer groups is symmetric in **11** and far from symmetric in **6**. The sequence of dihedral angles formed between adjacent aromatic rings gives a quantitative measure of the deviation from a centrosymmetric distribution of these groups. Thus, the dihedral angles formed between the C(4)−C(9) and C(28)−C(33) rings is 116.4°, C(28)−C(33) and C(16)−C(21) 61.2°, C(16)−C(21) and C(40)−C(45) 53.8°, and C(40)−C(45) and C(4)−C(9) 75.4°. The comparable sequence of angles for the structure of centrosymmetric **11** is 69.5°.

Thus, while previous examples of double ladder structures (A) may be thought of as being comprised of two enantiomeric halves, this description is not valid for **6**, which may be described as adopting a helical motif.



6 11·toluene

Figure 3. Views of the double ladders in **6** and **11**·toluene, highlighting the relative distribution of the spacer groups. Terminal methyl groups and hydrogen atoms have been omitted for clarity.

We are currently investigating the influence of other R groups and the variation of the bridging spacers on the twist of the double ladder structure.

Experimental Section

All solvents were dried and purified by standard procedures. NMR spectra were obtained using a Varian 300 MHz Unity Plus NMR spectrometer. ^{1}H, ^{13}C, and ^{119}Sn chemical shifts δ are given in ppm and are referenced against Me_4Si and Me_4Sn, respectively. Uncorrected melting points were determined on a Kofler hot stage. Microanalyses were performed using a CE 1106 elemental analyzer.

Synthesis of 1,4-Bis(chloromethyldimethylsilyl)benzene, 1. A solution of the di-Grignard of 1,4-dibromobenzene (24.12 g, 84.77 mmol) in THF (700 mL) was added during 2.5 h via a cannula to a magnetically stirred solution of $ClSiMe_2CH_2Cl$ (22.28 mL, 24.20 g, 169.3 mmol) in THF (100 mL).[25] The resulting reaction mixture was stirred overnight and hydrolyzed with saturated NH_4Cl solution. After removing the THF in vacuo Et_2O was added; the organic layer was separated and dried over Na_2SO_4. The Et_2O was evaporated, and the remaining crude product (20.5 g yellow oil) was recrystallized from hexane to give **1** as a colorless solid (11.4 g, 46% yield, mp 56−58 °C). ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.40 (s, 3H, $SiMe_2$), 2.93 (s, 1H, CH_2), 7.54 (s, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.44 MHz, $CDCl_3$): δ −4.6 [$^1J(^{29}Si-^{13}C) = 55$, $SiMe_2$], 30.2 [$^1J(^{29}Si-^{13}C) = 53$, CH_2], 133.2 (C_o), 137.8 (C_i). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ −2.9 ($SiMe_2$). Anal. Calcd for $C_{12}H_{20}Cl_2Si_2$: C 49.49, H 6.87. Found: C 49.63, H 6.94.

Synthesis of Bis[(triphenylstannylmethyl)dimethylsilyl]benzene, 2. To a magnetically stirred suspension (−78 °C) of Ph_3SnNa (10.25 g, 27.49 mmol) in a mixture of THF (50 mL) and NH_3 (200 mL) prepared from sodium (1.26 g, 54.78 mmol) and Ph_3SnCl (10.59 g, 27.49 mmol) was added dropwise a solution of **1** (4 g, 13.74 mmol) in THF (60 mL) over 20 min. The reaction mixture was stirred at −78 °C for 3 h and allowed to warm to room temperature overnight. After removing the THF in vacuo Et_2O was added and the precipitate (NaCl) was filtered off. The Et_2O was evaporated and the remaining crude product (12.5 g, colorless solid) recrystallized from CH_2Cl_2/hexane to give **2** (10.3 g, 81.5% yield, mp 141−143 °C) as a colorless solid. ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.35 (s, 6H, $SiMe_2$), 0.86 [s, 2H, $^2J(^{117/119}Sn-^1H) = 74/77$, CH_2], 7.35−7.98 (m, 17H, C_6H_4, $SnPh_3$). $^{13}C\{^1H\}$ NMR (75.44 MHz, $CDCl_3$): δ −5.9 [$^1J(^{117/119}Sn-^{13}C) = 263/275$, $^1J(^{29}Si-^{13}C) = 49$, CH_2], −0.1 [$^1J(^{29}Si-^{13}C) = 53$, $SiMe_2$], 128.4 [$^3J(^{117/119}Sn-^{13}C) = 50$, C_m], 128.8 (C_p), 132.59 (C_{oSi}), 136.9 [$^2J(^{117/119}Sn-^{13}C) = 38$, C_o], 139.4 [$^1J(^{117/119}Sn-^{13}C) = 484/507$, C_I], 141.3 (C_{iSi}). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ −2.9 [$^2J(^{117/119}Sn-^{29}Si) = 21$, $SiMe_2$]. $^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3$): δ −89.0 [$^1J(^{13}C-^{119}Sn) = 506$]. Anal. Calcd for $C_{48}H_{50}Si_2Sn_2$: C 62.63, H 5.47. Found: C 62.81, H 5.59.

Synthesis of Bis{[(trimethylsilylmethyl)diphenylstannylmethyl]dimethylsilyl}benzene, 3. To a magnetically stirred solution (0 °C) of **2** (7.8 g, 8.49 mmol) in CH_2Cl_2 (80 mL) was added I_2 (4.275 g, 16.95 mmol) in small portions over 30 min. The reaction mixture was stirred for 2 h, the solvent removed in vacuo, and the resulting yellow oil kept for 3 h at 130 °C and 10^{-3} Torr to remove all volatile byproducts. The oily residue (8.64 g, 8.49 mmol) was dissolved in THF (120 mL) and added dropwise at room temperature during 1 h to a Grignard solution prepared from chloromethyltrimethylsilane (3.00 g, 24.45 mmol) and Mg (588 mg, 24.48 mmol) in THF (120 mL). The reaction mixture was refluxed overnight and the THF removed in vacuo. To the resulting colorless solid was added Et_2O and the suspension hydrolyzed with saturated NH_4Cl solution. The organic layer was washed twice with water and dried over Na_2SO_4. After filtration the organic solvent was evaporated in vacuo and the resulting yellow oil kept for several hours at 130 °C and 10^{-3} Torr to remove all volatile byproducts to give 7.32 g crude product that could be used without further purification. $^{13}C\{^1H\}$ NMR (75.44 MHz, $CDCl_3$): δ −4.6 [$^1J(^{117/119}Sn-^{13}C) = 247/258$, $^1J(^{29}Si-^{13}C) = 49$, CH_2], −3.8 [$^1J(^{117/119}Sn-^{13}C) = 257/269$, $^1J(^{29}Si-^{13}C) = 47$, CH_2], −0.0 [$^1J(^{29}Si-^{13}C) = 53$, $SiMe_3$], 1.6 [$^1J(^{29}Si-^{13}C) = 51$, $SiMe_2$], 128.2 (C_m), 128.5 (C_p), 132.6 (C_{oSi}), 136.3 [$^2J(^{117/119}Sn-^{13}C) = 38$, C_o], 141.2 [$^1J(^{117/119}Sn-^{13}C) = 458/479$, C_I], 141.5 (C_{iSi}). $^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3$): δ −48.9 [$^1J(^{13}C-^{119}Sn) = 480$, $^1J(^{13}C-^{119}Sn) = 269$].

Synthesis of Bis{[(trimethylsilylmethyl)dichlorostannylmethyl]dimethylsilyl}benzene, 4. To a magnetically stirred solution (0 °C) of **3** (7.32 g, 7.80 mmol) in acetone (70 mL) was added dropwise a solution of $HgCl_2$ (8.46 g, 31.20 mmol) in acetone (70 mL) over 30 min. The reaction mixture was stirred overnight and the resulting precipitate (PhHgCl) filtered off. After removing the acetone in vacuo Et_2O (120 mL) was added and the suspension stirred for 10 min. The PhHgCl was removed by filtration and the organic solvent evaporated in vacuo to give 5.4 g of crude product that was recrystallized from Et_2O/hexane to give **4** as a colorless solid (3.15 g, 52% yield, mp 87−90 °C). ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 0.49 (s, 6H, $SiMe_2$), 0.52 [s, 2H, $^2J(^{117/119}Sn-^1H) = 88/92$, CH_2], 1.03 [s, 2H, $^2J(^{117/119}Sn-^1H) = 90/94$, CH_2], 7.57 (s, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.44 MHz, $CDCl_3$): δ −0.6 [$^1J(^{29}Si-^{13}C) = 55$, $^3J(^{117/119}Sn-^{13}C) = 22$, $SiMe_3$], 1.0 [$^1J(^{29}Si-^{13}C) = 52$, $^3J(^{117/119}Sn-^{13}C) = 27$, $SiMe_2$], 12.5 [$^1J(^{117/119}Sn-^{13}C) = 325/340$, $^1J(^{29}Si-^{13}C) = 45$ CH_2], 12.6 [$^1J(^{117/119}Sn-^{13}C) = 309/323$, $^1J(^{29}Si-^{13}C) = 46$, CH_2], 133.1 (C_o), 140.3 (C_i). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$): δ −4.2 [$^2J(^{117/119}Sn-^{29}Si) = 30$, $SiMe_2$], 1.5 [$^2J(^{117/119}Sn-^{29}Si) = 40$, $SiMe_3$]. $^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3$): δ 140.9. Anal. Calcd for $C_{20}H_{42}Cl_4Si_4Sn_2$: C 31.05, H 5.43. Found: C 31.28, H 5.54.

Synthesis of Bis{[(trimethylsilylmethyl)dihydroxystannylmethyl]dimethylsilyl}benzene, 5. To a magnetically stirred solution (0 °C) of NaOH (1.0 g, 25 mmol) in 15 mL of H_2O was added dropwise a solution of **4** (1.0 g, 1.29 mmol) in 20 mL of MeOH. The reaction mixture was stirred for 24 h and the resulting colorless precipitate filtered off and washed with water, MeOH, and EtOH to give **5** as a colorless solid (850 mg, 99% yield, mp 130−140 °C). The compound was insufficiently soluble to allow NMR spectroscopic investigation. IR (KBr): νOH 3600 cm^{-1} (br). Anal. Calcd for $C_{20}H_{46}O_4Si_4Sn_2$: C 34.30, H 6.62. Found: C 34.24, H 6.10.

Reaction of Compound 4 with Compound 5. 5 (327 mg, 0.467 mmol) and **4** (361 mg, 0.467 mmol) were combined with $CHCl_3$ (12 mL) and stirred for 48 h at 60 °C to give a clear solution. After removing the organic solvent in vacuo the crude

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product was recrystallized from a toluene/hexane/CH_2Cl_2 mixture (35 mL, 8 mL, 5 mL) to give **6′** as a colorless solid (520 mg, 78% yield, mp 225−235 °C). IR (Nujol): νOH 3652 cm^{-1}. Anal. Calcd for $C_{80}H_{169}Cl_7O_5Si_{16}Sn_8$: C 33.42, H 5.84; Cl, 8.68. Found: C 33.40, H 6.01; Cl 8.25.

Synthesis of 1,3-Bis[(2-triphenylstannyl)ethyl]benzene, 7. A solution of Ph_3SnH (15.39 g, 43.85 mmol) and AIBN (0.36 g, 2.19 mmol) in benzene (50 mL) was added dropwise to a magnetically stirred solution of 1,3-divinylbenzene (2.85 g, 21.92 mmol) in benzene (50 mL) at reflux. The resulting reaction mixture was stirred at reflux for 2 h. After removing the benzene in vacuo the crude product was crystallized from dichloromethane/hexane to give **7** as a colorless solid (15.1 g, 83% yield, mp 143−146 °C). ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 1.98 [t, 4H, $^2J(^{117/119}Sn-^1H)$ = 52, $SnCH_2$], 3.14 [t, 4H, $^3J(^{117/119}Sn-^1H)$ = 54, CH_2], 7.09 (s, 1H, C_6H_4), 7.18 (d, 2H, C_6H_4), 7.34 (t, 1H, C_6H_4), 7.45−7.80 (m, 30H, $SnPh_3$). ^{13}C{^{1}H} NMR (75.44 MHz, $CDCl_3$): δ 13.0 [$^1J(^{117/119}Sn-^{13}C)$ = 367/384, $SnCH_2$], 32.4 [$^2J(^{117/119}Sn-^{13}C)$ = 19, CH_2], 125.5 (C_6H_4), 127.6 (C_6H_4), 128.4 [$^3J(^{117/119}Sn-^{13}C)$ = 47, C_m], 128.6 (C_6H_4), 128.8 [$^4J(^{117/119}Sn-^{13}C)$ = 11, C_p], 137.0 [$^2J(^{117/119}Sn-^{13}C)$ = 35, C_o], 138.7 [$^1J(^{117/119}Sn-^{13}C)$ = 466/488, C_i], 144.9 [$^3J(^{117/119}Sn-^{13}C)$ = 57, C_6H_4]. ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): δ −100.1 [$^1J(^{13}C-^{119}Sn)$ = 386, $^1J(^{13}C-^{119}Sn)$ = 488]. Anal. Calcd for $C_{46}H_{42}Sn_2$: C 66.39, H 5.09. Found: C 66.15, H 4.72.

Synthesis of 1,3-Bis{[2-(trimethylsilylmethyl)diphenylstannyl]ethyl}benzene, 8. To a magnetically stirred solution (0 °C) of **7** (10.00 g, 12.01 mmol) in $CHCl_3$ (100 mL) was added I_2 (6.10 g, 24.02 mmol) in small portions over 30 min. The reaction mixture was stirred for 2 h, the solvent removed in vacuo, and the resulting yellow oil kept for 3 h at 130 °C and 10^{-3} Torr to remove all volatile byproducts. The oily residue (11.19 g, 12.01 mmol) was dissolved in THF (100 mL) and added dropwise at room temperature during 1 h to a Grignard solution prepared from chloromethyltrimethylsilane (4.42 g, 36.05 mmol) and Mg (1.75 g, 72.10 mmol) in THF (100 mL). The reaction mixture was refluxed overnight and the THF removed in vacuo. To the resulting colorless solid was added Et_2O and the suspension hydrolyzed with saturated NH_4Cl solution. The organic layer was washed twice with water and dried over Na_2SO_4. After filtration the organic solvent was evaporated in vacuo and the resulting yellow oil kept for several hours at 130 °C and 10^{-3} Torr to remove all volatile byproducts to give 8.57 g of crude product that could be used without further purification. ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.25 (s, 18H, $SiMe_3$), 0.45 [s, 4H, $^2J(^{117/119}Sn-^1H)$ = 72/75, $SiCH_2$], 1.87 [t, 4H, $^2J(^{117/119}Sn-^1H)$ = 45, $SnCH_2$], 3.13 [t, 4H, $^3J(^{117/119}Sn-^1H)$ = 51, CH_2], 7.22 (d, 2H, C_6H_4), 7.26 (s, 1H, C_6H_4), 7.41 (t, 1H, C_6H_4), 7.50−7.85 (m, 20H, $SnPh_2$). ^{13}C{^{1}H} NMR (75.44 MHz, $CDCl_3$): δ −5.5 [$^1J(^{117/119}Sn-^{13}C)$ = 244/255, $SiCH_2$], 1.6 [$^3J(^{117/119}Sn-^{13}C)$ = 16, $SiMe_3$], 13.7 [$^1J(^{117/119}Sn-^{13}C)$ = 350/366, $SnCH_2$], 32.5 [$^2J(^{117/119}Sn-^{13}C)$ = 17, CH_2], 125.3 (C_6H_4), 127.5 (C_6H_4), 128.2 [$^3J(^{117/119}Sn-^{13}C)$ = 47, C_m], 128.4 (C_6H_4), 128.5 (C_p), 136.6 [$^2J(^{117/119}Sn-^{13}C)$ = 35, C_o], 140.5 [$^1J(^{117/119}Sn-^{13}C)$ = 440/462, C_i], 145.1 [$^3J(^{117/119}Sn-^{13}C)$ = 57, C_6H_4]. ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): δ −59.0 [$^1J(^{13}C-^{119}Sn)$ = 463, $^1J(^{13}C-^{119}Sn)$ = 368, $^1J(^{13}C-^{119}Sn)$ = 254].

Synthesis of 1,3-Bis{[2-(trimethylsilylmethyl)dichlorostannyl]ethyl}benzene, 9. To a magnetically stirred solution (0 °C) of **8** (8.57 g, 10.05 mmol) in acetone (100 mL) was added dropwise a solution of $HgCl_2$ (10.92 g, 40.20 mmol) in acetone (100 mL) over 30 min. The reaction mixture was stirred overnight and the resulting precipitate (PhHgCl) filtered off. After removing the acetone in vacuo Et_2O (100 mL) was added and the suspension stirred for 10 min. The PhHgCl was removed by filtration and the organic solvent evaporated in vacuo to give the crude product, which was recrystallized from hexane to give **9** as a colorless solid (3.7 g, 54% yield, mp 64−67 °C). ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.12 (s, 18H, $SiMe_3$), 0.55 [s, 4H, $^2J(^{117/119}Sn-^1H)$ = 87/91, $SiCH_2$], 2.08 [t, 4H, $^2J(^{117/119}Sn-^1H)$ = 54, $SnCH_2$], 3.11 [t, 4H, $^3J(^{117/119}Sn-^1H)$ = 112, CH_2], 7.14 (d, 2H, C_6H_4), 7.16 (s, 1H, C_6H_4), 7.31 (t, 1H, C_6H_4). ^{13}C{^{1}H} NMR (75.44 MHz, $CDCl_3$): δ 1.0 [$^1J(^{29}Si-^{13}C)$ = 52, $^3J(^{117/119}Sn-^{13}C)$ = 26, $SiMe_3$], 11.7 [$^1J(^{29}Si-^{13}C)$ = 43, $^1J(^{117/119}Sn-^{13}C)$ = 284/297, $SiCH_2$], 29.4 [$^1J(^{117/119}Sn-^{13}C)$ = 450/471, $SnCH_2$], 30.5 [$^2J(^{117/119}Sn-^{13}C)$ = 30, CH_2], 126.5 (C_6H_4), 127.9 (C_6H_4), 129.7 (C_6H_4), 143.1 [$^3J(^{117/119}Sn-^{13}C)$ = 76, C_6H_4]. ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): δ 130.6. Anal. Calcd for $C_{18}H_{34}Cl_4Si_2Sn_2$: C 31.52, H 5.00. Found: C 31.15, H 5.05.

Table 1. Crystallographic Data for 6 and 11·Toluene

	6	**11·**toluene
formula	$C_{80}H_{168}Cl_8O_4Si_{16}Sn_8$	$C_{79}H_{144}Cl_8O_4Si_8Sn_8$
fw	2876.7	2615.8
cryst size, mm	0.10 × 0.10 × 0.18	0.10 × 0.10 × 0.15
cryst syst	monoclinic	monoclinic
space group	*Pc*	$P2_1/n$
a, Å	22.913(1)	19.091(1)
b, Å	12.680(1)	13.155(1)
c, Å	22.019(1)	24.413(1)
β, deg	101.592(1)	104.945(1)
V, Å^3	6266.9(5)	5923.7(5)
Z	2	2
D_{calcd}, g cm^{-3}	1.524	1.466
F(000)	2880	2596
μ, cm^{-1}	19.28	19.55
no. of data colld	24 166	34 550
θ_{max}, deg	25.7	25.7
no. of unique data	18 138	10 509
no. of unique data with $I \geq 3.0\sigma(I)$	6261	10 031
R	0.090	0.063
R_w	0.105	0.034

Synthesis of the Organotin Oxide 10. To a magnetically stirred solution (0 °C) of NaOH (1 g, 25 mmol) in 15 mL of H_2O was added dropwise a solution of **C** (1.0 g, 1.46 mmol) in 20 mL of MeOH. The reaction mixture was stirred for 24 h and the resulting white precipitate filtered off, washed with water, and dried at 60 °C and 10^{-3} Torr to give **10** as a colorless solid (840 mg, 100% yield, mp 290 °C dec). Anal. Calcd for $C_{18}H_{34}O_2Si_2Sn_2$: C 37.53, H 5.95. Found: C 37.60, H 6.28.

Synthesis of the Tetrameric Tetraorganodistannoxane 11. 9 (595 mg, 0.868 mmol) and **10** (500 mg, 0.868 mmol) were combined, toluene (20 mL) was added, and reaction mixture was stirred for 24 h at reflux to give a clear solution. The solution was concentrated to 2 mL to give **11** as colorless crystals (790 mg, 72% yield, mp 278−279 °C). ^{1}H NMR (299.98 MHz, $CDCl_3$): δ 0.23 (s, 18H, $SiMe_3$), 0.23 (s, 18H, $SiMe_3$), 0.98 [s, 4H, $^2J(^{117/119}Sn-^1H)$ = 123, $SiCH_2$], 1.02 [s, 4H, $^2J(^{117/119}Sn-^1H)$ = 123, $SiCH_2$], 1.93 [m, 4H, $SnCH_2$], 2.23 [m, 4H, $SnCH_2$], 2.89 [t, 4H, CH_2], 3.23 [t, 4H, CH_2], 6.10 (s, 1H, C_6H_4), 6.98 (d, 2H, C_6H_4), 7.01 (s, 1H, C_6H_4), 7.18−7.26 (m, 4H, C_6H_4). ^{13}C{^{1}H} NMR (75.44 MHz, $CDCl_3$): δ 1.4 [$^1J(^{29}Si-^{13}C)$ = 52, $^3J(^{117/119}Sn-^{13}C)$ = 32, $SiMe_3$], 2.0 [$^1J(^{29}Si-^{13}C)$ = 52, $^3J(^{117/119}Sn-^{13}C)$ = 30, $SiMe_3$], 18.4 [$^1J(^{29}Si-^{13}C)$ = 43, $^1J(^{117/119}Sn-^{13}C)$ = 402/420, $SiCH_2$], 19.5 [$^1J(^{29}Si-^{13}C)$ = 43, $^1J(^{117/119}Sn-^{13}C)$ = 377/394, $SiCH_2$], 30.9 [$^2J(^{117/119}Sn-^{13}C)$ = 33, CH_2], 31.1 [$^2J(^{117/119}Sn-^{13}C)$ = 33, CH_2], 32.3 [$^1J(^{117/119}Sn-^{13}C)$ = 569/595, $SnCH_2$], 34.9 [$^1J(^{117/119}Sn-^{13}C)$ = 612/640, $SnCH_2$], 124.8 (C_6H_4), 125.4 (C_6H_4), 126.9 (C_6H_4), 127.6 (C_6H_4), 128.8 (C_6H_4), 129.7 (C_6H_4), 143.2 [$^3J(^{117/119}Sn-^{13}C)$ = 76, C_6H_4], 143.5 [$^3J(^{117/119}Sn-^{13}C)$ = 76, C_6H_4]. ^{119}Sn{^{1}H} NMR (111.85 MHz, $CDCl_3$): δ −79.1 [$^2J(^{119}Sn-^{117/119}Sn)$ = 72], −141.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 72]. Anal. Calcd for $C_{72}H_{136}Cl_8O_4Si_8Sn_8$: C 34.26, H 5.43. Found: C 34.25, H 5.55.

X-ray Crystallography. Data were collected for colorless crystals of **6** and **11·**toluene at 173 K employing graphite-monochromatized Mo Kα radiation, λ = 0.7107 Å, on a Nonius KappaCCD diffractometer. Corrections were made for Lorentz and polarization effects[26] and for absorption using an empirical procedure (SORTAV). Crystal data are given in Table 1.

The structures were solved by heavy-atom methods[27] and refined by a full-matrix least-squares procedure based on F.[26] The analysis for **6** was nontrivial, but successful refinement was achieved in space group *Pc*. Considerable difficulties were encountered in the refinement with several atomic positions being poorly resolved; however, the molecular connectivity has been established unambiguously. The tin atoms were refined anisotropically with all other atoms being treated isotropically. It was not possible to determine the absolute structure, as there were no significant differences between Friedel pairs included in the data set. A residual electron density peak (4.1 e Å^{-3}) was located in a chemically nonsensible position, and it is concluded that this was an artifact of the data. It should be noted that some 15 different crystals were examined over the course of the examination. All samples showed the same metric symmetry and the same systematic extinctions, lending support to the choice of space group. The data reported here for **6** represents the best that we were able to obtain. For **11**·toluene, non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms were included in the model in their calculated positions (C−H 0.95 Å) with two exceptions. The Si(3)-bound methyl groups were found to be disordered, and each was modeled (isotropic, no hydrogens) over two positions with 50% site occupancy (from refinement). In addition, a disordered molecule of toluene was located in difference maps toward the end of refinement so that the asymmetric unit comprises one-half of a tetranuclear double ladder and one solvent molecule. This molecule was modeled as three approximately superimposed molecules such that three positions (33% occupancy) were found for the methyl groups and seven positions for the aromatic carbons (86% occupancy). The refinements were continued until convergence with the application of a weighting scheme of the form $w = 1/[\sigma^2(F_o)]$, and final refinement details are given in Table 1. Numbering schemes (ORTEP,[28] at the 50% probability level) are shown in Figures 1 and 2.

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Supporting Information Available: Further details of the structure determination including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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