Organostannanes Derived from (−)-Menthol: Controlling Stereochemistry during the Preparation of (1*R*,2*S*,5*R*)-Menthyldiphenyltin Hydride and Bis((1*R*,2*S*,5*R*)-menthyl)phenyltin Hydride

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Reaction of (1*R*,2*S*,5*R*)-menthylmagnesium chloride (MenMgCl) with triphenyltin chloride in THF proceeds with epimerization of the C-1 carbon of the menthyl group and results in a mixture of (1*R*,2*S*,5*R*)-menthyltriphenyltin (**1**) and (1*S*,2*S*,5*R*)-menthyltriphenyltin (**2**). Addition of Lewis bases such as triphenylphosphine to the THF solution of triphenyltin chloride prior to addition of the Grignard reagent suppresses epimerization and enables isolation of pure **1**. An epimerization mechanism involving one-electron-transfer reactions is postulated. Compound **1** is the precursor for reactions that lead to the formation of a series of compounds, namely, (1*S*,2*S*,5*R*)-menthyldiphenyltin iodide (**4**), (1*S*,2*S*,5*R*)-menthyldiphenyltin fluoride (**5**), (1*S*,2*S*,5*R*)-menthyldiphenyltin hydride (**6**), (1*S*,2*S*,5*R*)-menthylphenyltin dibromide (**7**), and (1*S*,2*S*,5*R*)-menthylphenyltin dichloride (**8**). The synthesis of the dimenthyl derivatives bis((1*S*,2*S*,5*R*)-menthyl)diphenyltin (**9**), bis((1*S*,2*S*,5*R*)-menthyl)-phenyltin iodide (**10**), bis((1*S*,2*S*,5*R*)-menthyl)phenyltin hydride (**11**), and bis((1*S*,2*S*,5*R*)-menthyl)tin di(chloroacetate) (**12**) is described. Crystal structure determinations of **7**, **8**, and **12** confirm the absolute configuration of the menthyl groups.

Introduction

Over recent years there has been a growing interest in the preparation of organostannanes that contain chiral organic substituents as well as organostannanes in which the tin center itself is chiral. This interest arises primarily because of the enormous potential of such compounds as chiral information transfer agents in a range of organic syntheses.[1−3] Very recently the surface organometallic chemistry of chiral organostannanes[4] has been investigated, as has their utility in heterogeneous catalysis.[5] Our own interest is in development of organotin hydrides as enantioselective free radical reducing agents for rational organic synthesis.[6,7]

Despite the potential uses of organostannanes containing elements of chirality, there are still few such compounds which are well characterized, and most of these contain the naturally occurring menthyl group as an organo substituent.[8−11] In some cases there has been crystallographic evidence for retention of configuration of the menthyl group after reaction with the tin center; in other cases spectroscopic data are used to support retention of configuration during the transfer of the organic group. The syntheses of triorganostannanes containing the (1*R*,2*S*,5*R*)-menthyl substituent (Men) have been achieved previously from reaction between triorganotin chlorides, R_3SnCl (R = methyl, neophyl) and the corresponding Grignard reagent. In both cases transfer of the menthyl group is reported to occur with retention of configuration of the C-1 stereocenter. To the best of our knowledge there have been no reports of corresponding syntheses starting from other triorganotin chlorides containing other organic substituents. In

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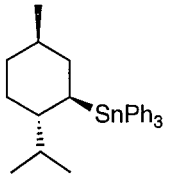
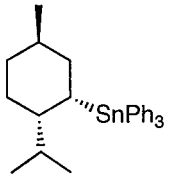
this paper we report the synthesis of (1*R*,2*S*,5*R*)-menthyltriphenyltin ($MenPh_3Sn$), as well as a series of related compounds containing one or more menthyl substituents on the tin center. We also report the X-ray structure analyses of three compounds that confirm retention of the configuration of stereogenic centers of the menthyl group during the synthetic transformations described.

Results and Discussion

Preparation of (1*R*,2*S*,5*R*)-Menthyltriphenyltin, $MenPh_3Sn$ (1). Reaction of 1.1 molar equiv of the Grignard reagent MenMgCl with Ph_3SnCl in tetrahydrofuran (THF) results in substantial epimerization of the C-1 carbon of the menthyl group, and the two compounds ((1*R*,2*S*,5*R*)-menthyl)triphenyltin (**1**) and ((1*S*,2*S*,5*R*)-menthyl)triphenyltin (**2**) are formed in the ratio of 3:2, as evidenced by ^{119}Sn NMR spectroscopy (δ −111.2, −108.1). Also evident in the reaction mixture are significant quantities of hexaphenylditin, $(Ph_3Sn)_2$. Changing the reaction solvent to toluene, hexane, diethyl ether, or di-*n*-butyl ether has little effect on the ratio of the two isomeric products. Attempts at the preparation of $MenPh_3Sn$ (**1**) from reaction of Ph_3SnM (M = Na or Li) with MenCl produced only hexaphenylditin, $(Ph_3Sn)_2$. Addition of MenCl to magnesium and Ph_3SnCl in THF[12] gave no reaction.



1



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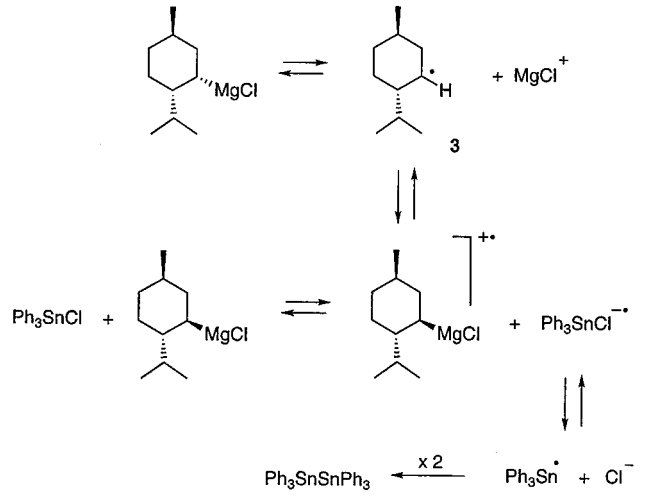
It was reported previously[13] that MenMgCl reacts with chlorodiphenylphosphine (Ph_2PCl) with retention of configuration at the C-1 of the menthyl group to form exclusively $MenPh_2P$. In that report the product was purified by distillation prior to NMR characterization, which allows for the possibility that any of the epimeric ((1*S*,2*S*,5*R*)-menthyl)diphenylphosphine isomer that formed could have been removed and therefore remain undetected. We repeated the reaction of MenMgCl with Ph_2PCl and investigated the reaction mixture prior to any purification. The ^1H NMR ($CDCl_3$) spectrum of the reaction mixture showed that only $MenPh_2P$ was produced, confirming that the Grignard reagent itself is configurationally stable, thereby eliminating it as the source of epimerization in its reaction with triorganotin halides.

We find that the reaction of the MenMgCl with $^nBu_3SnCl$ in THF or diethyl ether gives a 3:1 mixture of Men^nBu_3Sn and (1*S*,2*S*,5*R*)-menthyltributyltin, as well as quantities of hexabutylditin. In contrast, it has been reported that reaction of MenMgCl with Me_3SnCl results in no change of stereochemistry within the menthyl group, and a single compound $MenMe_3Sn$ was obtained in good yield.[9] The different ratios of isomers obtained from reaction of MenMgCl with the three different triorganotin chloride precursors, Me_3SnCl, $^nBu_3SnCl$, and Ph_3SnCl, suggest that the nature of the triorganotin reagent may influence the configurational stability of the C-1 carbon atom within the menthyl group.

Scheme 1



Reactions between Ph_3SnCl and MenMgCl were repeated in the presence of a number of Lewis bases such as LiI, $^nBu_4NI$, $(Ph_2P)_2(CH_2)_2$, Ph_3P, (cyclohexyl)$_3$P, and $^nBu_3P(O)$ in order to probe whether epimerization is related to the Lewis acidity of the triorganotin precursor. In each case the addition of 1 molar equiv of Lewis base to the solution of Ph_3SnCl prior to reaction with MenMgCl suppressed epimerization within the menthyl group, and only a single isomer was observed in the ^{119}Sn NMR spectrum of the reaction mixture (δ −111.2).

The Lewis base of choice was Ph_3P because of low cost and ease of removal, which was achieved by recrystallization and oxidative removal of residual Ph_3P by treatment with *tert*-butylhydroperoxide. There was no formation of (1*S*,2*S*,5*R*)-menthyltriphenyltin when the concentration of Ph_3P was reduced to 0.15 molar equiv; however, using less than 0.15 molar equiv of Ph_3P resulted in formation of significant quantities of the unwanted isomer, as did reaction times beyond 2 h.

Scheme 1 summarizes a plausible set of equilibria consistent with the above observations. The first step involves a one-electron transfer from the Grignard reagent to the Lewis acidic tin center in Ph_3SnCl. Subsequent dissociation of the radical cation ($MenMgCl^{+\cdot}$) gives rise to the menthyl radical (**3**), which has lost its original stereochemical integrity due to the planar geometry associated with the carbon-centered π-radical at C-1. The radical anion ($Ph_3Sn^{\bullet-}$) presumably undergoes dissociation to give the triphenylstannyl radical, which undergoes radical coupling to form hexaphenylditin, $(Ph_3Sn)_2$.

We speculate that addition of Ph_3P results in substantial interaction of the Lewis base with the Ph_3SnCl. The resulting adduct ($Ph_3SnCl{\cdot}PPh_3$) would be expected to have different electronic properties from those of Ph_3SnCl, which inhibit one-electron transfer from the Grignard reagent. Suppression of the radical pathways enables attachment of the menthyl substituent to tin without inversion and without formation of $(Ph_3Sn)_2$.

Compound **1** forms the basis for the synthesis of the series of new compounds outlined in Scheme 2.

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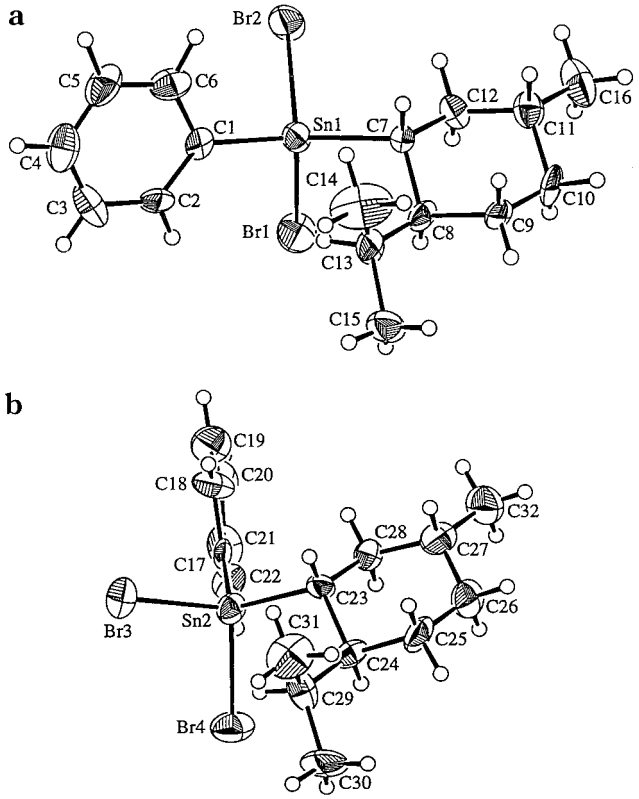
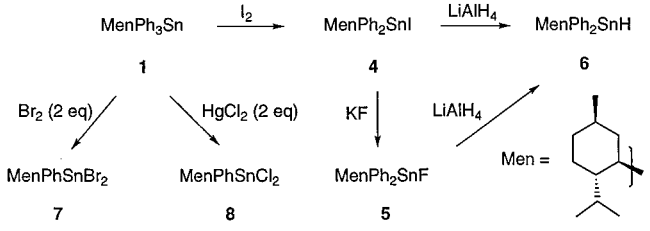


Figure 1. Molecular structures and atomic numbering scheme for the two independent molecules of $MenPhSnBr_2$ (**7**).

Table 1. Selected Interatomic (Å, deg) Parameters for $MenPhSnBr_2$ (7)

Sn(1)−Br(1)	2.489(3)	Sn(2)−Br(3)	2.486(3)
Sn(1)−Br(2)	2.510(3)	Sn(2)−Br(4)	2.491(3)
Sn(1)−C(1)	2.04(2)	Sn(2)−C(17)	2.12(2)
Sn(1)−C(7)	2.15(2)	Sn(2)−C(23)	2.20(2)
Br(1)−Sn(1)−Br(2)	105.2(1)	Br(3)−Sn(2)−Br(4)	103.6(1)
Br(1)−Sn(1)−C(1)	105.6(6)	Br(3)−Sn(2)−C(17)	107.2(5)
Br(1)−Sn(1)−C(7)	104.2(6)	Br(3)−Sn(2)−C(23)	115.5(6)
Br(2)−Sn(1)−C(1)	103.0(5)	Br(4)−Sn(2)−C(17)	103.5(6)
Br(2)−Sn(1)−C(7)	105.2(5)	Br(4)−Sn(2)−C(23)	110.8(6)
C(1)−Sn(1)−C(7)	131.4(8)	C(17)−Sn(2)−C(23)	115.0(8)

Scheme 2



Addition of 2 molar equiv of bromine to **1** afforded $MenPhSnBr_2$ (**7**) as a red oil in 95% yield, which solidified as clear crystals on standing. The molecular structures of the two independent molecules comprising the asymmetric unit of **7** are shown in Figure 1 and selected interatomic parameters are listed in Table 1. The tin atom in each molecule exists in a distorted tetrahedral geometry defined by a C_2Br_2 donor set. As can be seen from the orientation of the molecules in Figure 1, two distinct conformations about the tin atom are found in the solid state, and this is reflected in the spread of angles about the tin atoms. Thus, for **7a**, the widest angle subtended at tin is by the two organic substituents (131.4(8)°) compared with 115.5(6)° for Br(3)−Sn(2)−C(23) in **7b**. The narrower range of angles in **7b** suggests that there is reduced steric hindrance in this molecule. The crystal structure confirms that the menthyl group was attached to tin with complete retention of configuration.

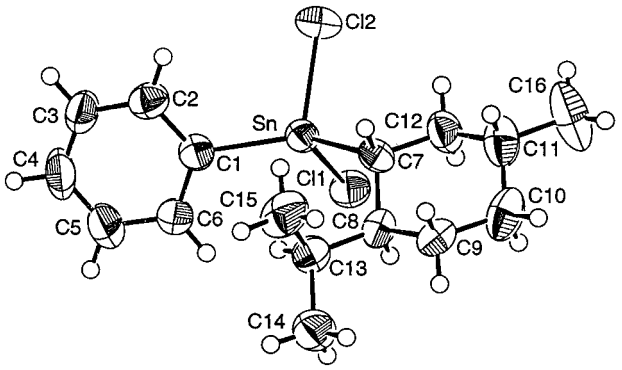


Figure 2. Molecular structure and atomic numbering scheme for $MenPhSnCl_2$ (**8**).

Table 2. Selected Interatomic (Å, deg) Parameters for $MenPhSnCl_2$ (8)

Sn−Cl(1)	2.378(3)	Sn−Cl(2)	2.351(3)
Sn−C(1)	2.127(9)	Sn−C(7)	2.174(9)
Cl(1)−Sn−C1(2)	99.1(1)	Cl(1)−Sn−C(1)	101.6(3)
Cl(1)−Sn−C(7)	103.6(3)	Cl(2)−Sn−C(1)	104.5(3)
Cl(2)−Sn−C(7)	105.1(3)	C(1)−Sn−C(7)	137.1(4)

The reaction of $HgCl_2$ with **1** afforded $MenPhSnCl_2$ (**8**), which also produced crystals suitable for X-ray structure analysis. The molecular structure of **8** is shown in Figure 2, and selected geometric parameters are collected in Table 2. The conformation about the tin atom is as found about the Sn(1) atom in **7**. The C−Sn−C angle of 137.1(4)° is greater than that found in **7a** and reflects the fact that the Cl−Sn−Cl angle of 99.1(1)° is more acute than the comparable angle of 105.2(1)° in **7a**.

The monohalogenation of **1** with 1 molar equiv of iodine afforded $MenPh_2SnI$ (**4**) in a 93% yield. The addition of potassium fluoride to this organotin iodide resulted in halide exchange, forming $MenPh_2SnF$ (**5**) in a 75% yield. Reaction of **4** and **5** with lithium aluminum hydride resulted in the formation of $MenPh_2SnH$ in 100% and 48% yields, respectively.

We repeated the previously reported synthesis of Men_2Ph_2Sn[5] and could obtain only a 34% yield of the optically pure organotin compound. Reaction of up to 3 molar equiv of MenMgCl with Ph_2SnCl_2 always gave mixtures of $Men_2PhSnCl$ and Men_2Ph_2Sn (**9**). Compound **9** was isolated and formed the basis for the syntheses described in Scheme 3.

Monohalogenation of **9** by the careful addition of 1 molar equiv of iodine gave Men_2PhSnI (**10**) as a yellow oil in 95% yield. Compound **10** displayed a single ^{119}Sn NMR chemical shift at 51.95 ppm. The ^{13}C NMR spectrum of **10** indicated 16 different carbon chemical shifts in the menthyl region associated with the 20 different carbon atoms resulting from the two menthyl groups at the diastereotopic tin center. Reduction of **10** with $LiAlH_4$ in diethyl ether afforded Men_2PhSnH (**11**) as a clear oil in 95% yield. A doublet was observed in

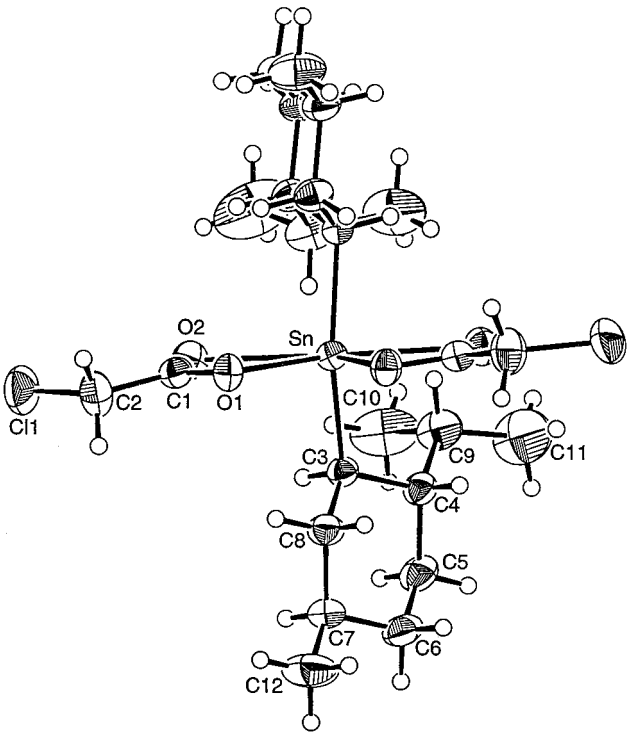
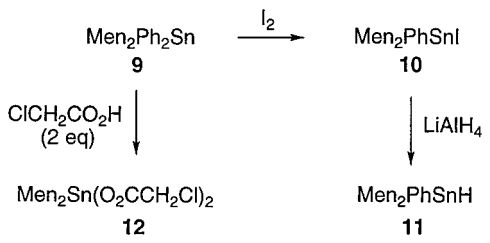


Figure 3. Molecular structure and atomic numbering scheme for $Men_2Sn(O_2CCH_2Cl)_2$ (**12**). Selected geometric parameters (primed atoms are related by 2-fold axis): Sn−O(1) 2.112(2), Sn−O(2) 2.628(3), Sn−C(3) 2.158(3) Å, O(1)−Sn−O(2) 53.62(8), O(1)−Sn−O(1′) 84.2(1), O(2)−Sn−O(2′) 168.5(1), C(3)−Sn−C(3′) 151.1(2)°.

Scheme 3



the ^{119}Sn NMR spectrum of **11** at −100.1 ppm [^1J(^{119}Sn−^{1}H) 1564 Hz].

Reaction of 2 molar equiv of chloroacetic acid with Men_2Ph_2Sn (**9**) afforded $Men_2Sn(O_2CCH_2Cl)_2$ (**12**) as white crystals in 40% yield. The molecular structure of **12** is shown in Figure 3, and selected interatomic parameters are listed in the figure caption. The molecule has 2-fold symmetry and the menthyl substituents have the *R* configuration at C-1, indicating retention of configuration at the reaction center. The tin atom exists in a skew-trapezoidal bipyramidal geometry with the menthyl groups disposed over the weaker Sn−O(2) bonds. The coordination geometry reported here for **12** is as found in related $R_2Sn(O_2CR')_2$ systems[14,15] with the noteworthy feature being the magnitude of the C−Sn−C angle (151.1(2)°), which is wider than is usually found. The diorganotin dicarboxylates are readily hydrolyzed to tetraorganodistannoxanes $(R'CO_2)R_2SnOSnR_2(OCOR')$ and $(R'CO_2)R_2SnOSnR_2(OH)$.[16] A ^{119}Sn NMR of **12** after storage in a nonairtight jar for 9 months showed negligible decomposition.

Synthesis of $(Men_3Sn)_2$ (13), Men_3SnBr (14), and Men_3SnH (15). To complete the series we undertook the preparation of Men_3SnH, the latter compound having been previously synthesized from Men_3SnCl.[5] Interestingly, Men_3SnCl was obtained using the same experimental procedure as that previously described for the synthesis of $(Men_3Sn)_2$.[11] We obtained only $(Men_3Sn)_2$, **13**, by following this procedure.[11] The ^{119}Sn NMR (20 °C, $CHCl_3$) spectrum of **13** contains a single broad peak ($W_{1/2}$ approx 600 Hz) at δ 21.2, and no ^{117}Sn satellites were observed. At −80 °C, the ^{119}Sn NMR resonance sharpens considerably (δ 23.2, $W_{1/2} = 25$ Hz), and ^{117}Sn satellites are clearly visible [J(^{119}Sn−^{117}Sn) 2144 Hz]. The rotation of the two trimenthyltin moieties about the tin−tin bond is rapid at room temperature and becomes slow on the NMR time scale at −80 °C. Raising the temperature also causes the tin resonance to sharpen such that at 105 °C the ^{119}Sn− ^{117}Sn coupling is again clearly observed (δ 18.7, J(^{119}Sn−^{117}Sn) 1880 Hz). The smaller coupling value at the higher temperature is consistent with the small increase in the tin−tin bond length required to allow free rotation.

No electrospray mass spectrum could be obtained on a sample of **13** in acetonitrile. However, addition of a small amount of dilute hydrochloric acid to a sample of **13** in acetonitrile shows *m*/*z* peaks at Men_5Sn_2 consistent with the loss of a menthyl group from $(Men_3Sn)_2$.

Reaction of **13** with bromine gives Men_3SnBr (**14**), which in turn is easily reduced by $LiAlH_4$ to give the corresponding hydride Men_3SnH (**15**).

Experimental Section

General Methods. NMR spectra were obtained using a JEOL-GX 270 FT NMR spectrometer (^{119}Sn inverse-gated, ^{119}Sn proton coupled, and ^{19}F), referenced to Me_4Sn and $CFCl_3$, respectively, and a Varian 300 MHz Unity Plus NMR spectrometer (^{1}H and ^{13}C), referenced to TMS.

Uncorrected melting points were determined on a Kofler hot stage. Microanalyses were performed at the Australian National University (Canberra, Australia). Electrospray mass spectra were obtained on a Micromass (VG) Platform mass spectrometer. High-resolution electrospray mass spectra were obtained on a Bruker BioApex 47e FT mass spectrometer. All solvents and reagents used were of analytical reagent grade. Reactions were generally carried out in an atmosphere of dry nitrogen. (1*R*,2*S*,5*R*)-menthyl chloride was prepared by the reaction of Lucas reagent with (1*R*,2*S*,5*R*)-menthol as previously reported.[17]

$MenPh_3Sn$ (1). A solution of Ph_3SnCl (42.0 g, 109.0 mmol) and Ph_3P (4.5 g, 17.2 mmol) in THF (150 mL) was added to a solution of MenMgCl (prepared from magnesium (4.58 g, 188.4 mmol) and (1*R*,2*S*,5*R*)-menthyl chloride (29.9 g, 171.0 mmol) in THF (100 mL) at room temperature). The reaction mixture was stirred at room temperature for 1.5 h and then heated at reflux for a further 30 min. The reaction mixture was hydrolyzed with 2 M hydrochloric acid (5 mL) and extracted with CH_2Cl_2 (200 mL), the extract was washed with water (2 × 100 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo. Approximately 60 mL of hexane and 40 mL of dicloromethane were added to the residue and subsequently concentrated to 30 mL, at which time most of the Ph_3P crystallized and was removed by filtration. The remaining Ph_3P was converted to Ph_3PO by the addition of *tert*-butylhy-

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droperoxide (15 mL) to the above solution. After stirring for 15 min, 1 mL of water was added. The Ph_3PO was removed by column chromatography (silica gel 60, 70−230 mesh) (hexane/dichloromethane (80:20)) to give **1** as a clear oil: yield (39.14 g, 73%). ^{1}H NMR ($CDCl_3$): δ 0.90−1.88 (19H, m), 7.47−7.72 (15H, m). ^{13}C NMR ($CDCl_3$): δ 16.0, 21.9, 22.6, 26.9, 34.3, 35.4, 35.6, 35.9 [J(^{13}C−^{119}Sn) 436 Hz], 41.7, 46.6, 35.9 128.4, 128.7, 137.4, 139.7 [J(^{13}C-$^{-119}$Sn) 447 Hz]. ^{119}Sn NMR ($CHCl_3$): δ −111.4. Anal. Calcd for $C_{28}H_{34}Sn$: C, 68.7; H, 7.0. Found: C, 68.3; H, 7.2.

MenPh$_2$SnI (4). A solution of iodine (21.0 g, 82.8 mmol) in $CHCl_3$ (1.2 L) was added to a solution of **1** (40.5 g, 82.7 mmol) in $CHCl_3$ (250 mL) at 0 °C over 6 h. Removal of solvent in vacuo left a yellow oil (41.5 g, 93%) of sufficient purity for further use. ^{1}H NMR ($CDCl_3$): δ 0.73−2.34 (19H, m); 7.39−7.79 (10H, m). ^{13}C NMR ($CDCl_3$): δ 15.8, 21.8, 22.4, 26.6, 34.6, 35.0, 35.3, 40.5 [J(^{13}C−^{119}Sn) 430 Hz], 41.2, 46.5, 128.8, 129.6, 136.3, 138.5 [J(^{13}C−^{119}Sn) 444 Hz]. ^{119}Sn NMR ($CHCl_3$): δ −37.4.

MenPh$_2$SnF (5). A mixture of KF (4.5 g, 76.9 mmol) in water (30 mL) was added to a solution of **4** (25.2 g, 46.8 mmol) in acetonitrile (50 mL) and the mixture stirred at room temperature for 2 h. The white precipitate that formed was collected by filtration to afford **5** of sufficient purity for further use (26.9 g, 75%), mp > 230 °C. ^{1}H NMR (DMSO-d_6): δ 0.20−2.06 (19H, m), 7.27−7.64 (10H, m). ^{13}C NMR (DMSO-d_6): δ 15.7, 21.9, 22.7, 25.9, 32.6, 34.8, 35.0, 40.0, 44.1 [d, J(^{13}C−^{119}Sn) 664 Hz, ^2J(^{13}C−^{19}F) 5.2 Hz], 44.3, 128.0, 128.5, 135.9, 136.3, 145.3 [d, J(^{13}C−^{19}F) 16 Hz] [J(^{13}C−^{119}Sn) 657 Hz], 146.1 [d, J(^{13}C−^{19}F) 14 Hz] [J(^{13}C−^{119}Sn 657 Hz]. ^{119}Sn (DMSO-d_6): δ −202.8 [d, J(^{119}Sn−^{19}F) 2133 Hz]. ^{19}F NMR ($CHCl_3$): δ −226.5. Anal. Calcd for $C_{22}H_{29}SnF$: C, 61.3; H, 6.8. Found: C, 61.0; H, 7.2.

MenPh$_2$SnH (6). Solid **5** (0.063 g, 0.15 mmol) was added to a suspension of $LiAlH_4$ (0.10 g, 0.26 mmol) in ether (30 mL), and the mixture was stirred at room temperature for 28 h. Water (0.25 mL) was added, the solids were filtered off, and the solvent was removed in vacuo to give **6** as a colorless oil (0.03 g, 48%). ^{1}H NMR (C_6D_6): δ 0.70−2.12 (19H, m), 6.46 (1H, s, J(^{1}H−^{119}Sn) 1730 Hz), 7.00−7.60 (10H, m). ^{13}C NMR (C_6D_6): δ 15.5, 21.6, 22.2, 26.6, 33.9, 34.6 [J(^{13}C−^{119}Sn) 432 Hz], 35.2, 35.3, 41.8, 46.7, 128.8, 128.9, 137.8, 138.7. ^{119}Sn NMR (C_6D_6): δ −133.5 [d, J (^{119}Sn−^{1}H) 1743 Hz]. HRMS (ESI): m/z (M − H)$^+$ Calcd for $C_{22}H_{29}Sn$: 413.1298. Found: 413.1284.

MenPhSnBr$_2$ (7). Bromine (4.28 g, 26.80 mmol) in methanol (8 mL) was added to a solution of **1** (6.59 g, 13.40 mmol) in chloroform (50 mL), over 5 min. The solution was stirred at room temperature for 24 h. The solvent was removed in vacuo to yield a red oil, which crystallized on standing to give **7** (6.30 g, 95%), mp 52−53°C. ^{1}H NMR ($CDCl_3$), δ 0.83−2.66 (19H, m), 7.50−7.79 (5H, m). ^{13}C NMR ($CDCl_3$): δ 15.5, 21.6, 22.2, 26.4, 34.4, 35.1, 35.4, 39.4, 45.9, 50.1 [J(^{13}C−^{119}Sn) 480 Hz], 129.2, 130.9, 134.4, 140.6; 140.6 [J(^{13}C−^{119}Sn) 518 Hz. ^{119}Sn NMR ($CHCl_3$): δ 4.7. Anal. Calcd for $C_{16}H_{24}SnBr_2$: C, 38.8; H, 4.9. Found: C, 38.4; H, 5.1.

MenPhSnCl$_2$ (8). A solution of $HgCl_2$ (9.91 g, 36.5 mmol) in acetone (250 mL) was added slowly to a solution of **1** (9.41 g, 19.2 mmol) in acetone (50 mL) at 0 °C, after which the reaction mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo and the PhHgCl removed by precipitation from chloroform/hexane to afford crude **8** as a colorless oil (6.49 g, 72%). A sample of the crude product was crystallized from hexane to give pure **8** as colorless crystals, mp 71−73 °C. ^{1}H NMR ($CDCl_3$): δ 0.83−2.69 (19H, m), 7.44−7.68 (5H, m).^{13}C NMR ($CDCl_3$): δ 15.5, 21.65, 22.2, 26.4, 34.4, 35.2, 36.1, 38.7, 45.6, 50.4 [J(^{13}C−^{119}Sn) 516 Hz], 129.4, 131.1, 134.5, 140.7 [J(^{13}C−^{119}Sn) 565 Hz]. ^{119}Sn NMR ($CDCl_3$): δ 26.8. Anal. Calcd for $C_{16}H_{24}SnCl_2$: C, 47.3; H, 6.0. Found: C, 47.6; H, 6.2.

Men$_2$Ph$_2$Sn (9). A solution of Ph_2SnCl_2 (7.40 g, 36.88 mmol) in THF (15 mL) was added to a solution of MenMgCl (prepared from Mg (3.0 g, 110.6 mmol) and menthyl chloride (19.40 g, 111.1 mmol in THF (20 mL)) and the mixture stirred at room temperature for 44 h. Water (50 mL) was added, and the resultant mixture was extracted with ether (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and the solvent removed in vacuo. The residue was purified by column chromatography (silica gel 60, 230−400 mesh) using hexane/dichloromethane (97:3) as the eluent (R_f 0.46). Removal of solvent left a colorless oil (6.96 g, 34% which was crystallized from acetone to afford **9** (4.41 g, 22%), mp 75 °C. ^{1}H NMR ($CDCl_3$): δ 0.79−2.23 (38H, m) 7.40−7.68 (10H, m). ^{13}C NMR ($CDCl_3$): δ 16.4, 21.9, 22.6, 26.9, 33.9, 35.1, 35.3, 35.8 [J(^{13}C−^{119}Sn) 382 Hz], 41.3, 46.2, 127.87, 127.94, 137.5, 141.3 [J(^{13}C−^{119}Sn) 382 Hz]. ^{119}Sn NMR ($CHCl_3$): δ −89.8. Anal. Calcd for $C_{32}H_{48}Sn$: C, 69.7; H, 8.8. Found: C, 69.8; H, 8.9.

Men$_2$PhSnI (10). A solution of iodine (2.50 g, 9.85 mmol) in $CHCl_3$ (500 mL) was added to a solution of **9** (5.43 g, 9.85 mmol) in $CHCl_3$ (20 mL) at 0 °C over 8 h. Removal of the solvent in vacuo yielded **10** as a yellow oil (5.63 g, 95%). ^{1}H NMR ($CDCl_3$): δ 0.11−2.22 (38H, m), 7.27−7.63 (5H, m). ^{13}C NMR ($CDCl_3$): δ 16.2, 16.3, 21.9, 22.0, 22.4, 26.7, 34.5, 34.9, 35.0, 35.1, 35.26, 35.31, 41.3, 41.8 [J(^{13}C−^{119}Sn) 350 Hz], 42.0, 42.2 [J(^{13}C−^{119}Sn) 350 Hz], 46.2, 46.6, 128.4, 128.8, 136.6, 139.6 [J(^{13}C−^{119}Sn) 340 Hz]. ^{119}Sn NMR ($CHCl_3$): δ 52.0. Anal. Calcd for $C_{26}H_{43}SnI$: C, 51.9; H, 7.2. Found: C, 52.5; H, 6.9.

Men$_2$PhSnH (11). A solution of **10** (1.27 g, 2.11 mmol) in ether (5 mL) was added to a suspension of $LiAlH_4$ (0.18 g, 4.75 mmol) in ether (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 h, the solids were filtered off, and the solvent was removed in vacuo to afford **11** as a colorless oil (0.95 g, 95%). ^{1}H NMR ($CDCl_3$): δ 0.87−2.26 (38H, m), 6.05 (1H, s, J(^{1}H−^{119}Sn) 1564 Hz), 7.21−7.71 (5H, m). ^{13}C NMR ($CDCl_3$): δ 16.0, 16.1, 22.1, 22.2, 22.68, 22.72, 27.1, 34.1, 34.3, 35.1 [J(^{13}C−^{119}Sn) 385 Hz], 35.3 [J(^{13}C−^{119}Sn) 385 Hz], 35.7, 42.8, 42.8, 47.4, 47.5, 128.5, 128.6, 138.1, 140.6. ^{119}Sn NMR (C_6D_6): δ −100.1 (d, J(^{119}Sn−^{1}H) 1566 Hz]. HRMS (ESI): Calcd for $C_{26}H_{43}Sn$ (M − H$^+$): 475.2376. Found: 475.2398.

Men$_2$Sn(O$_2$CCH$_2$Cl)$_2$ (12). A mixture of **9** (2.90 g, 5.26 mmol) and chloroacetic acid (0.99 g, 10.52 mmol) was heated to 160 °C with stirring for 20 min. The reaction mixture was allowed to cool and hexane (10 mL) added. The solution was heated at reflux for 30 min and then allowed to cool to room temperature, after which crystals formed (0.73 g, 38%), mp 121−123 °C. ^{1}H NMR ($CDCl_3$): δ 0.79−2.58 (38H, m), 4.14 (4H, s). ^{13}C NMR ($CDCl_3$): δ 15.5, 21.7, 22.1, 26.4, 34.2, 34.8, 35.3, 38.3, 40.8, 44.9, 53.5 [J(^{13}C−^{119}Sn) 471 Hz], 176.2. ^{119}Sn ($CDCl_3$): δ −180.4. Anal. Calcd for $C_{24}H_{42}SnO_4Cl_2$: C, 49.3; H, 7.3. Found: C, 49.3; H, 7.3.

(Men$_3$Sn)$_2$ (13). A solution of MenMgCl (0.71 M), prepared from magnesium (9.35 g, 385 mmol) and **1** (60.85 g, 384 mmol) in THF (250 mL) was added to a solution of $SnCl_4$ (4.18 mL, 35.70 mmol) in benzene (20 mL). The reaction mixture was heated at reflux for 5 h and stirred at room temperature for a further 16 h. The reaction was quenched with 10% hydrochloric acid (10 mL) and water (200 mL). The mixture was extracted with ether (4 × 50 mL), the combined extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. The residue was recrystallized from ethanol to afford **13** as a white solid (19.27 g, 50%), mp > 280 °C. ^{1}H NMR ($CDCl_3$): δ 0.82−2.23 (114H, m). ^{13}C NMR ($CDCl_3$): 17.4, 22.2, 22.5, 27.7, 34.5, 35.7, 36.6, 39.6 [J(^{13}C−^{119}Sn) 427 Hz], 45.6, 46.4. ^{119}Sn NMR ($CDCl_3$): δ 21.2 ($W_{1/2}$ approx 600 Hz) (cf. 18.8, ref 11). ^{119}Sn NMR (hexane, −80 °C): δ 23.2 [J(^{119}Sn−^{117}Sn) 2144 Hz]. ^{119}Sn NMR (toluene, 105 °C): δ 18.7 [J(^{119}Sn−^{117}Sn) 1880 Hz]. Anal. Calcd for $C_{60}H_{114}Sn_2$: C, 67.2; H, 10.7. Found: C, 67.1; H, 11.1.

Men$_3$SnBr (14). A solution of bromine (0.45 g, 2.82 mmol) in benzene (20 mL) was added to a solution of **13** (3.00 g, 2.80

Table 3. Crystallographic Data for $MenPhSnBr_2$ (7), $MenPhSnCl_2$ (8), and $Men_2Sn(O_2CCH_2Cl)_2$ (12)'

	7	8	12
formula	$C_{16}H_{24}Br_2Sn$	$C_{16}H_{24}Cl_2Sn$	$C_{24}H_{42}Cl_2O_4Sn$
fw	494.9	406.0	584.2
cryst size, mm	0.016 × 0.18 × 0.32	0.13 × 0.18 × 0.32	0.39 × 0.39 × 0.65
color	colorless	colorless	colorless
temp, K	293	293	293
cryst syst	triclinic	orthorhombic	orthorhombic
space group	$P1$	$P2_12_12_1$	$P2_12_12$
a, Å	9.417(3)	10.926(7)	9.782(5)
b, Å	12.846(6)	18.661(10)	17.454(3)
c, Å	9.084(4)	8.824(7)	8.350(3)
α, deg	98.86(4)	90	90
β, deg	114.94(2)	90	90
γ, deg	70.90(3)	90	90
V, Å^3	941.5(7)	1799(2)	1425.5(7)
Z	2	4	2
D_{calcd}, g cm^{-3}	1.746	1.499	1.361
$F(000)$	480	816	604
μ, cm^{-1}	56.02	17.03	11.08
transmission factors	0.288−1	0.446−1	0.523−1
no. of data colld	4592	2394	1901
θ_{max}, deg	27.5	27.5	27.5
no. of unique data with $I \geq 3.0\sigma(I)$	1764	1306	1706
R	0.046	0.037	0.022
R_w	0.040	0.036	0.025
residual electron density, Å^{-3}	0.74	0.45	0.31

mmol) in benzene (10 mL) at 6 °C with further stirring at room temperature for 3 h. Removal of the solvent in vacuo and crystallization from ethanol afforded **14** as a white solid (1.66 g, 96%), mp 137 °C. ^{1}H NMR ($CDCl_3$): 0.82−2.17 (57H, m).^{13}C NMR ($CDCl_3$): δ 16.8, 22.1, 22.6, 27.1, 35.0, 35.2, 35.4, 40.9, 43.5 [$J(^{13}C-^{119}Sn)$ 292 Hz], 46.4; 43.5. ^{119}Sn NMR ($CDCl_3$): δ 108.6 (cf. 105.5, ref 11). Anal. Calcd for $C_{30}H_{57}SnBr$: C, 58.5; H, 9.3. Found: C, 58.1; H, 10.0.

Men_3SnH (15). A solution of Men_3SnBr (0.45 g, 0.73 mmol) in THF (10 mL) and benzene (5 mL) was added to a suspension of $LiAlH_4$ (0.20 g, 5.26 mmol) in THF (5 mL) and the mixture stirred at room temperature for 30 min. The reaction mixture was quenched with water (20 mL) and extracted with ether (3 × 20 mL). The combined extracts were dried ($MgSO_4$), and the solvent was removed in vacuo to yield a colorless oil which crystallized on standing (0.36 g, 80%), mp 25−30 °C. ^{1}H NMR ($CDCl_3$): 0.79−2.15 (58H, m), 5.39 (1H, s).^{13}C NMR ($CDCl_3$): 16.3, 22.4, 23.0, 27.2, 33.8, 34.4 [$J(^{13}C-^{119}Sn)$ 338 Hz], 35.8, 36.0, 43.2, 41.6. ^{119}Sn NMR ($CDCl_3$): −103.12 (d, $J(^{119}Sn-^1H)$ 1456 Hz (cf. −102.9, ref 5).

Crystal and Molecular Structures of 7, 8, and 12. Intensity data were measured on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å and employing the $\omega-$scan technique. The data sets were corrected for Lorentz and polarization effects,[18] and an empirical absorption correction was applied in each case.[19] Relevant crystal data are given in Table 3.

The structures were solved by direct methods employing DIRDIF[20] and refined by a full-matrix least-squares procedure based on F.[18] Non-H atoms were refined with anisotropic displacement parameters, and H atoms were included in the models in their calculated positions. Absolute configurations were confirmed by refining the opposite hands, which resulted in a higher value for R_w in each case. Final refinement details are collected in Table 3, and the numbering schemes employed are shown in Figures 1−3, which were drawn with ORTEP[21] with 50% probability ellipsoids. The teXsan[18] package, installed on an Iris Indigo workstation, was employed for all calculations.

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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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