Optically Active Organotin Compounds Derived from β-Pinene. The Quest for Chiral Polystannanes†

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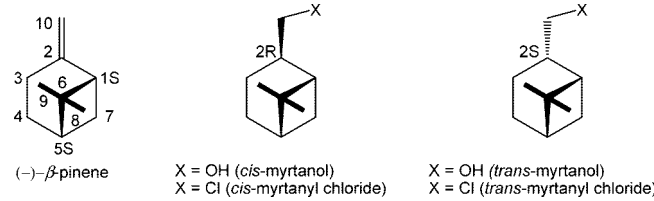
series of enantiomerically pure bis(myrtanyl)tin compounds, *cis*-Myr_2SnX_2 (**1**, X = Ph; **3**, X = Cl; **5**, X = H) and *trans*-Myr_2SnX_2 (**2**, X = Ph; **4**, X = Cl; **6**, X = H) were prepared starting from (–)-1S-β-pinene and characterized by multinuclear NMR spectroscopy and in case of **3** and **4** also by X-ray crystallography. The reduction of **3** and **4** with Mg selectively produced pentastannane rings, *cyclo*-(*cis*-$Myr_2Sn)_5$ (**7**) and *cyclo*-(*trans*-$Myr_2Sn)_5$ (**8**), while the dehydropolymerization of **5** and **6** produced a mixture of polystannanes, poly(*cis*-$Myr_2Sn)_n$ (**9**) or poly(*trans*-$Myr_2Sn)_n$ (**10**), and oligomers that could not be separated. The pentastannane rings gave rise to UV absorptions at λ_{max} 219 and 217 nm, which were assigned to $\sigma \rightarrow \sigma^*$ transitions of the Sn−Sn bonds. Due to the increased σ-electron delocalization, the polystannanes **9** and **10** show red-shifted UV absorptions at λ_{max} 416 and 417 nm. The CD spectra of the polystannanes **9** and **10** reveal a positive cotton effect at λ_{max} 422 and 425 nm, consistent with the idea that the chiral information is transferred from the UV-inactive myrtanyl groups to the polymer backbone, which most likely adopts a helical conformation with the right-handed screw sense being in excess.

Introduction

Synthetic macromolecular[1] and supramolecular[2] polymers with dynamically racemic helical structures have attracted considerable attention in recent years due to their ability to transfer and even amplify chiral information from nonracemic chiral pendant groups, guest molecules, and solvents. The principle for the transfer of chiral information is based on the fact that the helix is a chiral structure, which can exist as right- and left-handed mirror images. In the absence of any other chiral information there is no bias for either of the two screw senses as they are energetically equal and occur with the same probability. Incorporation of an external chiral distortion, e.g., by nonracemic pendant groups, creates diastereomers usually differing in energy. At sufficiently low temperatures, dynamic helices may adopt the conformation that accommodates the structure of the diastereomer with the lowest energy. Consequently, the parity of the chiral nonracemic pendant group will control the preferential screw sense of the helix. While chiral transfer experiments have been carried out for a great number of organic polymers including polyisocyanates and polyacetylenes, there are fewer reports on chiral organometallic polymers.[1] Chiral polysilanes[3] and more recently polygermanes[4] have been reported to transfer chiral information from an alkyl side chain to the group 14 element backbone, which can be elegantly probed by CD spectroscopy by using the UV active, delocalized

Scheme 1



$\sigma \rightarrow \sigma^*$ transitions of the E−E bonds (E = Si, Ge). To the best of our knowledge chiral polystannanes have not yet been described.

We are currently exploring routes for the preparation of chiral polystannanes. In this paper we report on the synthesis of a series of enantiomerically pure dialkyltin compounds using inexpensive terpene residues derived from β-pinene. We also describe our initial attempts to polymerize these monomeric precursors and provide the first evidence that the chiral information of the terpenoid pendant groups can be transferred onto the Sn−Sn backbone of the polystannanes obtained.

Results and Discussion

Preparation of Chiral Tin Precursors 1−6. According to modified literature procedures,[5] a large batch of (–)-β-pinene

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† Dedicated to Professor Dainis Dakternieks on the occasion of his 60th birthday.

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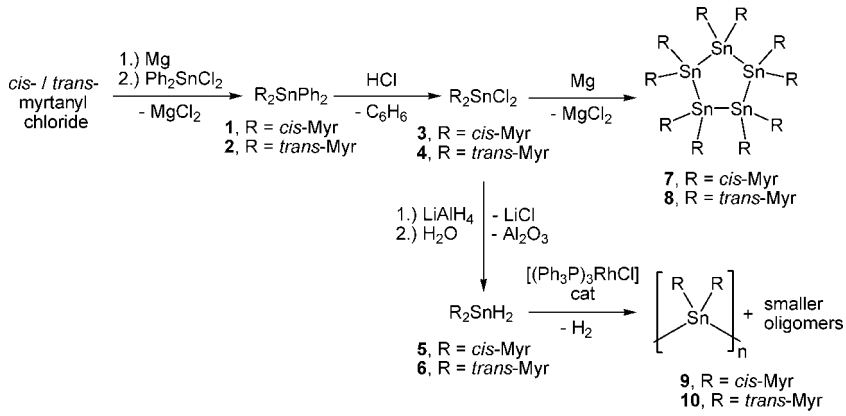
Scheme 2



was converted via oxidative hydroboration into either *cis*- or *trans*-myrtanol depending on the reaction conditions applied (Scheme 1). Unlike in the original procedures,[5] the large quantities of borane needed were generated in situ by using sodium borohydride and dimethyl sulfate, which is an inexpensive alternative to the commercially available $BH_3 \cdot THF$. The diastereomeric purity of the crude *cis*-myrtanol (95% de) and *trans*-myrtanol (74% de) estimated by ^1H NMR spectroscopy was improved by recrystallization of the monophthalic esters. Base hydrolysis of the phthalic esters provided enantiomerically pure *cis*-myrtanol (>98% de) and *trans*-myrtanol (>98% de), which were converted into *cis*- and *trans*-myrtanyl chloride by using the Apple reagent (PPh_3/CCl_4) without affecting the stereochemical integrity of the chiral centers (Scheme 1).[6]

The reaction of diphenyltin dichloride with 2 equiv of the Grignard reagent prepared form *cis*- or *trans*-myrtanyl chloride and Mg produced the enantiomerically pure bis(myrtanyl)diphenylstannanes *cis*-Myr_2SnPh_2 (**1**) and *trans*-Myr_2SnPh_2 (**2**) in high yields as colorless oils (Scheme 2).

The bis(myrtanyl)diphenylstannanes **1** and **2** give rise to ^{119}Sn NMR signals ($CDCl_3$) at δ –78.7 and –79.2, respectively. The relative configuration of the myrtanyl residues was confirmed by a full assignment of all ^{13}C and ^1H resonances (see the Experimental Section). The reaction of **1** and **2** with concentrated hydrochloric acid proceeds with the complete cleavage of the phenyl groups and provided the corresponding bis(myrtanyl)tin dichlorides *cis*-Myr_2SnCl_2 (**3**) and *trans*-Myr_2SnCl_2 (**4**) in nearly quantitative yields as colorless crystalline solids (Scheme 2). Compounds **3** and **4** are characterized by ^{119}Sn NMR chemical shifts ($CDCl_3$) of δ 116.3 and 118.3. The molecular structure of **3** and **4** are shown in Figures 1 and 2. Selected bond parameters are listed in the caption of the figures and relevant crystal and refinement data are collected in Table 1. The molecular structures of **3** and **4** confirm the identity of the compounds as well as the relative and absolute (Flack parameter) configuration of the *cis*- and *trans*-myrtanyl residues. The spatial arrangement around the Sn atom of **3** is tetrahedral with a weak additional intermolecular Sn···Cl interaction (3.890(2) Å; symmetry code: $a = 0.5 + x$, $0.5 - y$, $1 - z$) of an adjacent molecule in the crystal lattice (4 + 1 coordination). It is noteworthy that **4** reveals six crystallographically independent conformers in the solid state, four of which show a similar 4 + 1 coordination (3.573(2)−3.664(3) Å), whereas two lack additional Sn···Cl contacts. To the best of our knowledge such a large number of independent conformers in the unit cell is unprecedented and presumably due to packing effects associated with the asymmetric substituents and the intermolecular Sn···Cl contacts. The number and lengths of intermolecular Sn···Cl interactions have been investigated in detail for diorganotin dichlorides having various substituents.[7] Nevertheless, the structural differences of all six conformers of **4** are marginal. The reduction of **3** and **4** with use of $LiAlH_4$ produced the corresponding bis(myrtanyl)tin dihydrides *cis*-Myr_2SnH_2 (**5**) and *trans*-Myr_2SnH_2 (**6**) in virtually quantitative yield as colorless air-sensitive oils (Scheme 2). The proton-coupled ^{119}Sn spectra (C_6D_6) of **5** and **6** give rise to triplets at δ –223.2 and –225.7 with $^1J(^{119}Sn-^1H)$ couplings of 1667 and 1674 Hz. The IR

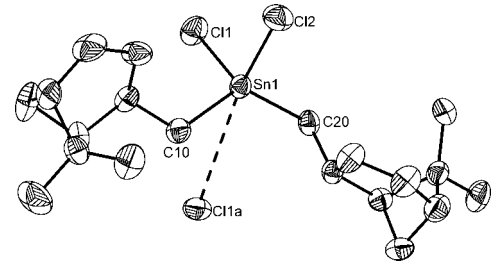


Figure 1. Molecular structure of *cis*-Myr_2SnCl_2 (**3**) showing 30% probability displacement ellipsoids and the numbering scheme. Symmetry code used to generate equivalent atoms: $a = 0.5 + x$, $0.5 - y$, $1 - z$. Selected bond parameters (Å, deg): Sn1−Cl1 2.363(2), Sn1−Cl2 2.348(2), Sn1−C10 2.131(6), Sn1−C20 2.141(5), Sn1−Cl1a 3.890(2), Cl1−Sn1−Cl2 99.87(7), Cl1−Sn1−C10 106.62(17), Cl1−Sn1−C20 106.60(16), Cl2−Sn1−C10 109.81(17), Cl2−Sn1−C20 105.77(15), C10−Sn1−C20 125.28(22).

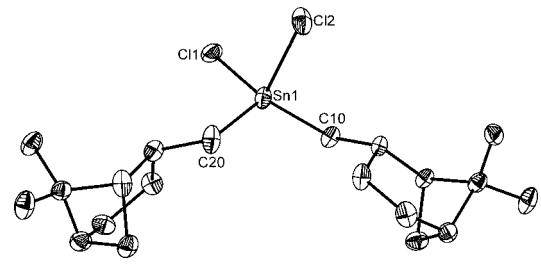


Figure 2. Molecular structure of one of six independent conformers of *trans*-Myr_2SnCl_2 (**4**) showing 30% probability displacement ellipsoids and the numbering scheme. The other five independent conformers are not shown. Selected bond parameters (Å, deg): Sn1−Cl1 2.343(5), Sn1−Cl2 2.352(3), Sn1−C10 2.122(6), Sn1−C20 2.156(8), Cl1−Sn1−C10 107.24(17), Cl1−Sn1−C20 111.93(17), Cl2−Sn1−C10 105.05(19), Cl2−Sn1−C20 107.14(21), C10−Sn1−C20 122.97(23).

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Table 1. Crystal Data and Structure Refinement of 3 and 4

	3	4
formula	$C_{20}H_{34}Cl_2Sn$	$C_{20}H_{34}Cl_2Sn$
formula wt, g mol^{-1}	464.06	464.06
cryst system	orthorhombic	monoclinic
cryst size, mm^3	0.23 × 0.18 × 0.04	0.65 × 0.30 × 0.06
space group	$P2_12_12_1$	$P2_1$
a, Å	6.9891(8)	19.346(5)
b, Å	15.683(2)	11.282(3)
c, Å	19.816(3)	30.018(7)
α, deg	90	90
β, deg	90	102.351(5)
γ, deg	90	90
V, Å^3	2172.0(5)	6400(3)
Z	4	12
ρ_{calcd}, Mg m^{-3}	1.419	1.445
T, K	133	133
μ(Mo $K\alpha$), mm^{-1}	1.421	1.447
F(000)	952	2856
θ range, deg	0.98 to 29.24	0.98 to 30.56
index ranges	$-9 \le h \le 8$	$-13 \le h \le 13$
	$-21 \le k \le 21$	$-17 \le k \le 19$
	$-26 \le l \le 27$	$-22 \le l \le 27$
no. of reflns collected	17755	77895
completeness to θ_{max} (%)	98.4	98.2
no. of indep. reflns	5744	37726
no. obsd reflns ($I > 2\sigma(I)$)	3952	28022
no. of refined params	208	1243
goodness of fit, F^2	1.000	1.014
R_1 (F) ($I > 2\sigma(I)$)	0.0428	0.0508
wR_2 (F^2) (all data)	0.1062	0.1150
Flack parameter	0.00(4)	0.00(2)
$(\Delta/\sigma)_{max}$	>0.001	>0.001
largest diff peak/hole, e Å^{-3}	0.343/−0.777	1.710/−1.320

spectra (neat) of **5** and **6** show one absorption at $\tilde{\nu}$ 1827 and 1832 cm^{-1}, which was assigned to Sn−H stretching vibrations.

Attempted Polymerization of 3−6. There are two principal routes for the preparation of polystannanes, namely the reductive dehalogenation of diorganotin dichlorides with alkali or earth alkali metals[8–10] and the transition metal-catalyzed dehydropolymerization of diorganotin dihyrides.[11–14] Molloy et al. reported that the kinetically controlled reduction of Bu_2SnCl_2 using Na in toluene at 60 °C produced high molecular weight polymers poly$(Bu_2Sn)_n$ ($n \approx$ 4000–5000) as well as cyclic oligomers *cyclo*-$(Bu_2Sn)_5$ and *cyclo*-$(Bu_2Sn)_6$ in varying amounts.[9] It is worth mentioning that the reduction of bulkier diorganotin dichlorides, such as *t*-Bu_2SnCl_2, exclusively produces smaller oligostannane rings, e.g, *cyclo*-(*t*-$Bu_2Sn)_4$.[10] When we adopted the same reaction conditions for the reduction of *cis*-Myr_2SnCl_2 (**3**) and *trans*-Myr_2SnCl_2 (**4**), we obtained a complex mixture of ill-defined products. The ^{119}Sn NMR spectra of the crude reaction mixtures revealed more than 10 signals in each case. A possible explanation may involve the disintegration of the strained bicylic *cis*- and *trans*-myrtanyl skeletons under these harsh reaction conditions. Jousseaume et al. described the milder

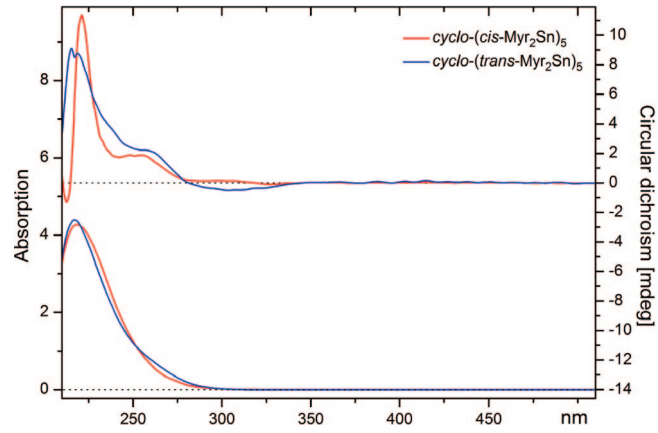

Figure 3. CD and UV spectra (THF) of *cyclo*-(*cis*-$Myr_2Sn)_5$ (**7**) and *cyclo*-(*trans*-$Myr_2Sn)_5$ (**8**).

reduction of Bu_2SnCl_2 with Mg activated by 1,2-dibromomethane in THF at 60 °C, which provided an approximately equimolar mixture of *cyclo*-$(Bu_2Sn)_5$ and *cyclo*-$(Bu_2Sn)_6$ in very high yield, but no high molecular weight fraction.[8] When we carried out the reduction of *cis*-Myr_2SnCl_2 (**3**) and *trans*-Myr_2SnCl_2 (**4**) with Mg under similar conditions at room temperature, we obtained the five-membered oligostannane rings *cyclo*-(*cis*-$Myr_2Sn)_5$ (**7**) and *cyclo*-(*trans*-$Myr_2Sn)_5$ (**8**) as slightly off-white, air-sensitive solids in almost quantitative yields (Scheme 2). A GPC analysis of the crude products indicated a low molecular weight fraction, but no evidence of high molecular weight materials. ^{119}Sn NMR spectroscopy ($CDCl_3$) reveals that only one product had formed. The ^{119}Sn NMR spectra of **7** and **8** show signals at δ –209.9 and –218.1, which compare well with the chemical shift reported for *cyclo*-$(Bu_2Sn)_5$ (–201.9). The signals of **7** and **8** are accompanied by two equally intense pairs of tin satellites indicative for $^1J(^{119}Sn-^{117}Sn)$ and $^2J(^{119}Sn-^{117}Sn)$ couplings of 471 and 328 Hz for **7** and 494 and 437 Hz for **8**, which are comparable with those of *cyclo*-$(Bu_2Sn)_5$ (468 and 465 Hz). The magnitude and relative intensity of the tin satellites with respect to the main signal are unambiguous proof for the five-membered ring structure.[15] Independent confirmation of the ring size stems from mass spectrometry. The EI MS spectra of **7** and **8** recorded at 220 °C reveal the highest mass cluster at 1966.2 g mol^{-1}, which was assigned to the molecular peak of the pentamers. Both spectra also showed a peak at 1572.9 g mol^{-1}, which is consistent with the transient formation of tetramers during the fragmentation processes at elevated temperatures. The UV spectra and CD spectra (THF) of **7** and **8** are shown in Figure 3. Consistent with the five-membered-ring structure, the UV spectra of **7** and **8** reveal absorption peaks at λ_{max} 219 and 217 nm, which were assigned to $\sigma \rightarrow \sigma^*$ transitions of the Sn−Sn bonds.[16] The CD spectrum of **7** reveals a positive Cotton effect at λ 221 and 255 (shoulder) nm as well as a negative cotton effect at λ 213 nm, while the CD spectrum of **7** shows only a positive Cotton effect at λ 216, 219, and 257 (shoulder) nm. The coincidence of UV and CD signals and the unambiguous assignment indicate that the Sn−Sn bonds sense the chiral environment of the UV-inactive myrtanyl substituents.

Since the seminal work of Tilley et al. a number of polystannanes have been prepared by the dehydropolymerisation

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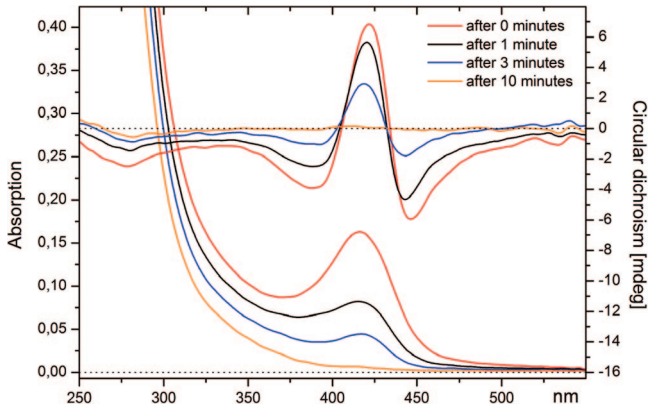

Figure 4. CD and UV spectra (THF) of poly(*cis*-$Myr_2Sn)_n$ (**9**) and related smaller oligomers. Exposure of the sample to ambient light for 0 to 10 min.

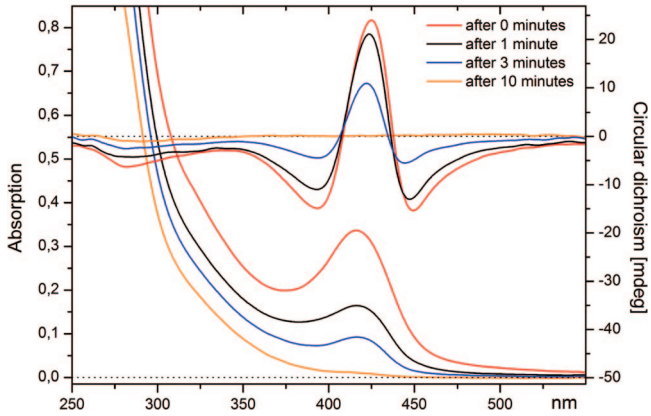

Figure 5. CD and UV spectra (THF) of poly(*trans*-$Myr_2Sn)_n$ (**10**) and related smaller oligomers. Exposure of the sample to ambient light for 0 to 10 min.

route.[11–14] Arguably, the highest polymer yields and molecular weights were obtained with Bu_2SnH_2 and Wilkinson's catalysts [$(Ph_3P)_3RhCl$] in THF.[14] When we adopted the same conditions for the dehydropolymerisation of *cis*-Myr_2SnH_2 (**5**) and *trans*-Myr_2SnH_2 (**6**), we obtained an inseparable very viscous, light- and air-sensitive, yellow mixture of polystannanes, poly(*cis*-$Myr_2Sn)_n$ (**9**) and poly(*trans*-$Myr_2Sn)_n$ (**10**), and oligomers. Unfortunately, due to the viscosity and sensitivity of the material, neither reasonable ^{119}Sn NMR spectra, nor GPC traces could be obtained. However, strong evidence for the presence of a high molecular weight fraction stems from the UV spectra of the diluted crude reaction mixtures. The UV spectra and CD spectra (THF) of **9** and **10** are shown in Figures 4 and 5. The UV spectra show absorption peaks at λ_{max} 416 nm for **9** and 417 nm for **10**, which are indicative of delocalized $\sigma \rightarrow \sigma^*$ transitions of long-chain polystannanes.[11–14]

Solutions containing **9** and **10** are extremely sensitive to the exposure of ambient light. After a few minutes of exposure the yellow color is completely faded and the absorption peaks at around λ_{max} 400 nm cannot be detected anymore (Figure 4). The CD spectra reveal a positive Cotton effect at λ_{max} 422 nm for **9** and 425 nm for **10**, which is consistent with the idea that the chiral information is transferred from the UV-inactive myrtanyl substituents to the polymer backbone. The polymer backbone most likely adopts a helical conformation with a right-handed screw sense being in excess. Unfortunately, the isolation of the polystannanes **5** and **6**, for instance by precipitation from methanol at –80 °C, the procedure that works well for most polysilanes,[3] failed.

In summary, we have prepared two series of enantiomerically pure and functionalized bis(myrtanyl)tin compounds, *cis*-Myr_2SnX_2 (**1**, R = Ph; **3**, R = Cl; **5**, R = H) and *trans*-Myr_2SnX_2 (**2**, R = Ph; **4**, R = Cl; **6**, R = H), derived from β-pinene. Reduction of **3** and **4** with Mg provided access to the five-membered pentastannane rings, *cyclo*-(*cis*-$Myr_2Sn)_5$ (**7**) and *cyclo*-(*trans*-$Myr_2Sn)_5$ (**8**). The [$(Ph_3P)_3RhCl$]-catalyzed dehydropolymisation of **5** and **6** produced an inseparable mixture of polystannanes, poly(*cis*-$Myr_2Sn)_n$ (**9**) and poly(*trans*-$Myr_2Sn)_n$ (**10**), and oligomers. The first evidence was presented that the chiral information of the myrtanyl residues is transferred onto the polymer backbone, which most likely adopts a helical conformation with the right-handed screw sense being in excess.

Experimental Section

Air-sensitive materials were handled under Argon, using standard Schlenk and glovebox techniques. (1*S*)-(–)-β-Pinene (98%), $(Ph_3P)_3RhCl$, and all reagents were commercially available and used as received. Ph_2SnCl_2 was prepared according to a literature procedure.[17] The synthesis of *cis*- and *trans*-myrtanyl chloride is described in the Supporting Information. Solvents were freshly distilled prior to use. NMR spectra were collected by using a Jeol JNM-LA 400 FT spectrometer and Jeol Eclipse+ 500 FT spectrometer are referenced against Me_4Si and Me_4Sn. IR spectra were recorded with a Nicolet Nexus FT-IR spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The circular dichroism was measured at 20 °C with use of a JASCO J-810 spectrometer, while the UV spectra were obtained with a Perkin-Elmer Lambda 9 spectrometer at room temperature. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of Bis(*cis*-myrtanyl)diphenyltin (1) and Bis(*trans*-myrtanyl)diphenyltin (2). Mg turnings (1.29 g, 53.2 mmol) covered with dry THF (5 mL) were activated by addition of 1,2-dibromoethane (150 μL). To this suspension was slowly added the appropriate myrtanyl chloride (8.00 g, 46.3 mmol) dissolved in THF (50 mL). The reaction mixture was refluxed for 18 h. After cooling to room temperature the Grignard reagent was decanted from the unreacted Mg to another flask via cannula. To the Grignard reagent was dropwise added a solution of diphenyltin dichloride (6.05 g, 17.6 mmol) in THF (50 mL). The mixture was stirred for 18 h at room temperature before Et_2O (40 mL), *n*-pentane (20 mL), and water (80 mL) were added. The organic layer was washed with water (2 × 80 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The remaining viscous oil was distilled, using a Kugelrohr apparatus at 245 °C/1 mbar.

1: Yield 9.23 g, 16.9 mmol, 96%. $[\alpha]_D$ –29.1 (*c* 0.18, $CHCl_3$). ^1H NMR (500.16 MHz, $CDCl_3$) δ 7.70–7.60 (4H, m; H-phenyl$_{(ortho)}$), 7.49–7.42 (6H, m; H-phenyl$_{(para)}$, H-phenyl$_{(meta)}$), 2.58–2.47 (2H, m; H-2), 2.45–2.40 (2H, m; Hs(e)-7), 2.18–2.09 (2H, m; Ha(e)-3), 2.10–2.03 (2H, m; Hs(e)-4), 2.02–2.01 (4H, m; H-1, H-5), 1.95–1.89 (2H, m; Ha(a)-4), 1.68 (4H, d, $^3J(^1H-^1H) = 8$ Hz; H-10), 1.69–1.61 (2H, m; Hs(a)-3), 1.27 (6H, s; H-8), 1.23 (6H, s; H-9), 0.95 (2H, d, $^2J(^1H-^1H) = 10$ Hz; Ha(a)-7). $^{13}C-\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 141.2 (C-phenyl$_{(ipso)}$), 136.8 (C-phenyl$_{(ortho)}$),128.2(C-phenyl$_{(para)}$),128.1(C-phenyl$_{(meta)}$),49.8($^3J(^{13}C-^{119/117}Sn) = 46$ Hz; C-1), 41.3 (C-5), 39.5 ($^2J(^{13}C-^{119/117}Sn) = 20$ Hz; C-2), 38.7 (C-6), 34.0 (C-7), 28.1 (C-8), 26.6 (C-4), 26.5 ($^3J(^{13}C-^{119/117}Sn) = 48$ Hz; C-3), 23.4 (C-9), 21.5 ($^1J(^{13}C-^{119}Sn) = 357$ Hz; C-10). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ –78.7. Anal. Calcd for $C_{32}H_{44}Sn$ (547.40): C, 70.21; H, 8.10. Found: C, 70.18; H, 8.22.

(17) Gilman, H.; Gist, L. A. *J. Org. Chem.* **1957**, *22*, 368.

2: Yield 9.25 g, 16.9 mmol, 96%. $[\alpha]_D$ –8.1 (*c* 0.21, $CHCl_3$). ^1H NMR (500.16 MHz, $CDCl_3$) δ 7.57–7.55 (4H, m; H-phenyl$_{(ortho)}$), 7.40–7.37 (6H, m; H-phenyl$_{(para)}$, H-phenyl$_{(meta)}$), 2.40−2.30 (2H, m; H-2), 2.11–2.07 (2H, m; Hs(e)-7), 1.94–1.90 (2H, m; H-5), 1.79–1.74 (8H, m; Hs(e)-3, H-4, H-1), 1.49 (2H, d, $^2J(^1H-^1H)$ = 10 Hz; Ha(a)-7), 1.45–1.41 (2H, m; H-10), 1.43–1.30 (2H, m; Ha(a)-3), 1.35–1.31 (2H, m; H-10′), 1.20 (6H, s; H-8), 0.75 (6H, s; H-9). $^{13}C-\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 141.3 (C-phenyl$_{(ipso)}$), 136.7 (C-phenyl$_{(ortho)}$), 128.2 (C-phenyl$_{(para)}$), 128.1 (C-phenyl$_{(meta)}$), 49.4 ($^3J(^{13}C-^{119/117}Sn)$ = 43 Hz; C-1), 40.7 (C-5), 39.7 (C-6), 32.8 ($^2J(^{13}C-^{119/117}Sn)$ = 18 Hz; C-2), 26.8 (C-8), 26.6 ($^3J(^{13}C-^{119/117}Sn)$ = 50 Hz; C-3), 24.6 (C-4), 22.9 (C-7), 20.0 ($^1J(^{13}C-^{119}Sn)$ = 364 Hz; C-10), 19.8 (C-9). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ –79.2. Anal. Calcd for $C_{32}H_{44}Sn$ (547.40): C, 70.21; H, 8.10. Found: C, 70.31; H, 8.17.

Synthesis of Bis(*cis*-myrtanyl)tin Dichloride (3) and Bis(*trans*-myrtanyl)tin Dichloride (4). The appropriate bis(myrtanyl)diphenyltin (7.00 g, 12.8 mmol) was stirred in concentrated HCl (80 mL) for 20 h. The crude product was extracted with CH_2Cl_2 (80 mL). The organic layer was washed with water (3 × 30 mL) and dried over Na_2SO_4. The solvent was removed in vacuo to give the bis(myrtanyl)diphenyltin dichloride as colorless solids. Crystallization from CH_2Cl_2/*n*-hexane afforded colorless crystals.

3: Yield 5.69 g, 12.3 mmol, 96%. Mp 110 °C. $[\alpha]_D$ –37.5 (*c* 0.12, $CHCl_3$). ^1H NMR (399.65 MHz, $CDCl_3$) δ 2.59–2.50 (2H, m; H-2), 2.40–2.34 (2H, m; Hs(e)-7), 2.19–2.10 (2H, m; Ha(e)-3), 2.00 (4H, d, $^3J(^1H-^1H)$ = 8 Hz; H-10), 1.99–1.92 (2H, m; Hs(e)-4), 1.96–1.91 (2H, m; H-5), 1.88–1.83 (2H, m; Ha(a)-4), 1.84–1.82 (2H, m; H-1), 1.54–1.44 (2H, m; Hs(a)-3), 1.21 (6H, s; H-8), 1.07 (6H, s; H-9), 0.92 (2H, d, $^2J(^1H-^1H)$ = 10 Hz; Ha(a)-7). $^{13}C-\{^1H\}$ NMR (100.40 MHz, $CDCl_3$) δ 49.3 ($^3J(^{13}C-^{119/117}Sn)$ = 78 Hz; C-1), 40.7 (C-5), 38.7 (C-6), 37.7 ($^2J(^{13}C-^{119/117}Sn)$ = 30 Hz; C-2), 37.0 ($^1J(^{13}C-^{119}Sn)$ = 398 Hz; C-10), 33.6 (C-7), 27.9 (C-8), 26.0 (C-4), 25.2 ($^3J(^{13}C-^{119/117}Sn)$ = 70 Hz; C-3), 23.2 (C-9). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ 116.3. Anal. Calcd for $C_{20}H_{34}Cl_2Sn$ (464.10): C, 51.76; H, 7.38. Found: C, 51.82; H, 7.25.

4:Yield 5.56 g, 12.0 mmol, 94% yield. Mp 57–58 °C, $[\alpha]_D$ +8.3 (*c* 0.20, $CHCl_3$). ^1H NMR (500.16 MHz, $CDCl_3$) δ 2.57–2.46 (2H, m; H-2), 2.13–2.08 (2H, m; Hs(e)-7), 1.94–1.90 (2H, m; H-5), 1.87–1.83 (2H, m; H-10), 1.87–1.78 (2H, m; Hs(e)-3), 1.85–1.75 (4H, m; H-4), 1.79–1.75 (2H, m; H-10′), 1.70–1.68 (2H, m; H-1), 1.37 (2H, d, $^2J(^1H-^1H)$ = 10 Hz; Ha(a)-7), 1.34 – 1.25 (2H, m; Ha(a)-3), 1.21 (6H, s; H-8), 0.84 (6H, s; H-9). $^{13}C-\{^1H\}$ NMR (125.77 MHz, $CDCl_3$) δ 48.9 ($^3J(^{13}C-^{119/117}Sn)$ = 75 Hz; C-1), 40.5 (C-5), 40.0 (C-6), 36.4 ($^1J(^{13}C-^{119}Sn)$ = 405 Hz; C-10), 32.1 ($^2J(^{13}C-^{119/117}Sn)$ = 27 Hz; C-2), 26.7 (C-8), 25.5 ($^3J(^{13}C-^{119/117}Sn)$ = 67 Hz; C-3), 24.2 (C-4), 22.9 (C-7), 19.9 (C-9). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ 118.3. Anal. Calcd for $C_{20}H_{34}Cl_2Sn$ (464.10): C, 51.76; H, 7.38. Found: C, 51.89; H, 7.24.

Synthesis of Bis(*cis*-myrtanyl)tin Dihydride (5) and Bis(*trans*-myrtanyl)tin Dihydride (6). To a suspension of $LiAlH_4$ (0.13 g, 3.4 mmol) in dry Et_2O (15 mL) was added a solution of the appropriate bis(myrtanyl)tin dichloride (1.00 g, 2.2 mmol) in dry Et_2O (15 mL). The solution was stirred for 15 h at room temperature before it was cooled on an ice bath. Degassed water (10 mL) was added carefully. After complete addition the mixture was allowed to warm to room temperature and the organic layer was thoroughly washed with degassed water (3 × 10 mL), dried over Na_2SO_4, and filtered. Removal of the solvent in vacuo gave the product as highly viscous colorless oil.

5: Yield 0.83 g, 2.10 mmol, 98%. $[\alpha]_D$ –45.5 (*c* 1.55, THF). ^1H NMR (500.16 MHz, C_6D_6) δ 4.76 – 4.74 (2H, m, $^1J(^1H-^{119}Sn)$ = 1667 Hz, $^3J(^1H-^1H)$ = 2 Hz; Sn-*H*), 2.33–2.29 (2H, m; Hs(e)-7), 2.27–2.20 (2H, m; H-2), 2.07–1.99 (2H, m; Ha(e)-3), 1.94–1.88 (2H, m; Hs(e)-4), 1.87–1.86 (4H, m; H-5, H-1), 1.81–1.75 (2H, m; Ha(a)-4), 1.46–1.39 (2H, m; Hs(a)-3), 1.23–1.19 (4H, m; H-10), 1.20 (6H, s; H-8), 1.04 (6H, s; H-9), 0.84 (2H, d, $^2J(^1H-^1H)$ = 10 Hz; Ha(a)-7). $^{13}C-\{^1H\}$ NMR (125.78 MHz, C_6D_6) δ 50.1 ($^3J(^{13}C-^{119/117}Sn)$ = 52 Hz; C-1), 41.7 (C-5), 41.2 ($^2J(^{13}C-^{119/117}Sn)$ = 23 Hz; C-2), 39.0 (C-6), 34.4 (C-7), 28.5 (C-8), 26.9 (C-4), 26.5 ($^3J(^{13}C-^{119/117}Sn)$ = 45 Hz; C-3), 23.5 (C-9), 18.2 ($^1J(^{13}C-^{119}Sn)$ = 366 Hz; C-10). ^{119}Sn NMR (148.95 MHz, C_6D_6) δ –223.2 (t, $^1J(^{119}Sn-^1H)$ = 1667 Hz). IR (neat): $\tilde{\nu}$ = 1827 cm^{-1}. Anal. Calcd for $C_{20}H_{36}Sn$ (395.21): C, 60.78; H, 9.18; Found: C, 60.85; H, 9.12.

6: Yield 0.83 g, 2.10 mmol, 97%. $[\alpha]_D$ +10.1 (*c* 2.06, THF). ^1H NMR (399.65 MHz, C_6D_6) δ 4.61–4.57 (2H, m, $^1J(^1H-^{119}Sn)$ = 1675 Hz, $^3J(^1H-^1H)$ = 2 Hz; Sn-*H*), 2.14–2.03 (2H, m; H-2), 1.97–1.91 (2H, m; Hs(e)-7), 1.78–1.74 (2H, m; H-5), 1.68−1.57 (8H, m; Hs(e)-3, H-4, H-1), 1.28 (2H, d, $^2J(^1H-^1H)$ = 10 Hz; Ha(a)-7), 1.18–1.04 (2H, m; Ha(a)-3), 1.11 (6H, s; H-8), 1.00–0.93 (2H, m; H-10), 0.88–0.82 (2H, m; H-10), 0.71 (6H, s; H-9). $^{13}C-\{^1H\}$ NMR (100.40 MHz, C_6D_6) δ 49.9 ($^3J(^{13}C-^{119/117}Sn)$ = 52 Hz; C-1), 41.2 (C-5), 40.0 (C-6), 34.4 ($^2J(^{13}C-^{119/117}Sn)$ = 22 Hz; C-2), 27.2 (C-8), 26.5 ($^3J(^{13}C-^{119/117}Sn)$ = 42 Hz; C-3), 25.0 (C-4), 23.4 (C-7), 20.4 (C-9), 16.7 ($^1J(^{13}C-^{119}Sn)$ = 371 Hz; C-10). ^{119}Sn NMR (148.95 MHz, C_6D_6) δ –225.7 (t, $^1J(^{119}Sn-^1H)$ = 1674 Hz). IR (neat): $\tilde{\nu}$ = 1832 cm^{-1}. Anal. Calcd for $C_{20}H_{36}Sn$ (395.21): C, 60.78; H, 9.18; Found: C, 60.89; H, 9.10.

Synthesis of Dodekakis(*cis*-myrtanyl)cyclopentastannane (7) and Dodekakis(*trans*-myrtanyl)cyclopentastannane (8). Mg turnings (1.05 g, 43 mmol) covered with dry THF were activated with 1,2-dibromoethane (100 μL). To this vigorously stirred suspension was added the appropriate bis(myrtanyl)tin dichloride (2.00 g, 4.3 mmol) dissolved in THF (15 mL). The reaction mixture turned dark green to almost black within 10 min. After 20 h, the solution was decanted from the unreacted Mg and hydrolyzed with degassed water (15 mL). The organic layer was washed with degassed water (3 × 15 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo gave the product as an off-white solid.

7: Yield 1.64 g, 0.834 mmol, 97%. Mp 178 °C (softens at 105 °C). $[\alpha]_D$ –31.4 (*c* 0.35, $CHCl_3$). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ –209.9 ($^1J(^{119}Sn-^{117}Sn)$ = 471 Hz, $^2J(^{119}Sn-^{117}Sn)$ = 328 Hz)). UV λ_{max} 219 nm. Anal. Calcd for $C_{100}H_{170}Sn_5$ (1965.97): C, 61.09; H, 8.72. Found: C, 59.74; H, 8.58.

8: Yield 1.62 g, 0.826 mmol, 96%. Mp 159 °C (softens at 93 °C). $[\alpha]_D$ –51.7 (*c* 0.35, $CHCl_3$). $^{119}Sn-\{^1H\}$ NMR (148.95 MHz, $CDCl_3$) δ –218.1 ($^1J(^{119}Sn-^{117}Sn)$ = 494, $^2J(^{119}Sn-^{117}Sn)$ = 437 Hz). UV λ_{max} 217 nm. Anal. Calcd for $C_{100}H_{170}Sn_5$ (1965.97): C, 61.09; H, 8.72. Found: C, 59.82; H, 8.55.

Dehydropolymerization of 5 and 6. In an argon-flooded glovebox an open Schlenk tube wrapped in aluminum foil (as light protection) was charged with the appropriate bis(myrtanyl)tin dihydride (200 mg, 0.51 mmol) and $(Ph_3P)_3RhCl$ (19 mg, 0.02 mmol) was added. The Schlenk tube was shaken occasionally and left to stand for 5 d. During this time the viscosity increased significantly and the bright yellow color intensified.

Crystallography. Intensity data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[18] The structures were solved by direct methods and difference Fourier synthesis by using SHELXS-97 implemented in the program WinGX 2002.[19] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached were included in geometrically calculated positions for all structures by using a riding model and were refined isotropically. The figure were

(18) SMART, SAINT, and SADABS, Siemens Analytical X-ray Instruments Inc.: Madison, WI, **1999**.
(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(20) *DIAMOND*, V2.1d, Crystal Impact; K. Brandenburg & M. Berndt & GbR, **2002**.

created with DIAMOND.[20] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 675780 (**3**) and 675781 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44–1223–336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Procedures for the synthesis and spectral data of *cis*- and *trans*-myrtanol and *cis*- and *trans*-myrtanyl chloride, figures of the other five crystallographically independent conformers of **4**, and crystallographic data (CIF files) for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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