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FULL PAPER

Synthesis of chiral organotin hydrides containing menthyl and oxazoline substituents †

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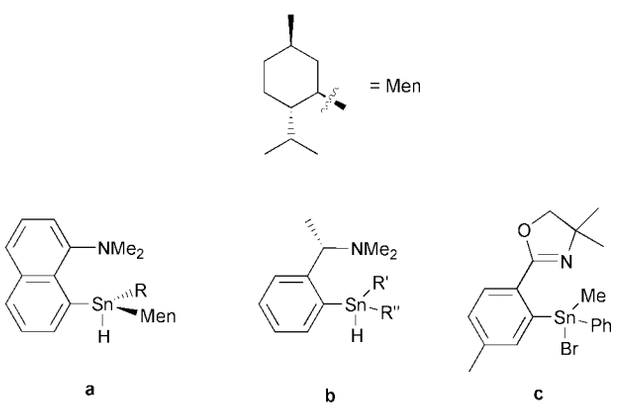
A series of chiral non-racemic triorganotin halides and triorganotin hydrides containing one or two (1*R*,2*S*,5*R*)-menthyl (Men) substituents as well as 2-(4,4-dimethyl-2-oxazolinyl)-5-(methyl)phenyl (L) or chiral 2-(4-isopropyl-2-oxazolinyl)-5-(methyl)phenyl ligand (L*) have been synthesized and characterised. Each of SnCl(Men)PhL and SnH(Men)PhL has a stereogenic tin centre and were isolated in diastereomeric ratios of 70 : 30 and 50 : 50, respectively; SnCl(Men)PhL* and SnH(Men)PhL* were synthesized in diastereomeric ratios of 50 : 50 and 66 : 34, respectively. Single crystal X-ray analysis of $SnCl(Men)_2L$ and SnCl(Men)PhL reveals a tendency towards five co-ordination at the tin centre as a result of N→Sn interactions. AM1 calculations provide good qualitative predictability of the molecular geometries observed in the solid state as well as the diastereomeric ratios in solution.

Introduction

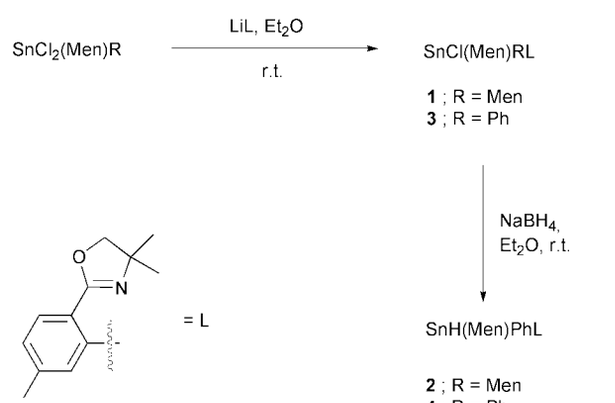
In recent years there has been increased interest in the synthesis of chiral organotin hydrides as enantioselective free radical reducing agents.[1–7] Only a small number of chiral organotin hydrides have been synthesized previously. Even fewer chiral organotin hydrides containing potentially intramolecular co-ordinating groups have been described. These encompass organotin hydrides (**a**) containing the bidentate dimethylaminonaphthyl substituent[8,9] and a series of organotin hydrides (**b**) containing the chiral 2-[(1*S*)-1-dimethylaminoethyl]benzene ligand.[10] Although organotin halides (**c**) containing the 2-(4,4-dimethyl-2-oxazolinyl)-5-(methyl)phenyl group (L) have also been synthesized,[11] there have been no reports of the synthesis of any corresponding organotin hydrides.



As part of our ongoing interest in the synthesis of various classes of chiral organotin hydrides,[6,7] we recently reported the synthesis of a range of chiral organotin hydrides containing both of the aforementioned 8-(dimethylamino)naphthyl and 2-[(1*S*)-1-dimethylaminoethyl]benzene intramolecular substituents in combination with the chiral (1*R*,2*S*,5*R*)-menthyl (Men) moiety.[12] Recent work by us has demonstrated significant enhancement in enantioselectivities during asymmetric reductions involving these chiral organotin hydrides and achiral Lewis acids.[7] We now report the synthesis and characterisation of a series of chiral organotin hydrides containing the Men substituent as well as the 2-(4,4-dimethyl-2-oxazolinyl)-5-(methyl)phenyl (L) ligand or the chiral 2-(4-isopropyl-2-oxazolinyl)-5-(methyl)phenyl (L*) ligand.

Results and discussion

Reaction of one molar equivalent of 2-[4,4-dimethyl-2-oxazolinyl]-5-methylphenyllithium (LiL) with $SnCl_2(Men)_2$ in diethyl ether afforded $SnCl(Men)_2L$ **1** in 79% yield (Scheme 1). The ^{119}Sn NMR ($CDCl_3$) spectrum of **1** contains a single resonance (δ −94.8) whilst the corresponding ^{13}C and ^1H NMR ($CDCl_3$) spectra each contain two resonances (δ 28.10, 28.38 and 1.43, 1.46 respectively) corresponding to the diastereotopic



Scheme 1

† Electronic supplementary information (ESI) available: AM1 calculations of the heat of formation of compounds **3** and **7**. See http://www.rsc.org/suppdata/dt/b0/b004259p/

Table 1 Selected interatomic (Å, °) parameters for $SnCl(Men)_2L$ **1** and SnCl(Men)PhL **3**

	1	**3**
Sn–Cl	2.487(2)	2.467(2)
Sn–C(1)	2.163(5)	2.13(1)
Sn–C(13)	2.162(5)	2.160(7)
Sn–C(23)	2.177(6)	2.11(1)
Sn–N	2.531(4)	2.552(6)
Cl–Sn–C(1)	98.4(2)	95.7(3)
Cl–Sn–C(13)	96.7(1)	96.3(2)
Cl–Sn–C(23)	94.2(1)	96.4(3)
Cl–Sn–N(1)	170.8(1)	169.1(4)
C(1)–Sn–C(13)	112.5(2)	128.3(6)
C(1)–Sn–C(23)	108.0(2)	113.0(4)
C(1)–Sn–N(1)	72.5(2)	74.0(4)
C(13)–Sn–C(23)	135.7(2)	115.3(6)
C(13)–Sn–N(1)	88.2(2)	87.7(2)
C(23)–Sn–N(1)	87.6(2)	91.0(5)
Sn–N(1)–C(7)	106.8(3)	106.4(7)
Sn–N(1)–C(9)	143.4(3)	144.5(8)
Sn–C(1)–C(6)	117.8(4)	117.4(7)

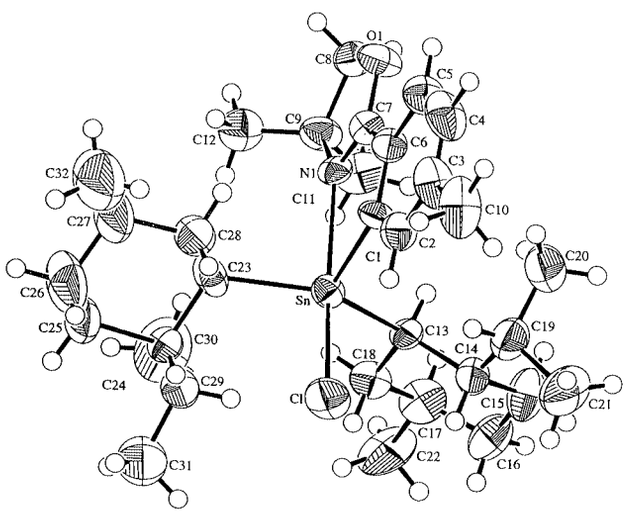


Fig. 1 Molecular structure and atomic numbering scheme for $SnCl(Men)_2L$ **1**.

methyl groups on the oxazoline ring. On heating a solution of **1** (toluene-d8) to 100 ºC two methyl signals are still observed in the ^1H NMR spectrum indicating intramolecular co-ordination of the oxazoline ring nitrogen to the tin center.

The molecular structure of compound **1** is shown in Fig. 1 and selected interatomic parameters are collected in Table 1. The Sn atom is best described as being five-co-ordinate and exists in a distorted trigonal bipyramidal geometry. In this description, the axial positions are defined by the N(1) and Cl atoms with Cl–Sn–N(1) of 170.8(1) °; the Sn atom lies 0.2370(4) Å above the trigonal C_3 plane in the direction of the Cl atom. The two halves of the L ligand are essentially coplanar as seen in the C(1)/C(6)/C(7)/N(1) torsion angle of 0.3(9)° which has the consequence that there is only minor puckering in the five-membered chelate ring (*e.g.* Sn/N(1)/C(7)/C(6) –3.2(7) °).

Reduction of compound **1** with $NaBH_4$ in ethanol afforded $SnH(Men)_2L$ **2** in 64% yield (Scheme 1). The ^{119}Sn NMR (C_6D_6) spectrum comprises a doublet (δ −62.1, $^1J(^{119}Sn–^1H)$ 1238 Hz) whilst the ^{13}C and ^1H NMR ($CDCl_3$) spectra contain two sets of resonances (δ 28.13, 28.32 and 1.15, 1.16 respectively) corresponding to the diastereotopic methyl groups on the oxazoline ring.

Reaction of one molar equivalent of LiL with $SnCl_2(Men)Ph$ in diethyl ether gives SnCl(Men)PhL **3** in 68% yield (Scheme 1). The ^{119}Sn NMR (Et_2O) spectrum of the reaction mixture of **3**, 18 hours after the commencement of the reaction, shows two resonances (δ −156.7 and −181.2) in a ratio of 50 : 50 corresponding to the two possible diastereomers which differ in stereochemistry at the tin center. Addition of methanol to the crude product afforded **3** as a white solid. The ^{119}Sn NMR ($CDCl_3$) spectrum of a freshly prepared analytically pure sample of **3** shows two resonances (δ −156.2 and −180.4) now in a 30 : 70 ratio. After 3 days at room temperature ^{119}Sn NMR ($CDCl_3$) spectroscopy revealed that the 50 : 50 ratio had reestablished itself. This result indicates that one diastereomer of **3** crystallises preferentially from methanol. Another example of preferential crystallisation yielding an asymmetric transformation has previously been reported.[13] The ^{13}C and ^1H NMR spectra (toluene-d8) of **3** show two sets of resonances for the methyl groups of the oxazoline ring, both at room temperature and at 105 °C, indicating Sn–N association is slow on the NMR timescale.

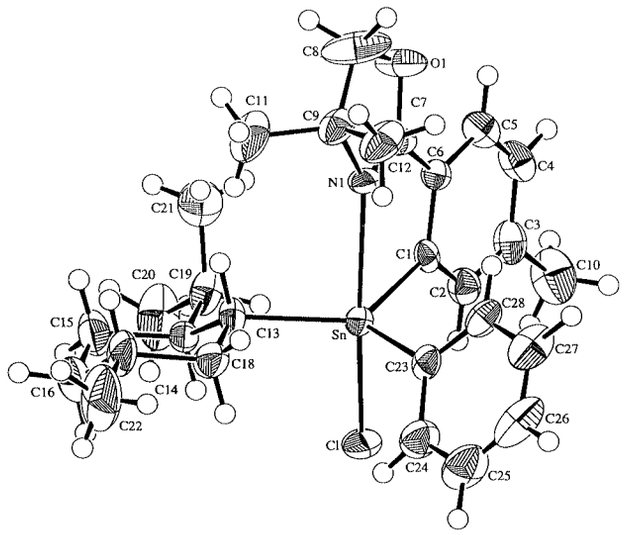
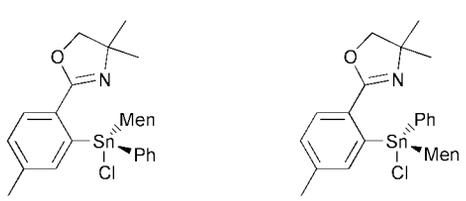
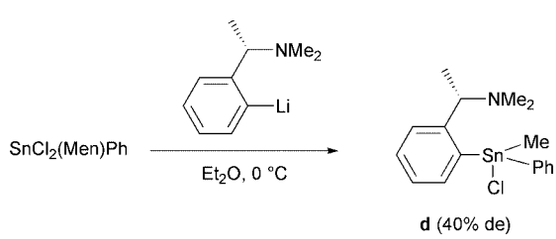


Fig. 2 Molecular structure and atomic numbering scheme for SnCl(Men)PhL **3**.



3

We previously reported that the reaction of 2-[(1*S*)-1-dimethylaminoethyl]phenyl lithium with $SnCl_2(Men)Ph$ in diethyl ether at 0 °C resulted in the formation of the two distereomers of a similar organotin halide, **d**, in a 70 : 30 ratio.[12] A lower reaction temperature of −78 °C resulted in the same 70 : 30 ratio of the two isomers of **d** as evidenced by ^{119}Sn NMR spectroscopy (Scheme 2). Consequently, there was no further



Scheme 2

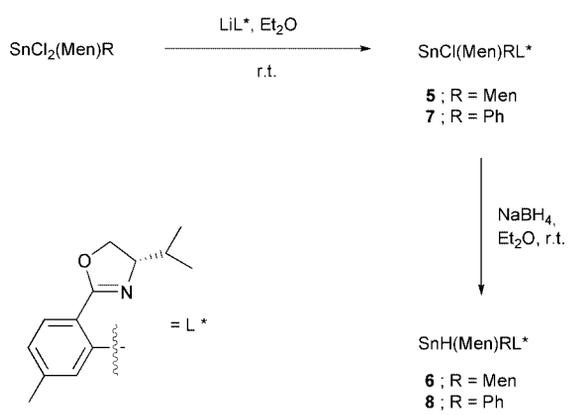
investigation of the change in reaction conditions on the formation of the organotin halide, **3**.

Slow evaporation of a methanol–dichloromethane solution of compound **3** gave crystals suitable for X-ray analysis. The molecular structure is shown in Fig. 2 and Table 1 collects

important geometric parameters. The X-ray analysis shows that the molecule is the (S_{Sn}) diastereomer and thus suggests that this is the predominant species in the freshly prepared solution. The geometry found for **3** resembles closely that described earlier for **1**. The Sn–N distance is 2.552(6) Å which suggests that the magnitude of this interaction is marginally weaker than that in **1**, consistent with the reduced Lewis acidity of the Sn atom in **3**, the relatively large errors notwithstanding. This conclusion is supported by the difference between the Sn–Cl bond distances for the two structures. Thus, that in **3** is significantly shorter than in **1**, consistent with the stronger Sn–N interaction in **1**. The substitution of a menthyl group for a phenyl also relieves some of the steric pressure in the C_3 trigonal plane as there is a narrower range of C–Sn–C angles in the structure of **3**. The Sn atom lies 0.2276(4) Å above the C_3 plane in the direction of the Cl atom.

Reduction of compound **3** with $NaBH_4$ afforded SnH(Men)PhL **4** in 79% yield (Scheme 1). The inverse-gated ^{119}Sn NMR (C_6D_6) spectrum **4** shows two resonances in a 50 : 50 ratio (δ −122.6 and −148.2) corresponding to the two possible diastereomers. The ^{13}C and ^{1}H NMR (C_6D_6) spectra of the diatereomeric mixture display four separate signals corresponding to the two diastereomeric methyl groups of each isomer on the oxazoline ring indicating that dissociation of the Sn–N bond is slow on the NMR timescale.

Attention was then directed towards the synthesis of organotin hydrides containing the chiral 2-(4-(*S*)-isopropyl-2-oxazolinyl)-5-methylphenyl substituent (L*). The L* ligand contains an isopropyl group at the oxazoline ring which provides the source of chirality. Incorporation of such a chiral intramolecular co-ordinating ligand may influence the enantioselective outcome of organotin hydride radical reductions. Reaction of one molar equivalent of n-BuLi with HL* resulted in the formation of LiL*. ^{1}H NMR spectroscopy of the subsequent D_2O exchange reaction gave evidence for the formation of LiL* although it could not be purified by precipitation. Reaction of one molar equivalent of n-BuLi followed by *in situ* reaction with $SnCl_2(Men)_2$ gave $SnCl(Men)_2L$* **5** (Scheme 3) in 58% yield in the crude reaction mixture as evident by ^{119}Sn



Scheme 3

NMR spectroscopy. The ^{119}Sn NMR spectrum (Et_2O) of this mixture indicated the presence of several tin containing species which could not be identified. Purification *via* chromatography and crystallisation afforded analytically pure **5** in 30% yield; ^{119}Sn NMR ($CDCl_3$) δ −106.2. No attempts were made to optimise the yield for this reaction. Reduction of **5** with $NaBH_4$ afforded $SnH(Men)_2L$* **6** in 61% yield; ^{119}Sn NMR (C_6D_6): δ −64.4.

Analogously, the reaction of one molar equivalent of n-BuLi with HL* followed by *in situ* reaction with $SnCl_2(Men)Ph$ afforded SnCl(Men)PhL* **7** in 36% yield in the crude reaction mixture. The ^{119}Sn NMR spectrum (Et_2O) of the reaction mixture indicated the presence of several tin containing species which could not be identified. Purification by chromatography and crystallisation afforded analytically pure **7** in 16% yield. No attempts were made to optimise the yield obtained. The ^{119}Sn NMR ($CDCl_3$) spectrum showed two separate resonances in a 45 : 55 ratio (δ –159.2 and −178.5) corresponding to the two diastereoisomers. Reduction of **7** with $NaBH_4$ afforded SnH(Men)PhL* **8** in 93% yield. The proton-coupled ^{119}Sn NMR (C_6D_6) spectrum showed two doublet resonances in an approximate ratio of 34 : 66 (δ –133.8, $J(^{119}Sn–^{1}H)$ 1772 Hz, and −139.7, $J(^{119}Sn–^{1}H)$ 1645 Hz respectively).

In order to provide further insight into the structures and energies of the two tin epimeric diastereomers of SnCl(Men)PhL **3** and SnCl(Men)PhL* **7**, their geometries were optimised using the AM1 semiempirical molecular modelling technique.[14] The calculated lowest-energy structures are displayed in Fig. 3 together with the AM1 calculated relative energy of each isomer; full details are available as ESI.† Inspection of Fig. 3 reveals that the calculated structures of **3** bear a striking resemblance to the crystal structure displayed in Fig. 2. The tin atom in each molecule is calculated to be co-ordinated to the amino-nitrogen atom, with calculated N–Sn separations in (R_{Sn})-**3** and (S_{Sn})-**3** of 2.62 and 2.59 Å respectively, in good agreement with the X-ray determined value of 2.55 Å for (S_{Sn})-**3** (see above). In addition, energy partitioning[15–17] within the AM1 framework provides an (attractive) N–Sn bicentric energy of −2.08 and −2.21 eV for the (*R*) and (*S*) isomer respectively. More importantly, these calculations predict that (R_{Sn})-**3** lies 0.6 kJ mol^{-1} below (S_{Sn})-**3** in energy. Assuming that this enthalpy difference is reflected in the difference in free energies, this value translates into an approximately equal proportion of isomers at 25 °C, a result which is in excellent agreement with the experimental data (see above).

Fig. 3 reveals that the AM1 calculated geometries of the isomers of compound **7** are remarkably similar to the analogous structures calculated for **3**. Both structures are, once again, calculated to have significant N–Sn bonding, with calculated separations of 2.78 and 2.79 Å for (R_{Sn})-**7** and (S_{Sn})-**7** respectively, and calculated associated bicentric energies of −1.48 and −1.43 eV. Clearly, the N–Sn interactions in structures **7** are predicted to be marginally weaker than the corresponding interactions in **3**, presumably due to increased steric interactions in **7** as a result of the extra bulk associated with the iso-propyl substituent. AM1 calculations predict that (R_{Sn})-**7** is more stable than (S_{Sn})-**7** by some 2.5 kJ mol^{-1}. Using the same argument presented above, this difference translates into an approximate 70 : 30 ratio of isomers at 25 °C.

Providing accurate predictions of relative ratios of isomers is subject to influence by subtle changes in free energy. If it is accepted that AM1 has an associated error of about 4 kJ mol^{-1} in calculated relative energies[18] then this value is also consistent with an approximately equal ratio of isomers.

Organotin hydrides containing oxazoline substituents could not be stored for long periods of time under argon. Compound **8** had decomposed by 30% after storage under argon for 24 hours, 66% of **2** after storage under argon for 11 days and **4** had decomposed completely after storage under argon for only 7 days. The decomposition was probably due to the high reactivity with small traces of oxygen.

Experimental

General details

NMR spectra were obtained using a JEOL-GX 270 FT NMR spectrometer (^{119}Sn inverse-gated or ^{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 Dortmund University,

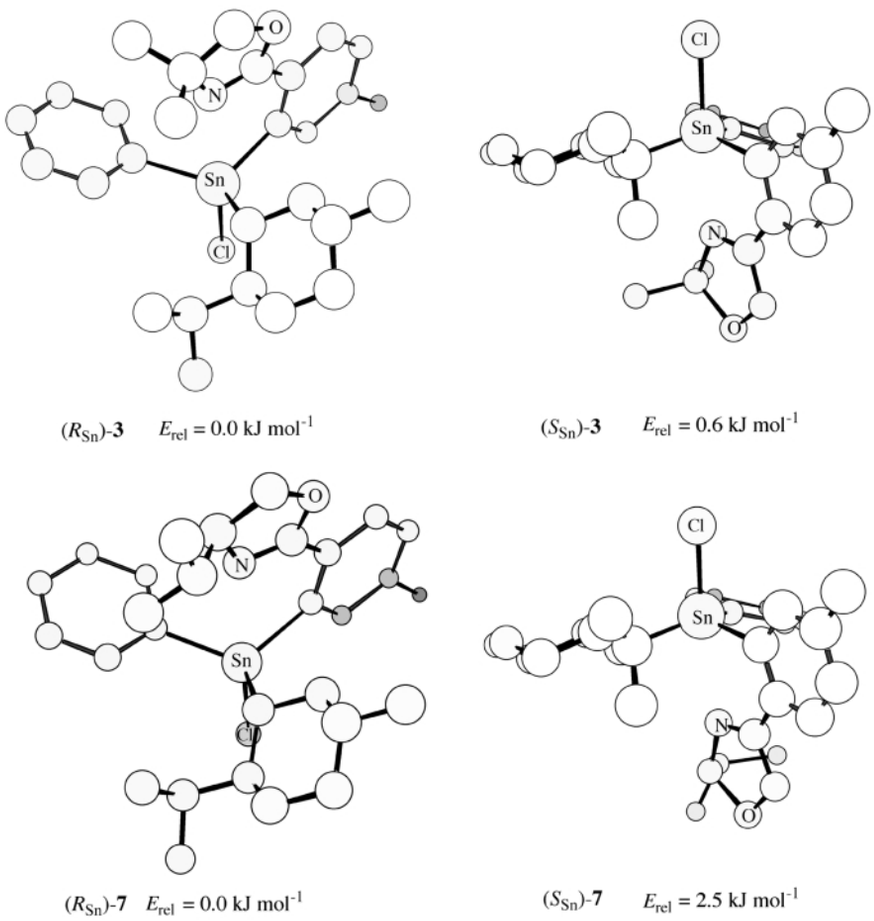


Fig. 3 AM1 calculated geometries of both diastereomers of compounds **3** and **7** (hydrogen atoms removed for clarity).

Germany. 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 argon. 2-[4,4-Dimethyl-2-oxazolinyl]-5-methylphenyllithium (LiL) and L were prepared based on literature methods,[19,20] $Cl_2(Men)_2Sn$[12] and $SnCl_2(Men)Ph$[6] as previously reported.

Syntheses

[2-(4,4-Dimethyl-2-oxazolinyl)-5-methylphenyl]bis[(1*R*,2*S*,5*R*)-menthyl]tin chloride $SnCl(Men)_2L$ 1. A solution of $SnCl_2(Men)_2$ (3.78 g, 8.08 mmol) in diethyl ether (30 mL) was added to a suspension of LiL (1.75 g, 8.97 mmol) in diethyl ether (50 mL) at 0 °C, and stirred at room temperature for 45 minutes. A saturated solution of ammonium chloride (3 mL) and then water (50 mL) were added. The residue was extracted with diethyl ether (3 × 50 mL), the combined extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. Crystallisation from methanol gave compound **1** as a white solid (3.96 g, 79%). mp 182–184 °C. ^{1}H NMR ($CDCl_3$): δ 0.06–2.32 (38 H, m), 1.43 (3 H, s), 1.46 (3 H, s), 2.41 (3 H, s), 4.30 (2 H, s), 7.16 (1 H, d), 7.63 (1 H, d) and 8.05 (1 H, s). ^{13}C NMR ($CDCl_3$): δ 14.65, 16.54, 21.41, 21.78, 21.90, 22.43, 22.53, 26.16, 26.51, 28.10, 28.38, 31.44, 33.70, 34.78, 34.84, 35.59, 35.70, 39.58, 41.27, 43.56 [J(^{13}C–^{119}Sn) 539 Hz], 43.79, 44.16, 45.00 [J(^{13}C–^{119}Sn) 531 Hz], 66.44, 81.30, 126.26, 127.44, 129.03, 137.26, 142.96, 150.42 [J(^{13}C–^{119}Sn) 471 Hz] and 168.80. ^{119}Sn NMR ($CDCl_3$): δ –94.8. Calc. for $C_{32}H_{52}ClNOSn$: C, 61.9; H, 8.4; N, 2.3. Found: C, 61.5; H, 8.6; N, 2.1%.

[2-(4,4-Dimethyl-2-oxazolinyl)-5-methylphenyl][bis(1*R*,2*S*,5*R*)-menthyl]tin hydride $SnH(Men)_2L$ 2. A solution of $NaBH_4$ (0.32 g, 8.46 mmol) in ethanol (10 mL) was added to a solution of compound **1** (0.28 g, 0.45 mmol) in ethanol (50 mL) and stirred at room temperature for 45 minutes. The solvent was removed *in vacuo* and a 20% solution of sodium/potassium (±)-tartrate (10 mL) added. The residue was extracted with diethyl ether (2 × 10 mL), dried (Na_2SO_4) and the solvent removed *in vacuo* to yield **2** as a white oil (0.17 g, 64%). ^{1}H NMR (C_6D_6): δ 0.23–2.39 (38 H, m), 1.15 (3 H, s), 1.16 (3 H, s), 2.02 (3 H, s), 3.69 (2 H, m), 6.32 [1 H, s, J(^{1}H–^{119}Sn) 1238 Hz], 6.90 (1 H, d), 7.87 (1 H, s) and 7.96 (1 H, d). ^{13}C NMR (C_6D_6): δ 15.31, 17.26, 21.41, 22.23, 22.74, 22.77, 22.97, 27.09, 27.56, 28.13, 28.32, 32.40, 33.82, 35.84, 36.00, 36.02 [J(^{13}C–^{119}Sn) 477 Hz], 36.10, 36.14, 38.20 [J(^{13}C–^{119}Sn) 467 Hz], 41.11, 42.86, 47.68, 47.77, 67.25, 79.50, 127.77, 129.08, 130.47, 140.37, 141.35, 148.28 [J(^{13}C–^{119}Sn) 420 Hz] and 164.97. ^{119}Sn NMR (C_6D_6): δ −62.1. HRMS (ESI): Calc. for $C_{32}H_{52}NOSn$ $(M - H)^+$ m/z 586.4048; found 586.3073. ^{119}Sn NMR (C_6D_6) indicated 66% of **2** decomposed after 11 days storage under argon.

[2-(4,4-Dimethyl-2-oxazolinyl)-5-methylphenyl][(1*R*,2*S*,5*R*)-menthyl]phenyltin chloride $SnCl(Men)PhL$ 3. A solution of $SnCl_2(Men)Ph$ (2.33 g, 5.76 mmol) in diethyl ether (30 mL) was added to a suspension of 2-[4,4-dimethyl-2-oxazolinyl]-5-methylphenyllithium (1.25, 6.40 mmol) in diethyl ether (50 mL) at 0 °C and then stirred at room temperature for 18 h. A saturated solution of ammonium chloride (2 mL) and then water (20 mL) were added. The residue was extracted with diethyl ether (20 mL) and then dichloromethane (2 × 20 mL). The combined organic fractions were dried (Na_2SO_4) and the solvent was removed *in vacuo*. The residue was purified by column chromatography (silical gel 60, 70– 230 mesh) using a gradient solvent system of first hexane–dichloromethane–triethylamine (70 : 30 : 1) followed by methanol. Removal of the solvent *in vacuo* left a yellow oil (2.19 g, 68%) which crystallised from

methanol to afford compound **3** in a 70 : 30 diastereomeric mixture (1.04 g, 32%), mp 177–184 °C. ^{1}H NMR ($CDCl_3$): both isomers, δ 0.39–2.35 (38 H, m), 0.98 (3 H, s), 1.00 (3 H, s), 1.43 (6 H, s), 2.45 (3 H, s), 2.46 (3 H, s), 4.31 (4 H, m) and 7.22–8.24 (16 H, m). ^{13}C NMR ($CDCl_3$): major isomer, δ 14.91, 21.39, 21.70, 22.43, 25.78, 28.19, 28.22, 32.65, 34.79, 35.43, 39.69, 43.62, 46.55 [J(^{13}C–^{119}Sn) 654], 66.35, 81.85, 126.26, 127.21, 127.68, 128.29, 129.74, 135.90, 137.13, 143.55, 144.13 [J(^{13}C–^{119}Sn) 680], 146.96 [J(^{13}C–^{119}Sn) 612], 168.84; minor isomer, δ 15.88, 21.61, 21.70, 22.21, 25.92, 28.01, 33.70, 34.68, 35.32, 38.77, 43.45, 45.98 [J(^{13}C–^{119}Sn) 650], 66.27, 81.60, 126.53, 127.68, 127.92, 128.39, 129.80, 134.98, 138.45, 143.04, 145.14 [J(^{13}C–^{119}Sn) 664 Hz], 145.42 [J(^{13}C–^{119}Sn) 619 Hz] and 168.90. ^{119}Sn NMR ($CDCl_3$): major isomer, δ (rel. intensity in %) −180.4 (70); minor isomer, δ −156.2 (30). Calc. for $C_{28}H_{38}$ClNOSn: C, 60.2; H, 6.9; N, 2.5. Found: C, 60.0; H, 7.1; N, 2.5%.

[2-(4,4-Dimethyl-2-oxazolinyl)-5-methylphenyl][(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride SnH(Men)PhL 4. A solution of the 70 : 30 diastereomeric mixture of compound **3** (0.20 g, 0.36 mmol) in ethanol (30 mL) was added to a solution of $NaBH_4$ (0.27 g, 7.14 mmol) in ethanol (5 mL) and stirred at room temperature for 1 h. The ethanol was removed *in vacuo* and then water (10 mL) added. The residue was extracted with diethyl ether (2 × 10 mL) and the solvent removed *in vacuo* to afford **4** as a yellow oil (0.15 g, 79%). ^{1}H NMR (C_6D_6): δ 0.25–2.23 (50 H, m), 1.89 (3 H, s), 1.95 (3 H, s), 3.56–3.67 (4 H, m), 6.89–8.01 (16 H, m), 6.85 [1 H, s, J(^{1}H–^{119}Sn) 1648] and 6.92 [1 H, s, J(^{1}H–^{119}Sn) 1648 Hz]. ^{13}C NMR (C_6D_6): δ 15.76, 16.02, 21.35, 21.37, 21.94, 22.24, 22.73, 22.80, 27.00, 27.03, 28.15, 28.32, 28.62, 28.63, 33.43, 34.40, 35.76, 36.00, 36.04, 36.22, 39.27, 39.44, 41.08, 41.32, 46.63, 46.83, 67.45 (2C), 79.70, 79.76, 127.87, 127.90, 128.11, 128.19, 128.32, 128.40, 129.56, 129.59, 130.76, 130.84, 137.73, 138.19, 139.72, 140.03, 141.49 (2C), 144.44, 144.61, 144.63, 144.95, 164.72 and 164.85. ^{119}Sn NMR (C_6D_6): δ (rel. intensity in %) −122.64 (50) and −148.20 (50). HRMS (ESI): *m*/*z* calc. for $C_{28}H_{38}NOSn$, $(M - H)^+$, *m*/*z* 524.1966; found 524.1972. ^{119}Sn NMR (C_6D_6) indicated **4** decomposed completely after 7 days storage under argon.

2-[4-(*S*)-isopropyl-2-oxazolinyl)-5-menthylphenyl]bis((1*R*,2*S*,5*R*)-menthyl)]tin chloride SnCl(Men)$_2$L* 5. A 1.5 M solution of n-butyllithium in pentane (2.72 mL, 4.08 mmol) was added to a solution of 2-[4-methylphenyl]-4-(*S*)-isopropyloxazoline (0.83 g, 4.08 mmol) in hexane (10 mL) and stirred at room temperature for 3 h. This solution was added to a solution of bis[(1*R*,2*S*,5*R*)-menthyl]tin dichloride (1.53 g, 3.27 mmol) in diethyl ether (10 mL) and stirred at room temperature for 2 h. A saturated solution of aqueous ammonium chloride (2 mL) and then water (10 mL) was added. The residue was extracted with dichloromethane (2 × 20 mL), the combined organic extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel 60, 230 mesh) using gradient elution with hexane–dichloromethane–triethylamine (70 : 30 : 1) followed by methanol as the eluents. Crystallisation from dichloromethane–methanol afforded the product as a white solid (0.62 g, 30%), mp 141–143 °C. ^{1}H NMR ($CDCl_3$): δ 0.44–2.00 (38 H, m), 0.85 (3 H, d), 0.99 (3 H, d), 2.14 (1 H, m), 2.43 (3 H, s), 4.22 (1 H, m), 4.43 (1 H, d of d), 4.58 (1 H, d of d), 7.16 (1 H, d), 7.63 (1 H, d) and 8.05 (1 H, s). ^{13}C NMR ($CDCl_3$): δ 15.05, 15.21, 16.42, 19.71, 21.86, 21.89, 21.98, 22.28, 22.42, 26.28, 26.63, 30.86, 32.95, 34.11, 34.72, 34.95, 35.47, 35.49, 40.51, 41.36, 43.85, 44.78 [J(^{13}C–^{119}Sn) 540], 45.16, 47.31 [J(^{13}C–^{119}Sn) 540], 69.62, 70.14, 126.43, 127.10, 129.03, 137.76, 143.03, 150.44 [J(^{13}C–^{119}Sn) 486 Hz] and 170.91. ^{119}Sn NMR ($CDCl_3$): δ −106.2. Calc. for $C_{33}H_{54}$ClNOSn: C, 62.4; H, 8.6; N, 2.2. Found: C, 62.6; H, 9.2; N, 2.2%.

2-4-(*S*)-Isopropyl-2-oxazoline)-5-methylphenyl]bis(1*R*,2*S*,5*R*)-menthyl)]tin hydride SnH(Men)$_2$L* 6. A solution of $NaBH_4$ (0.08 g, 2.11 mmol) in ethanol (5 mL) was added to a solution of compound **5** (0.14 g, 0.22 mmol) in ethanol (5 mL) and stirred at room temperature for 1 h. The solvent was removed *in vacuo*, water (3 mL) added and the residue extracted with diethyl ether (3 × 5 mL). The solvent of the combined organic extracts was removed *in vacuo* to afford a white oil (0.08 g, 61%). ^{1}H NMR (toluene-d8): δ 0.36–2.94 (38 H, m), 1.04 (3 H, d), 1.10 (3 H, d), 2.19 (3 H, s), 3.91 (1 H, m), 4.05 (2 H, m), 6.44 (1 H, s) [J(^{1}H–^{119}Sn) 1270 Hz], 7.00 (1 H, d), 7.94 (1 H, s) and 8.01 (1 H, d). ^{13}C NMR (toluene-d8): δ 15.31, 17.14, 17.81, 18.85, 21.33, 22.16, 22.62, 22.65, 22.97, 27.08, 27.52, 32.41 (2C), 33.86, 35.46 [J(^{13}C–^{119}Sn) 469], 35.89, 36.06 (2C), 36.32, 37.96 [J(^{13}C–^{119}Sn) 457 Hz], 41.43, 42.93, 47.57, 47.84, 69.86, 72.68, 128.00, 129.06, 130.46, 140.21, 141.17, 148.10 [J(^{13}C–^{119}Sn) 423 Hz] and 166.71. ^{119}Sn NMR (toluene-d8): δ −64.4. HRMS (ESI): calc. for $C_{33}H_{54}NOSn$, $(M - H)^+$, *m*/*z* 600.3280; found 600.3228.

[2-(4-(*S*)-Isopropyl-2-oxazoline)-5-methylphenyl][(1*R*,2*S*,5*R*)-menthyl]phenyltin chloride SnCl(Men)PhL* 7. A 1.5 M solution of n-BuLi in pentane (2.85 mL, 4.28 mmol) was added to a solution of 2-[4-methylphenyl]-4-(*S*)-isopropyloxazoline (0.87, 4.28 mmol) in diethyl ether (3 mL) and stirred at room temperature for 2.5 h. This reaction mixture was added to a solution of $SnCl_2$(Men)Ph (1.48 g, 3.65 mmol) in diethyl ether (5 mL) and stirred at room temperature for 2 h. A saturated aqueous solution of ammonium chloride (2 mL) was added and then water (2 mL). The layers were separated and the residue was further extracted with dichloromethane (2 × 20 mL). The combined organic extracts were washed with water (20 mL), dried (Na_2SO_4) and the solvent was removed *in vacuo* to afford a yellow oil. The crude product was purified by column chromatography using silica gel 60 (70–230 mesh) and acetone as the solvent system, followed by crystallisation from methanol to afford compound **7** as a white solid (0.34 g, 16%), mp 174–176 °C. ^{1}H NMR ($CDCl_3$): δ 0.57–2.40 (52 H, m), 2.44 (3 H, s), 2.47 (3 H, s), 4.05 (1 H, m), 4.17 (1 H, m), 4.38 (1 H, d of d), 4.45 (1 H, d), 4.48 (1 H, d of d), 7.24–7.34 (8 H, m), 7.53–7.77 (6 H, m), 8.17 (1 H, s) and 8.24 (1 H, s). ^{13}C NMR ($CDCl_3$): δ 14.49, 15.21, 16.04, 16.96, 19.57, 19.69, 21.71 (2C), 21.90, 21.92, 22.30, 22.48, 26.05, 26.18, 30.40, 31.59, 33.28, 33.49, 34.87, 35.01, 35.33 (2C), 39.41, 39.60, 43.88, 44.54, 44.60 [J(^{13}C–^{119}Sn) 641], 46.81 [J(^{13}C–^{119}Sn) 661], 68.68, 70.20, 70.49, 72.57, 126.59, 126.72, 126.94, 127.27, 127.96, 128.25, 128.50, 128.56, 129.82, 129.94, 135.25, 135.93, 137.73, 138.51, 143.45, 143.91, 144.22 [J(^{13}C–^{119}Sn) 662], 144.93 [J(^{13}C–^{119}Sn) 673 Hz], 146.39 [J(^{13}C–^{119}Sn) 627], 147.67 [J(^{13}C–^{119}Sn) 619 Hz], 170.81 and 171.08. ^{119}Sn NMR ($CDCl_3$): δ (rel. intensity %) −159.2 (50) and −178.5 (50). Calc. for $C_{29}H_{40}$ClNOSn: C, 60.8; H, 7.0; N, 2.4. Found: C, 61.2; H, 7.0; N, 2.4%.

[2-(4-(*S*)-Isopropyl-2-oxazoline)-5-methylphenyl][(1*R*,2*S*,5*R*)-menthyl]phenyltin hydride SnH(Men)PhL* 8. A solution of $NaBH_4$ (0.12 g, 3.17 mmol) in ethanol (5 mL) was added to a suspension of compound **7** (0.06 g, 0.10 mmol) in ethanol (5 mL) and stirred at room temperature for 1.5 h. The ethanol was removed *in vacuo* and water (5 mL) added. The residue was extracted with diethyl ether (2 × 5 mL) and the solvent removed *in vacuo* to afford **8** as a yellow oil (0.05 g, 93%). ^{119}Sn NMR (C_6D_6): δ (rel. intensity in %) −133.8 (34) [J(^{119}Sn–^{1}H) 1772 Hz] and −139.7 (66) [J(^{119}Sn–^{1}H) 1645 Hz]. HRMS (ESI): calc. for $C_{29}H_{40}NOSn$, $(M - H)^+$; *m*/*z* 538.2145. found 538.2133. ^{119}Sn NMR (C_6D_6) indicated 30% of **8** decomposed after 24 h storage under argon.

X-Ray crystallography[21–25]

Intensity data for colourless compounds **1** and **3** were collected on a Rigaku AFC7R diffractometer fitted with graphite mono-

Table 2 Crystallographic data for $Cl(Men)_2LSn$ **1** and $SnCl(Men)PhL$ **3**

	1	**3**
Formula	$C_{32}H_{52}ClNOSn$	$C_{28}H_{38}ClNOSn$
M	620.9	558.8
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a/Å	27.961(6)	8.052(2)
b/Å	11.809(8)	17.781(6)
c/Å	10.087(6)	10.304(3)
β/°		112.36(2)
V/Å^3	3331(3)	1364.3(7)
Z	4	2
T/K	173	173
μ/cm^{-1}	8.69	10.53
No.data collected	4314	3463
R_{int}	0.00	0.040
No.unique data with $I \geq 3.0\sigma(I)$	3018	2310
R	0.044	0.035
R_w	0.049	0.043

chromatised Mo-Kα radiation, $\lambda = 0.71073$ Å, such that θ_{max} was 27.5°. An empirical absorption correction was applied for **1** as was a correction for extinction. Absolute structures were determined on the basis of the known configuration of the menthyl groups. Crystallographic and refinement data are given in Table 2. Diagrams of the molecules were drawn with ORTEP plotted at the 50% probability level.

CCDC reference number 186/2178.

See http://www.rsc.org/suppdata/dt/b0/b004259p/ for crystallographic files in .cif format.

Molecular orbital methods

AM1 calculations were performed using MOPAC Version 7 (ref. 14) on an Apple Macintosh Powerbook G3 14.1TFT/266 computer. Geometry optimizations were performed using standard gradient techniques. Optimized geometries of all structures are available as ESI.†

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