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Chiral organotin hydrides containing intramolecular coordinating substituents

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Abstract

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 the 8-dimethylaminonaphthyl (L) or 2-[(1*S*)-1-dimethylaminoethyl]phenyl (L*) substituents has been synthesised and characterised. Each of the compounds MenPhLSnBr (**1**) and MenPhLSnH (**2**) has a stereogenic tin centre and the compounds were isolated in diastereomeric ratios of 60:40 and 66:33, respectively. Compounds MenPhL*SnCl (**3**) and MenPhL*SnH (**4**) were synthesised with diastereomeric ratios of 73:27 and 64:36, respectively. Single crystal X-ray analysis of MenPhL*SnCl (**3**), Men_2L*SnCl (**8**), and $MenPh_2$LSn (**10**) reveals that each structure has a tendency towards penta-coordination at the tin centre as a result of intramolecular N→Sn interactions. AM1 calculations successfully predict the molecular geometries observed in the solid state as well as the diastereomeric ratios observed in solution.

Keywords: Chiral; Organotin; Hydride

1. Introduction

Tri-*n*-butyltin hydride is an efficient, commonly utilised reagent in free radical chemistry [1]. Reduction reactions involving prochiral radicals must always result in racemic mixtures of the product owing to the inability of Bu_3SnH to differentiate between the two faces of the prochiral carbon radical during delivery of the hydrogen atom from tin to carbon. Over recent years there has been increased interest in the synthesis of chiral organotin hydrides as enantioselective free radical reducing agents [2]. For example, Metzger et al. [3] as well as Nanni and Curran [4] prepared organotin hydrides containing the C_2-symmetric binaphthyl moiety. These stannanes induced some degree of enantioselectivity during the free radical reduction of several racemic alkyl halides. A series of organotin hydrides containing the intramolecular coordinating chiral 2-[(1*S*)-1-dimethylaminoethylphenyl] ligand (L*) also displayed some enantioselectivity in free radical reductions [5]. The syntheses of several triorganostannanes containing the chiral (1*R*,2*S*,5*R*)-menthyl (Men) have been reported previously [6–11]. Amongst these was *t*-butyl-8-(dimethylaminonaphthyl)-(1*R*,2*S*,5*R*)-menthyltin hydride, which contains a stereogenic tin centre and was prepared in a 60:40 diastereomeric ratio [6]. Work in our group has demonstrated significant enhancement in enantioselectivities during asymmetric reductions involving chiral non-racemic stannanes by the incorporation of chiral and achiral Lewis acids [12]. As part of our ongoing interest [10,13,14] in the development of enantioselective free radical reducing agents, we now focus on the synthesis of a series of chiral organotin hydrides which contain the chiral (1*R*,2*S*,5*R*)-menthyl substituent (Men) as well as potentially intramolecular coordinating 8-(dimethylamino)naphthyl (L) (see Scheme 1) and L* (see Scheme 2) ligands. The enantioselectivity of organotin the hydrides in a cross-section of radical reactions is currently being evaluated.

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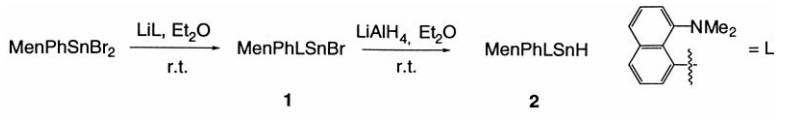
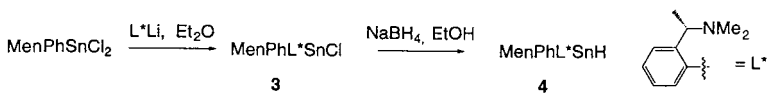


Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Monomenthyltin derivatives

The synthesis of the first target compound, namely 8 - (dimethylamino) - naphthyl - (1*R*,2*S*,5*R*) - menthylphenyltin hydride (**2**) was achieved as follows. Reaction of one molar equivalent of 8-(dimethylamino)-naphthyllithium (LiL), as the etherate, with $MenPhSnBr_2$ (Scheme 1) in diethyl ether results in a white solid, which has elemental analysis consistent with the formula MenPhLSnBr (**1**). The ^{119}Sn-NMR spectrum (C_6H_6) of the isolated product contains two signals at δ −89.4 and −119.6 and were observed in a 60:40 ratio which are assigned to the two possible diastereomers of **1** (Fig. 1). The ^{13}C-NMR spectra (toluene-d_8) of **1** at room temperature contains four sharp singlets (δ 47.12, 47.59, 49.98 and 50.62) corresponding to the two non-equivalent methyl groups at the nitrogen of the dimethylaminonaphthyl substituent for each diastereomer. These signals most likely indicate that the nitrogen is effectively coordinated to the tin centre. This is supported by the crystal structure of a similar compound, 8-(dimethylamino)naphthyl-(1*R*,2*S*,5*R*)-menthylmethyltin bromide (MenMeLSnBr) [15] which has a N–Sn bond distance of 2.55(1) Å. The ^{13}C-NMR spectrum of this product also exhibited separate signals for each methyl group. Attempts to obtain crystals of **1** suitable for X-ray study were not successful.

Interestingly, there is no substantive change in the ^{13}C-NMR spectra on heating solutions of **1** to 90°C. Furthermore there is no change in the ratio of the two ^{119}Sn resonances after a toluene solution of **1** had been heated at 115°C for 24 h. The remarkably high configurational stability of the two isomers of **1** can be largely ascribed to the rigid aromatic ring system which ensures that the nitrogen of the dimethylamino group is kept in close proximity to the tin atom.

Attempts to separate the two isomers of **1** using normal-phase chromatography, MPLC, HPLC and crystallisation were not successful.

Reaction of **1** with lithium aluminium hydride ($LiAlH_4$) results in formation of MenPhLSnH (**2**) (Scheme 1) in a diastereomeric ratio of 66:34, as evidenced by the ^{119}Sn proton-coupled NMR spectrum (C_6D_6) which exhibited two doublets; δ −115.0, $^1J(^{119}Sn-^1H)$ 1955 Hz and −140.0, $^1J(^{119}Sn-^1H)$ 1980 Hz.

The ^{1}H-NMR spectra (C_6D_6) of **2** at room temperature contains four singlets (δ 2.24, 2.28, 2.50, 2.54) corresponding to two non-equivalent methyl substituents attached to the nitrogen in the L moiety for each of the two isomers. As is the case for **1**, the nitrogen appears to be coordinated to the tin centre, even though the tin centre in **2** might be expected to have a lower Lewis acidity. Heating a toluene solution of **2** at 100°C for 20 minutes caused no change in the 66:34 diastereomeric ratio as evidenced by ^{119}Sn-NMR.

Attention was then directed to the preparation of MenPhL*SnH (**4**) which was prepared as described. Addition of L*Li to $MenPhSnCl_2$ in diethyl ether affords MenPhL*SnCl (**3**) in a 69% yield (Scheme 2). The ^{119}Sn-NMR spectrum ($CHCl_3$) of an analytically pure sample of **3** shows two resonances at δ −123.8 and −146.4 in the ratio 73:27 corresponding to the two diastereomers of **3**. The ^{13}C-NMR spectrum ($CDCl_3$) of **3** at room temperature displays two separate, somewhat broad, resonances for the nitrogen-bound methyl groups of the L* substituent of each isomer (δ 36.9 ($W_{1/2}$ 40 Hz) and 43.9 ($W_{1/2}$ 40 Hz) for the major isomer, δ 37.8 ($W_{1/2}$ 80 Hz) and 45.2 ($W_{1/2}$ 80 Hz) for the minor isomer). The difference in chemical shifts, i.e. approximately 7 ppm between the two methyl groups of each isomer, suggest that the two methyl groups exist in

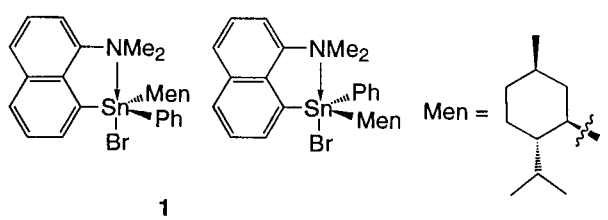


Fig. 1. Diagram representing the two diastereomers of compound **1**.

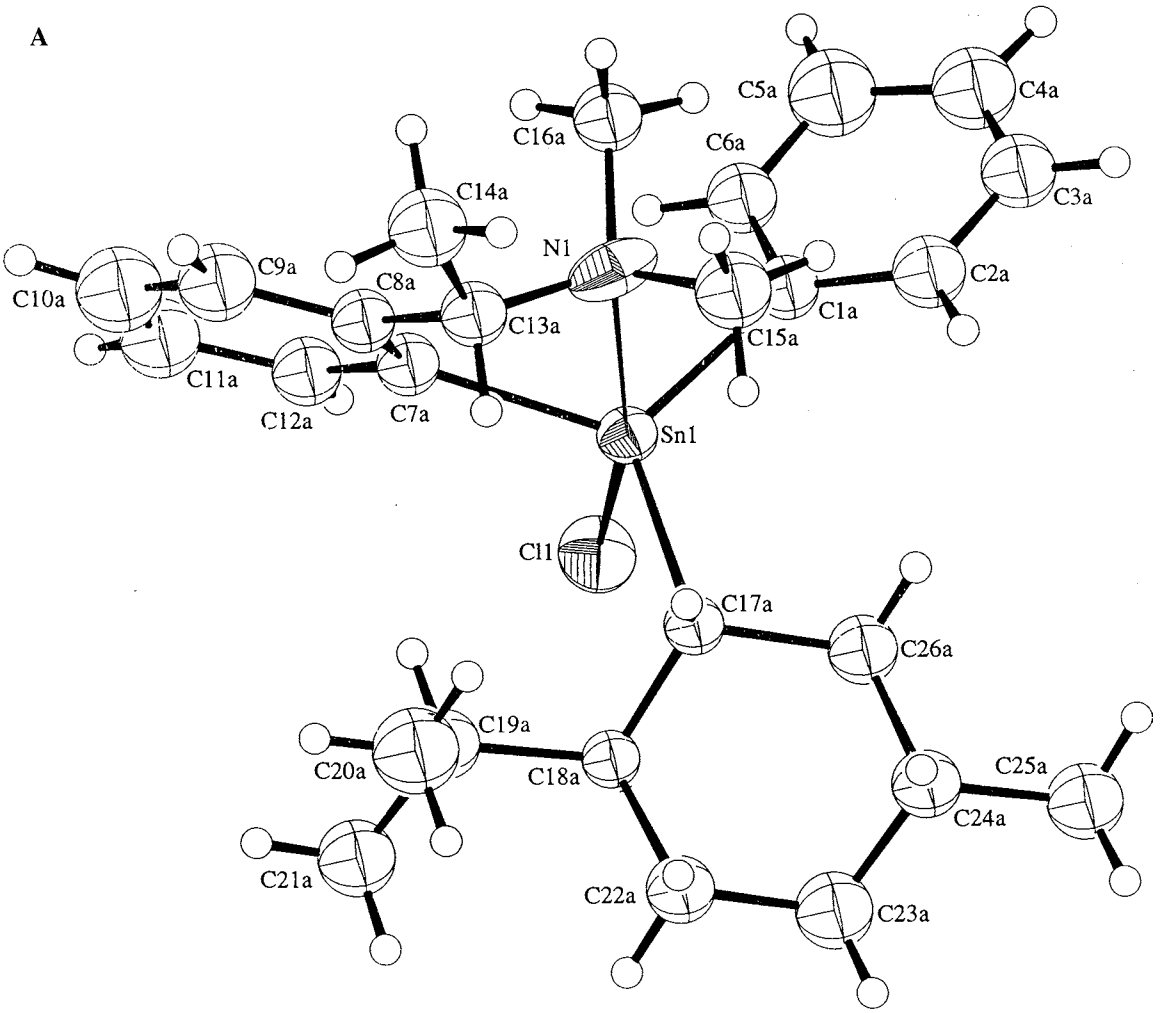


Fig. 2. Molecular structures and atomic numbering scheme for (A) molecule a, and (B) molecule c, of MenPhL*SnCl (**3**); the numbering scheme for molecule b follows that of molecule a.

significantly different chemical environments. A smaller difference of approximately 3 ppm is observed for the two methyl groups of the L moiety in compound **1**. On heating a solution of **3** in toluene to 105°C the four methyl ^{13}C-NMR (toluene-d_8) resonances coalesce into two signals, indicating dissociation of the N→Sn coordination. Heating the toluene solution of **3** at 105°C for 18 hours caused no change in the ratio of the two ^{119}Sn-NMR signals. The ^{119}Sn-NMR spectrum of a solution of compound **3** in dichloromethane showed no change in the diastereomeric ratio after two weeks a 20°C.

The X-ray analysis of **3** was carried out on a crystal obtained from the slow evaporation of a 1:1 dichloromethane–methanol solution. The unit cell comprises three independent molecules with two molecules, i.e. a and b, adopting an *S* configuration at the stereogenic tin centre and the third molecule, c, adopting a *R* configuration. Molecules a and c are illustrated in Fig. 2 and selected interatomic parameters are collected in Table 1. The tin atom in each molecule is bonded to three carbon atoms, a chlorine as well as the amino-nitrogen atom. The Sn···N distances lie in the range 2.58(2)–2.64(2) Å. The overall molecular structure for each molecule is consistent with a distorted trigonal bipyramidal geometry in which the tin atom lies 0.189(2) Å above the C_3 trigonal plane in the direction of the chlorine atom; the comparable values for molecules b and c are 0.173(2) and 0.237(2) Å, respectively. This is comparable with the compound of (R_{Sn})-[8-(dimethylaminonaphthyl]-(1*R*,2*S*,5*R*)-menthylmethyltin bromide which also had a distorted trigonal bipyramidal coordination geometry at the tin centre with a Sn···N distance of 2.55(1) Å [15]. The most significant consequence of the differing stereochemistry found for the tin atoms in molecules a and b and that observed in molecule c is found in the distortion in the C_3 trigonal plane. Thus, there is a significant (approximately 10°) expansion and contraction of the C(1)–Sn–C(7) and C(1)–Sn–C(17) angles, respectively, in molecule c compared with molecules a and b.

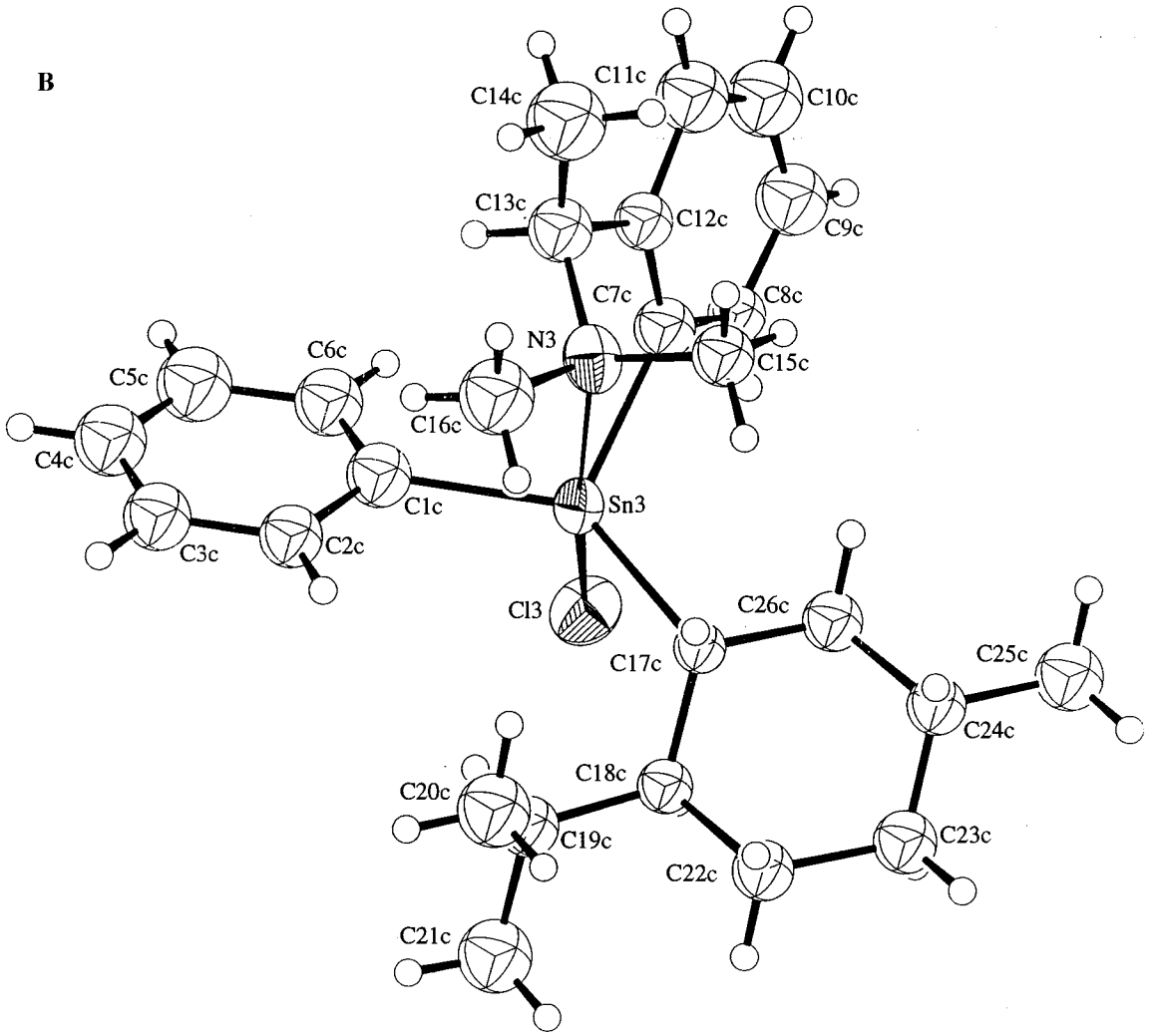


Fig. 2. (*Continued*)

The use of $LiAlH_4$ as a reducing agent appears to destroy compound **3**. The ^{119}Sn-NMR spectrum of the reaction mixture indicated the absence of any ^{119}Sn products. However, reaction of sodium borohydride ($NaBH_4$) with **3** in ethanol solution affords a diastereomeric mixture of MenPhL*SnH (**4**) in 95% yield (Scheme 2). The ^{119}Sn proton-coupled NMR spectrum of **4** displays two doublet resonances (δ −136.7, $^1J(^1H-^{119}Sn)$ 1920 Hz and −166.8, $^1J(^1H-^{119}Sn)$ 1904 Hz) in a 64: 36 ratio. The ^{13}C- and ^{1}H-NMR (C_6D_6) spectra of **4** at room temperature displays a single signal (δ 40.26, 40.82 and 1.86, 1.92, respectively) for the two methyl groups of the dimethylaminoethylphenyl substituent for each diastereomer of **4** indicating no N→Sn coordination. On cooling the ^{13}C-NMR signals corresponding to the methyl groups coalesce at approximately −50°C.

In order to provide further insight into the structures and energies of the two tin-epimeric diastereomers of MenPhLSnBr (**1**) and MenPhL*SnCl (**3**), the ge-

Table 1
Selected interatomic (Å, °) parameters for MenPhL*SnCl (**3**)

	Molecule a	Molecule b	Molecule c
Sn–Cl	2.496(5)	2.486(6)	2.464(7)
Sn–N	2.58(2)	2.64(2)	2.60(2)
Sn–C(1)	2.16(2)	2.16(2)	2.12(2)
Sn–C(7)	2.13(2)	2.14(2)	2.14(2)
Sn–C(17)	2.16(2)	2.15(2)	2.17(2)
Cl–Sn–N	166.3(4)	167.6(4)	168.8(4)
Cl–Sn–C(1)	92.1(5)	92.4(5)	96.0(7)
Cl–Sn–C(7)	95.6(5)	94.6(5)	97.8(6)
Cl–Sn–C(17)	97.4(5)	96.8(5)	95.5(5)
N–Sn–C(1)	87.2(7)	90.8(6)	87.8(8)
N–Sn–C(7)	73.0(6)	73.3(6)	71.0(7)
N–Sn–C(17)	94.8(6)	91.9(6)	89.7(7)
C(1)–Sn–C(7)	119.3(7)	116.0(8)	107.1(9)
C(1)–Sn–C(17)	119.9(7)	120.7(7)	131.7(7)
C(7)–Sn–C(17)	118.5(8)	121.4(8)	117.5(7)

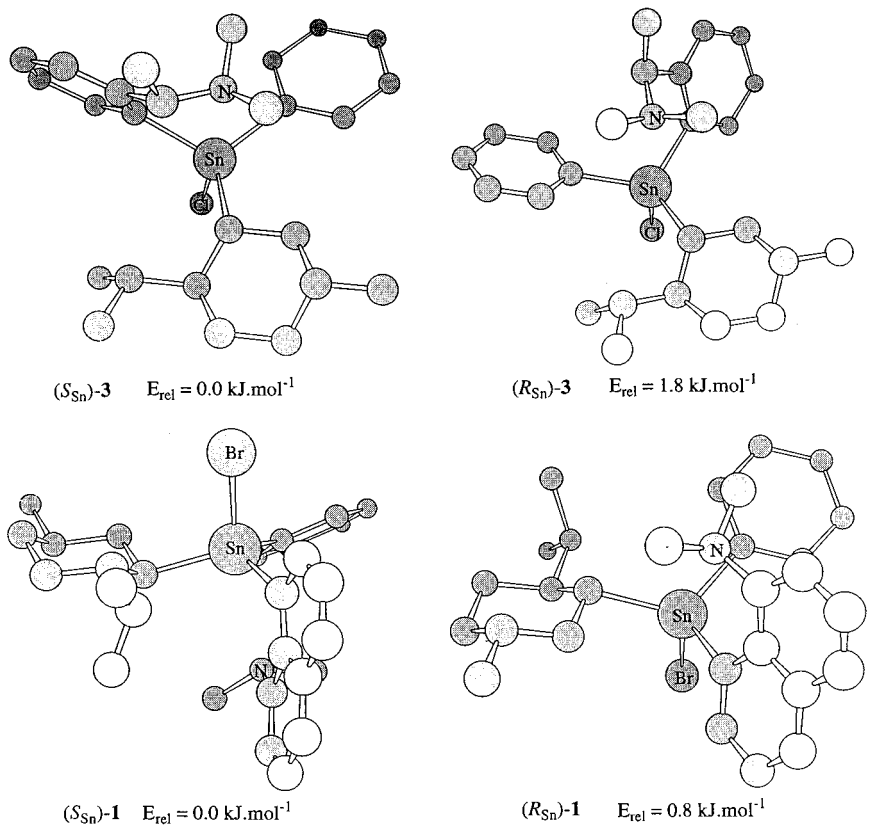


Fig. 3. AM1 calculated geometries of both diastereomers of compounds **1** and **3**.

ometries of **1** and **3** were optimised using the AM1 semiempirical molecular modelling technique [16]. 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 Supporting Information. Inspection of Fig. 3 reveals that the calculated structures of **3** bear a striking resemblance to the X-ray structures displayed in Fig. 2. The tin atom in each molecule is shown to be coordinated to the amino-nitrogen atom, with calculated N–Sn separations in (S_{Sn})-**3** and (R_{Sn})-**3** of 2.86 and 2.71 Å, respectively, in good agreement with the X-ray determined values, such as 2.55(1) Å for MenMeLSnBr [15]. In addition, energy partitioning [17–19] within the AM1 framework reveals an (attractive) N–Sn bicentric energy of -1.43 and -1.96 eV for the *S* and *R* isomers, respectively. More importantly, these calculations predict that (S_{Sn})-**3** lies 1.8 kJ mol^{-1} below (R_{Sn})-**3** in energy. Assuming that this enthalpy difference is reflected in the difference in free energies, this value of 1.8 kJ mol^{-1} translates into a 2:1 ratio of isomers at 25°C in favour of (S_{Sn})-**3**, a result which is in excellent agreement with the experimental data (vide supra).

These calculated data provide confidence in our ability to predict the structures and energies of the isomers of MenPhLSnBr (**1**) for which no X-ray data are available. Fig. 3 reveals that the AM1 calculated geometry of the *S* isomer of **1** is remarkably similar to the analogous X-ray structure of MenMeLSnBr reported by Schumann et al. [15]. Both structures are, once again, calculated to have significant N–Sn bonding, with separations of 2.99 and 3.04 Å for (S_{Sn})-**1** and (R_{Sn})-**1**, respectively, and calculated associated bicentric energies of -0.86 and -0.74 eV. Clearly, the N–Sn interactions in structures **1** are predicted to be marginally weaker than the corresponding interactions in **3**. To our delight, AM1 calculations predict that the *S* isomer of MenPhLSnBr (**1**) is more stable than (R_{Sn})-**1** by only 0.8 kJ mol^{-1}. Using the same argument presented above, this difference translates into a 60:40 ratio of isomers at 25°C, once again in excellent agreement with the available experimental data; the ^{119}Sn-NMR spectrum of **1** reveals two signals in approximately 60:40 ratio (vide supra). On the basis of the exceptional agreement between calculated and experimental data, we tentatively assign the major diastereomer of **1** to be (S_{Sn})-MenPhLSnBr.

2.2. Dimenthyltin derivatives

The addition of one molar equivalent of LiL to Men_2SnCl_2 (**5**) (prepared by treatment of $HgCl_2$ with Men_2Ph_2Sn in acetone) in diethyl ether affords Men_2LSnCl (**6**) (Scheme 3); ^{119}Sn-NMR ($CDCl_3$): δ

−49.6. The ^{13}C- and ^{1}H-NMR ($CDCl_3$) spectra of **6** contain two resonances (δ 48.51, 50.12 and 2.76, 2.88, respectively) corresponding to the diastereotopic methyl groups on the nitrogen of the L substituent.

Reduction of **6** with $LiAlH_4$ in diethyl ether gave the hydride, Men_2LSnH (**7**) (Scheme 3). The ^{119}Sn-NMR (C_6D_6) spectrum of **7** displays a doublet δ −104.6 ($^1J(^{119}Sn-^1H)$ 1729 Hz). The ^{13}C- and ^{1}H-NMR (toluene-d_8) spectra at 20 and 100°C of **7** contain two separate peaks (δ 46.33, 47.79 and 2.44, 2.48, respectively) associated with the two methyl groups of the L substituent, again indicating coordination of the nitrogen to the tin centre.

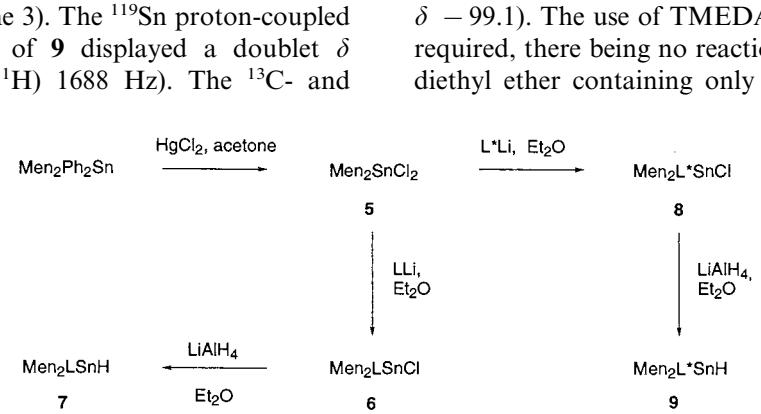
The reaction of L*Li with **5** afforded Men_2L^*SnCl (**8**) quantitatively as a white crystalline solid (Scheme 3). The ^{13}C- and ^{1}H-NMR ($CDCl_3$) spectra of **8** at room temperature contained a single broad resonance (δ 40.13 and 2.25, respectively) for the two methyl substituents of the L* moiety. Coalescence of the ^{13}C-NMR resonance was observed at 0°C, and two separate signals (δ 36.7 and 42.8) are visible at −55°C. We attribute this to a dynamic N→Sn dissociation/association process in solution, which is fast compared with the NMR time scale at room temperature. Coalescence occurs at a lower temperature compared with **3**, consistent with decreased Lewis acidity of the tin centre in **8**. The structure of **8** was determined by X-ray crystallography.

The structure of **8** is shown in Fig. 4 and selected interatomic parameters are listed in Table 2. The immediate geometry about the tin atom is defined by three carbon atoms and a chlorine atom. The close approach of the amino-nitrogen atom, i.e. Sn···N is 2.640(3) Å, has a significant structural impact, however, so that the molecular geometry may be described as being intermediate between tetrahedral and trigonal bipyramidal. In the latter description the tin atom lies 0.2293(2) Å above the trigonal C_3 plane in the direction of the chloride atom; the Cl–Sn···N(1) axial angle is 169.11(7)°.

Reduction of **8** with $LiAlH_4$ afforded Men_2L^*SnH (**9**) in a 78% yield (Scheme 3). The ^{119}Sn proton-coupled NMR spectrum (C_6D_6) of **9** displayed a doublet δ −141.3 ppm ($^1J(^{119}Sn-^1H)$ 1688 Hz). The ^{13}C- and ^{1}H-NMR spectra (C_6D_6) of **9** at room temperature each displayed a single resonance (δ 41.32 and 2.05, respectively) for the nitrogen-bound methyl groups of the dimethylaminoethylphenyl ligand indicating their equivalence and suggests that the N→Sn association/dissociation of **9** is fast on the NMR timescale. There are no substantial changes in the ^{13}C-NMR spectra at temperatures down to −70°C.

Some tetraorganotin compounds were synthesised to compare the degree of intramolecular coordination with the corresponding organotin halides and organotin hydrides. The reaction of an excess of LiL with $MenPh_2SnF$ in diethyl ether afforded $MenPh_2LSn$ (**10**) as a white solid in a 32% yield (^{119}Sn-NMR (C_6H_6): δ −107.1). The ^{13}C- and ^{1}H-NMR spectra indicated N→Sn coordination in solution and this was confirmed by a crystal structure of **10** (as a 1:2 chloroform solvate). Two molecules of **10** comprise the crystallographic asymmetric unit, however, there are only minor conformational differences between them as illustrated in Fig. 5; selected interatomic parameters are collected in Table 3. The tin atom in each molecule is bound by four carbon atoms and exists in a distorted tetrahedral geometry. The range of tetrahedral angles subtended at the Sn(1) atom of 102.5(3)–119.4(3)° (101.7(3)–119.2(3)° for the Sn(2) atom) suggests relatively little distortion from the ideal geometry. The maximum deviation in each case may be traced to the presence of close intramolecular N(1)→Sn(1) and N(2)→Sn(2) interactions of 2.882(7) and 2.899(7) Å, respectively. The overall molecular geometry, including the magnitude of the distortions, seen in **10** matches those found for the two independent molecules of the triphenyltin analogue [20]. The increased magnitude of the intramolecular Sn···N(1) interaction in **8** compared with that found in **10** may be related, in the first instance, to the enhanced Lewis acidity of the tin centre in **8** having a C_3Cl donor set as opposed to a C_4 donor set as in **10**.

Addition of an excess of LiL to Men_2PhSnI in tetramethylethylenediamine (TMEDA) afforded Men_2PhLSn (**11**) in a 33% yield (^{119}Sn-NMR ($CHCl_3$): δ −99.1). The use of TMEDA as a solvent system was required, there being no reaction in diethyl ether, nor in diethyl ether containing only one molar equivalent of



Scheme 3.

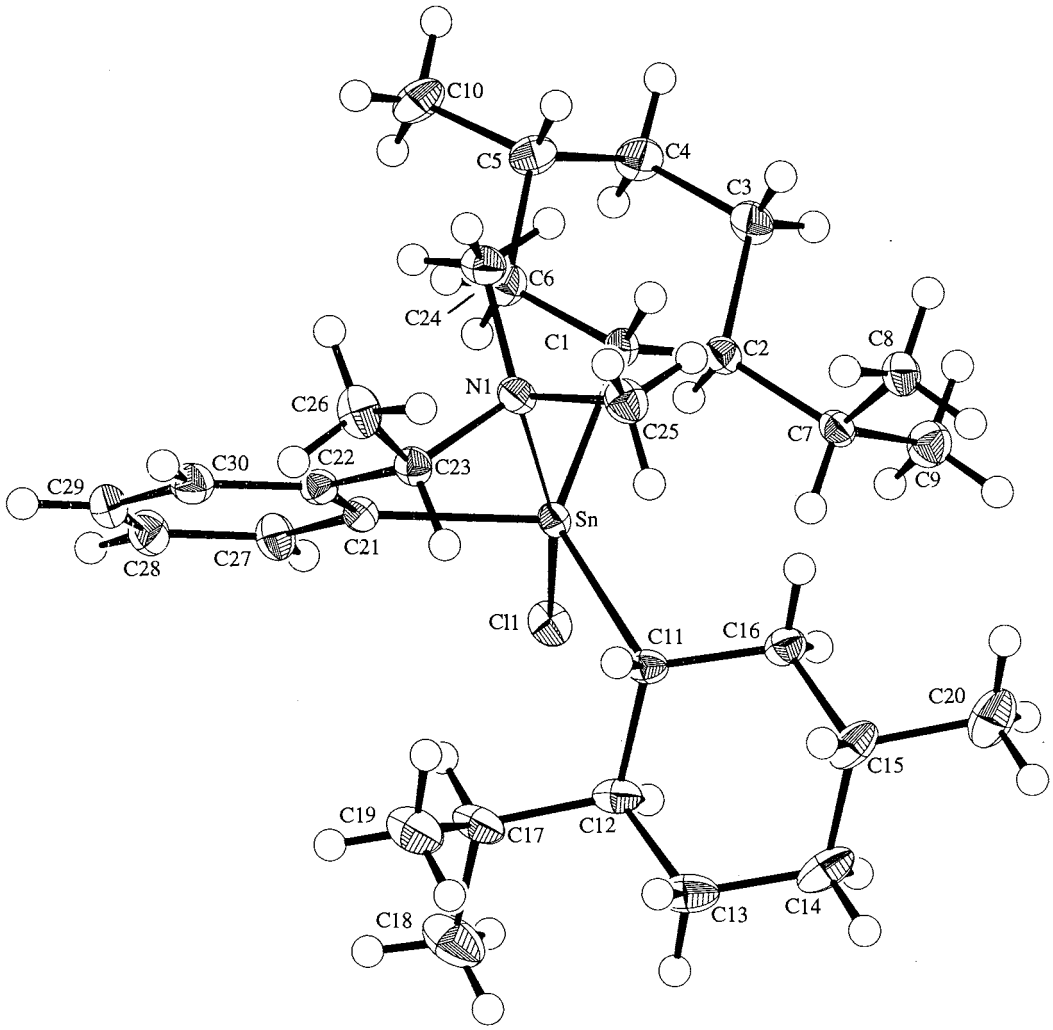


Fig. 4. Molecular structure and atomic numbering scheme for Men_2L^*SnCl (**8**).

TMEDA. The ^{13}C- and ^{1}H-NMR ($CDCl_3$) spectra for **11** displays two signals (δ 40.48, 50.98 and 2.47, 2.76, respectively) for the two diastereomeric methyl groups again indicating association of the nitrogen to the tin centre.

3. Experimental

3.1. General methods

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 (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 nitrogen or dry argon. LiL as the etherate [21], LiL* [22], $MenPh_2SnF$, $MenPhSnBr_2$ [10], Men_2PhSnI

Table 2
Selected interatomic (Å, °) parameters for Men_2L^*SnCl (**8**)

Sn–Cl	2.474(1)	Sn–C(1)	2.195(4)
Sn–C(11)	2.196(4)	Sn–C(21)	2.155(4)
Sn–N(1)	2.640(3)		
Cl–Sn–C(1)	92.56(9)	Cl–Sn–C(11)	97.6(1)
Cl–Sn–C(21)	98.4(1)	Cl–Sn–N(1)	169.11(7)
C(1)–Sn–C(11)	132.2(1)	C(1)–Sn–C(21)	112.2(1)
C(1)–Sn–N(1)	87.0(1)	C(11)–Sn–C(21)	112.2(1)
C(11)–Sn–N(1)	90.7(1)	C(21)–Sn–N(1)	71.8(1)

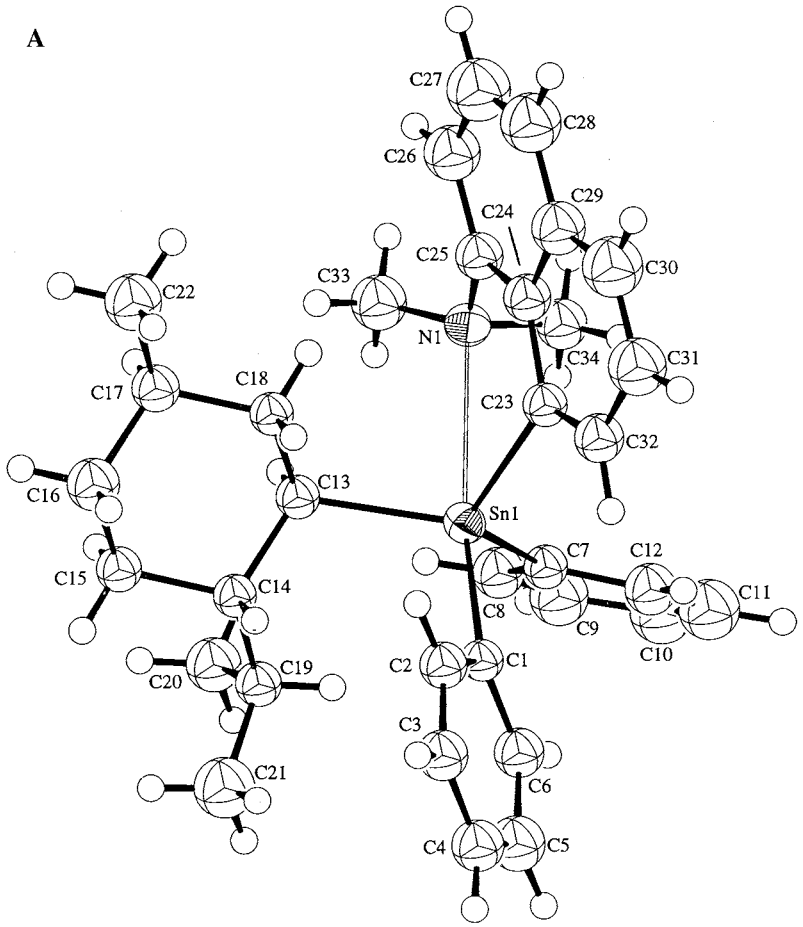


Fig. 5. Molecular structures and atomic numbering scheme for the two independent molecules of $MenPh_2LSn$ (**10**).

[10] and $MenPhSnCl_2$ [10] were prepared as previously reported.

3.2. Syntheses

3.2.1. *MenPhLSnBr* (*1*)

A suspension of $LiL{\cdot}Et_2O$ (1.22 g, 4.86 mmol) in diethyl ether (100 ml) was added to a stirred solution of $MenPhSnBr_2$ (1.5 g, 3.03 mmol) in diethyl ether (20 ml). The reaction mixture was stirred at room temperature (r.t.) for 86 h and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel 60, 70–230 mesh) using a 70:30 hexane–dichloromethane solvent system. Removal of the solvent in vacuo yielded a red crystalline solid (1.2 g, 68%); m.p. 49–52°C. ^{13}C-NMR ($CDCl_3$): major diastereomer: δ 15.73, 21.08, 21.56, 25.40, 32.86, 34.01, 34.27, 38.60, 41.84 ($J(^{13}C-^{119}Sn)$ 556 Hz), 43.59, 47.12, 50.62, 115.81, 124.96, 126.31, 126.47, 127.80 (2C), 128.21, 128.71, 132.28 ($J(^{13}C-^{119}Sn)$ 553 Hz), 133.43, 133.55, 134.32 (2C), 137.96, 145.70 ($J(^{13}C-^{119}Sn)$ 612 Hz), 149.09; minor diastereomer: δ 14.53, 20.85, 22.01, 25.40, 31.71, 34.05, 34.50, 40.31, 43.36 ($J(^{13}C-^{119}Sn)$ 567 Hz), 43.74, 47.59, 49.98, 115.67, 125.14, 126.31, 126.63, 127.70 (2C), 128.03, 128.61, 133.06, 133.43, 134.97 ($J(^{13}C-^{119}Sn)$ 616 Hz), 134.92 (2C), 136.57, 144.97 ($J(^{13}C-^{119}Sn)$ 636 Hz), 148.85. ^{119}Sn-NMR ($CDCl_3$): δ (R_{int}, %) −89.4 (60), −119.6 (40). Anal. Calc for $C_{28}H_{36}BrNSn$: C, 57.5; H, 6.2; N, 2.4. Found: C, 58.2; H, 6.3; N, 2.9%.

3.2.2. *MenPhLSnH* (*2*)

A solution of **1** (0.26 g, 0.45 mmol) in diethyl ether (10 ml) was added to a suspension of $LiAlH_4$ (0.18 g, 4.7 mmol) in diethyl ether (3 ml), and stirred at r.t. for 18 h. Water (2 ml) was carefully added, followed by a 20% solution of potassium/sodium-(+)-tartrate (2 ml). The residue was extracted with diethyl ether (2 × 5 ml) and the combined organic extracts were dried (Na_2SO_4) and the solvent removed in vacuo to yield **2** as a yellow oil (0.15 g, 66%). ^{1}H-NMR (C_6D_6): δ 0.07–2.19 (38H, m, both isomers), 2.24 (3H, s, minor isomer), 2.28 (3H, s, major isomer), 2.50 (3H, s, minor isomer), 2.54 (3H, s, major isomer), 6.77 (1H, s, minor isomer), 6.91 (1H,

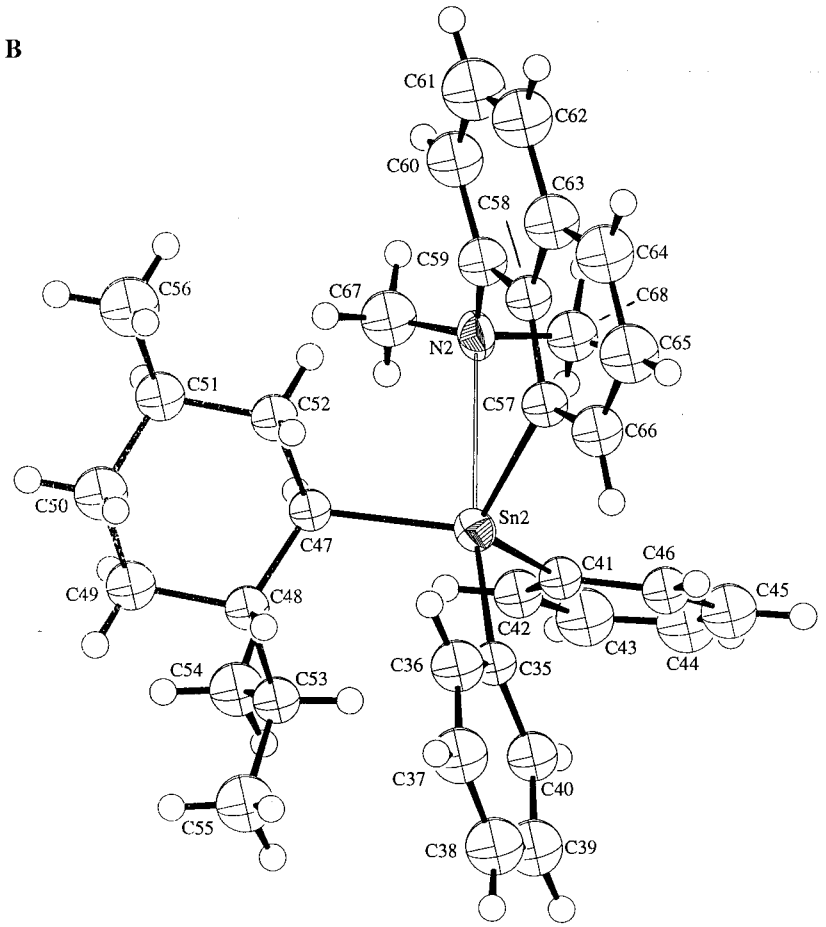


Fig. 5. (*Continued*)

s, major isomer), 6.82–8.34 (22H, m, both isomers). ^{119}Sn-NMR (C_6D_6): δ (R_{int}, %) −140.0 (66) (d, $J(^{119}Sn-^{1}H)$ 1980 Hz), −115.0 (33%) (d, $J(^{119}Sn-^{1}H)$ 1955 Hz). HRMS (ESI): m/z Calc. for $C_{28}H_{37}SnN$ $[M-H]^+$: 506.1861. Found: 506.1868.

3.2.3. MenPhL*SnCl (3)

A solution of LiL* (1.53 g, 9.79 mmol) in diethyl ether (20 ml) was added to a solution of $MenPhSnCl_2$ (3.31 g, 8.16 mmol) in diethyl ether (40 ml) at 0°C, and the resultant solution stirred at r.t. for 18 h. Saturated ammonium chloride (2 ml), then water (20 ml) were added. The mixture was extracted with dichloromethane (2 × 40 ml), the combined organic extracts were dried (Na_2SO_4) and the solvent removed in vacuo to afford **3** as an orange oil in quantitative yield which was triturated from methanol afforded a white crystalline solid (2.18 g, 52%); m.p. 144–145°C. ^{1}H-NMR ($CDCl_3$): δ 0.58–2.46 (50H, m, both isomers), 1.24 (3H, d, minor isomer), 1.28 (3H, d, minor isomer), 3.49 (1H, q, major isomer), 3.91 (1H, q, minor isomer), 7.21–7.65 (16H, m, both isomers), 8.34–8.36 (1H, m, major isomer), 8.45–8.48 (1H, m, minor isomer). ^{13}C-NMR ($CDCl_3$): major diastereomer: δ 8.53, 16.19, 21.80, 22.23, 25.97, 33.80, 34.77, 34.95, 36.90 (broad, $W_{1/2}$ 40 Hz), 39.78, 43.54 ($J(^{13}C-^{119}Sn)$ 600 Hz), 43.88, 43.90 (broad, $W_{1/2}$ 40 Hz), 61.31, 125.12, 127.11, 128.15 (2C), 128.64, 129.06, 135.63 (2C), 138.21, 139.78, 144.07 ($J(^{13}C-^{119}Sn)$ 607 Hz), 147.92; minor diastereomer: δ 10.58, 16.03, 21.50, 22.45, 26.27, 32.36, 34.56, 35.10, 37.8 (broad, half width 80 Hz), 40.41, 41.73 ($J(^{13}C-^{119}Sn)$ 576 Hz), 43.77, 45.2 (broad, half width 80 Hz), 63.54, 125.36, 127.38, 128.02 (2C), 128.27, 129.09, 135.79 (2C), 136.96, 141.67, 144.91 ($J(^{13}C-^{119}Sn)$ 653

Table 3
Selected interatomic (Å, °) parameters for $MenPh_2LSn$ (**10**)

Sn(1)–C(1)	2.162(8)	Sn(2)–C(35)	2.179(9)
Sn(1)–C(7)	2.156(8)	Sn(2)–C(41)	2.129(8)
Sn(1)–C(13)	2.176(8)	Sn(2)–C(47)	2.148(8)
Sn(1)–C(23)	2.160(9)	Sn(2)–C(57)	2.147(9)
Sn(1)–N(1)	2.882(7)	Sn(1)–N(1)	2.899(7)
C(1)–Sn(1)–C(7)	102.5(3)	C(35)–Sn(2)–C(41)	101.7(3)
C(1)–Sn(1)–C(13)	103.9(3)	C(35)–Sn(2)–C(47)	104.2(3)
C(1)–Sn(1)–C(23)	103.3(3)	C(35)–Sn(2)–C(57)	104.1(3)
C(7)–Sn(1)–C(13)	119.4(3)	C(41)–Sn(2)–C(47)	119.2(3)
C(7)–Sn(1)–C(23)	112.8(3)	C(41)–Sn(2)–C(57)	113.9(3)
C(13)–Sn(1)–C(23)	112.6(3)	C(47)–Sn(2)–C(57)	111.6(3)

Hz), 146.38. ^{119}Sn-NMR ($CHCl_3$): major diastereomer: δ (R_{int}, %) −123.8 (73); minor diastereomer: δ (R_{int}, %) −146.4 (27). Anal. Calc. for $C_{26}H_{38}ClNSn$: C, 60.2; H, 7.4; N, 2.7. Found: C, 60.2; H, 7.4; N, 2.8%.

3.2.4. MenPhL*SnH (4)

A solution of $NaBH_4$ (0.27 g, 7.14 mmol) in ethanol (30 ml) was added to a suspension of **3** as prepared above (0.20 g, 0.39 mmol) in ethanol (10 ml) and the reaction mixture was stirred at r.t. for 1 h. The solvent was removed in vacuo, water (3 ml) was added and the residue was extracted with diethyl ether (3 × 5 ml). The combined extracts were dried (Na_2SO_4) and the solvent removed in vacuo to afford **4** as a yellow oil (0.18 g, 95%). ^{1}H-NMR (C_6D_6): δ 0.66–2.19 (38H, m, both isomers), 1.05 (3H, d, minor isomers), 1.08 (3H, d, major isomer), 1.86 (6H, s, major isomer), 1.92 (6H, s, minor isomer), 3.22 (1H, q, minor isomer), 3.49 (1H, q, major isomer), 6.46 (1H, s, minor isomer) (J(^{1}H–^{119}Sn) 1904 Hz), 6.46 (1H, s, major isomer) (J(^{1}H–^{119}Sn) 1920 Hz), 7.00–7.85 (18H, m both isomers). ^{13}C-NMR (C_6D_6): major diastereomer: δ 13.31, 16.08, 22.11, 22.81, 27.06, 34.10, 35.41 (J(^{13}C–^{119}Sn) 456 Hz), 35.67, 35.98, 40.82 (2C), 42.92, 46.41, 64.64, 126.79, 126.89, 128.36 (2C), 128.39, 128.78, 137.89, 138.14, 140.83 (J(^{13}C–^{119}Sn) not observable), 144.15 (J(^{13}C–^{119}Sn) 387 Hz), 150.54; minor diastereomer: δ 11.23, 16.00, 22.04, 22.78, 27.06, 33.39, 35.90, 35.98 (J(^{13}C–^{119}Sn) 484 Hz), 36.09, 40.26 (2C), 42.15, 46.78, 63.37, 126.34, 126.75, 128.07 (2C), 128.39, 128.53, 138.05 (2C), 138.38, 140.94 (J(^{13}C–^{119}Sn) not observable), 144.33 (J(^{13}C–^{119}Sn) 359 Hz), 150.29. ^{119}Sn-NMR (C_6D_6): major diastereomer: δ (R_{int}, %) −136.7 (64); minor diastereomer: δ (R_{int}, %) −166.8 (36). HRMS (ESI): m/z Calc. for $C_{26}H_{38}SnN$ $[M-H]^+$: 484.2017. Found: 484.2014.

3.2.5. Men$_2$SnCl$_2$ (5)

A solution of $HgCl_2$ (4.99 g, 18.38 mmol) in acetone (100 ml) was added slowly to a solution of Men_2Ph_2Sn (5.06, 9.18 mmol) in acetone (100 ml) at 0°C. The reaction mixture was stirred at r.t. for a further 18 h. The solvent was removed in vacuo and the PhHgCl was removed by precipitation from diethyl ether. The residue was distilled (180°C, 1 Pa), to give **5** as a colourless oil which solidified on standing (3.47 g, 81%); m.p. 43–45°C. ^{1}H-NMR ($CDCl_3$): δ 0.83–2.33 (38H, m). ^{13}C-NMR ($CDCl_3$): δ 15.9, 21.9, 22.2, 26.7, 34.5, 35.3, 36.7, 38.9, 45.8, 52.6 (J(^{13}C–^{119}Sn) 385 Hz). ^{119}Sn-NMR ($CDCl_3$): δ 94.3. Anal. Calc. for $C_{20}H_{38}Cl_2Sn$: C, 51.3; H, 8.2. Found: C, 51.3; H, 8.0%.

3.2.6. Men$_2$LSnCl (6)

A suspension of LiL·etherate (1.33 g, 5.32 mmol) in diethyl ether (25 ml) was added to a solution of **5** (2.30 g, 4.91 mmol) in diethyl ether (25 ml) at 0°C, and the reaction mixture was stirred at r.t. for 18 h. Saturated ammonium chloride (2 ml) was added and the resultant mixture extracted with diethyl ether (3 × 20 ml). The combined extracts were dried ($MgSO_4$) and the solvent removed in vacuo. The residue was purified by column chromatography (silica gel 60, 70–230 mesh) using gradient elution with a 70:30:1 solution of hexane–dichloromethane–triethylamine followed by acetone and then methanol. Removal of solvent in vacuo yielded the crude product as a brown oil (2.07 g, 70%). The product was dissolved in dichloromethane (20 ml), washed with 1 M HCl (20 ml), dried (Na_2SO_4) and the solvent was removed in vacuo to obtain **6** as a maroon solid (0.58 g, 20%); m.p. 65–72°C. ^{1}H-NMR ($CDCl_3$): δ −0.28–2.07 (38H, m), 2.76 (3H, s), 2.88 (3H, s), 7.37–8.35 (10H, m). ^{13}C-NMR ($CDCl_3$): δ 14.62, 16.60, 21.38, 21.89, 22.30, 22.64, 26.34, 26.59, 30.95, 34.30, 34.75 (2C), 35.37, 35.53, 40.64, 42.12, 42.92 (J(^{13}C–^{119}Sn) 474 Hz), 44.12 (J(^{13}C–^{119}Sn) 482 Hz), 44.24, 44.42, 48.51, 50.12, 115.70, 125.01, 127.20 (2C), 128.26, 134.41, 135.07, 136.42, 140.05 (J(^{13}C–^{119}Sn) 467 Hz), 150.76. ^{119}Sn-NMR ($CDCl_3$): δ −49.6. Anal. Calc. for $C_{32}H_{50}ClNSn$: C, 63.8; H, 8.4; N, 2.3. Found: C, 63.4; H, 7.9; N, 2.2%.

3.2.7. Men$_2$LSnH (7)

A solution of **6** (0.42 g, 0.70 mmol) in diethyl ether (25 ml) was added to a suspension of $LiAlH_4$ (0.08 g, 4.61 mmol) in diethyl ether (50 ml). The reaction mixture was stirred at r.t. for 18 h. Water (1 ml) was cautiously added. The reaction mixture was filtered and a 20% potassium/sodium-(+)-tartrate solution (30 ml) was added. The residue was extracted with diethyl ether (3 × 30 ml), dried (Na_2SO_4) and the solvent removed in vacuo to yield a cream coloured oil (0.36 g, 86%). ^{1}H-NMR (C_6D_6): δ 0.40–2.17 (38H, m), 2.44 (3H, s), 2.48 (3H, s), 6.31 (1H, s), 6.99–8.01 (10H, m). ^{13}C-NMR (C_6D_6): δ 15.97, 16.47, 22.40, 22.46, 22.96, 23.03, 27.44 (2C), 32.77, 34.13, 35.02 (J(^{13}C–^{119}Sn) 475 Hz), 35.84, 36.04, 36.10, 36.15, 36.75 (J(^{13}C–^{119}Sn) 389 Hz), 42.23, 43.70, 46.33, 47.79 (2C), 47.96, 116.18, 125.57, 125.90, 125.94, 129.28, 135.15, 135.63, 136.93, 138.83 (J(^{13}C–^{119}Sn) 442 Hz), 152.48. ^{119}Sn-NMR (C_6H_6): δ −104.6 (d, J(^{119}Sn–^{1}H) 1729 Hz). HRMS (ESI): m/z Calc. for $C_{32}H_{49}NSn$ $[M-H]^+$: 568.2953. Found: 568.2967.

3.2.8. Men$_2$L*SnCl (8)

A solution of LiL* (1.26 g, 8.12 mmol) in diethyl ether (30 ml) was added to a solution of **5** (3.39 g, 7.24 mmol) in diethyl ether (20 ml) at 0°C, and the reaction stirred at r.t. for 18 h. Saturated NH_4Cl (2 ml), and water (50 ml) were added to the reaction mixture. The mixture was extracted with dichloromethane (2 × 30 ml), the combined extracts dried (Na_2SO_4) and the solvent removed in vacuo. The residue was triturated with methanol to give **8** a white crystalline solid (3.33 g,

79%); m.p. 183–187°C. ^{1}H-NMR ($CDCl_3$): δ 0.07–2.06 (38H, m), 1.41 (3H, d), 2.25 (6H, s, broad), 4.12 (1H, q), 7.17–8.06 (4H, m). ^{13}C-NMR ($CDCl_3$): δ 7.87, 15.29, 16.40, 21.49, 21.87, 22.37, 22.57, 26.43, 26.67, 30.88, 34.42, 34.85 (2C), 35.30, 35.42, 40.13 (broad) (2C), 40.92, 41.08 (J(^{13}C–^{119}Sn) 462 Hz), 41.94, 44.12, 44.96, 45.06 (J(^{13}C–^{119}Sn) 515 Hz), 61.75, 124.69, 127.28, 128.15, 136.53, 145.05 (J(^{13}C–^{119}Sn) 488 Hz), 146.55. ^{119}Sn-NMR (CH_2Cl_2): δ −75.2. Anal. Calc. for $C_{30}H_{52}ClNSn$: C, 62.0; H, 9.0; N, 2.4. Found: C, 62.0; H, 9.3; N, 2.2%.

3.2.9. *Men$_2$L*SnH (**9**)*

A solution of **8** (0.63 g, 1.09 mmol) in diethyl ether (20 ml) was added to a suspension of $LiAlH_4$ (0.70 g, 18.4 mmol) in diethyl ether (30 ml) and the mixture was stirred at r.t. for 18 h. The reaction mixture was filtered through a thin layer of filter aid and water (3 ml) was added carefully to the filtrate at 0°C. Sodium/potassium-(+/−)-tartrate (20%, 20 ml) was added and the product was extracted with diethyl ether (2 × 30 ml). The combined extracts were dried (Na_2SO_4) and the solvent removed in vacuo to yield **9** as a pale yellow oil (0.46 g, 78%). ^{1}H-NMR (C_6D_6): δ 0.81–2.28 (38H, m), 1.15 (3H, d), 2.05 (6H, s), 3.56 (1H, q), 5.99 (1H, s, J(^{1}H–^{119}Sn) 1671 Hz), 7.13–7.72 (4H, m). ^{13}C-NMR (C_6D_6): δ 13.64, 16.12, 16.24, 22.26, 22.31, 22.85, 22.89, 27.20, 27.29, 33.72 (2C), 35.61 (J(^{13}C–^{119}Sn) 362 Hz), 35.86 (J(^{13}C–^{119}Sn) 431 Hz), 35.98, 36.04, 36.07, 41.32 (2C), 42.30, 43.73, 47.15, 47.75, 65.30, 126.22, 126.73, 128.12, 138.30, 142.58 (J(^{13}C–^{119}Sn) 430 Hz), 151.36. ^{119}Sn-NMR (C_6D_6): δ −141.3 (d, J(^{119}Sn–^{1}H) 1688 Hz). HRMS (ESI): m/z Calc. for $C_{30}H_{52}NSn$ $[M-H]^+$: 546.3109. Found: 546.3112.

3.2.10. *MenPh$_2$LSn (**10**)*

A suspension of LiL·etherate (1.50 g, 6.20 mmol) in diethyl ether (50 ml) was added to a suspension of $MenPh_2SnF$ (0.74 g, 1.72 mmol) in diethyl ether (10 ml) at 0°C. The reaction mixture was stirred at r.t. for 60 h, after which the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel 60, 70–230 mesh) using a 20:80 solution of dichloromethane–hexane to afford **10** as a white solid (0.38 g, 32%); m.p. 82–85°C. ^{1}H-NMR ($CDCl_3$): δ 0.31–2.21 (19H, m), 1.87 (3H, s), 2.66 (3H, s), 7.24–7.86 (16H, m). ^{13}C-NMR ($CDCl_3$): δ 16.75, 21.56, 22.68, 26.94, 33.45, 35.40, 35.61, 36.60 (J(^{13}C–^{119}Sn) 509 Hz), 40.92, 45.12, 45.85, 50.40, 115.52, 125.48, 125.83, 125.93, 127.55, 127.74 (2C), 128.07 (2C), 128.15 (2C), 128.44 (2C), 135.22 (J(^{13}C–^{119}Sn) 537 Hz), 143.68 (J(^{13}C–^{119}Sn) 493 Hz), 145.23 (J(^{13}C–^{119}Sn) 360 Hz), ^{119}Sn-NMR (C_6H_6): δ −107.1. Anal. Calc for $C_{34}H_{41}NSn{\cdot}CHCl_3$: C, 59.9; H, 6.0; N, 2.0. Found: C, 60.7; H, 6.4; N, 1.8%.

Table 4
Crystallographic data for MenPhL*SnCl (**3**), Men$_2$L*SnCl (**8**) andMenPh$_2$LSn (**10**·2CHCl$_3$)

	3	**8**	**10**·2CHCl$_3$
Formula	$C_{26}H_{38}ClNSn$	$C_{30}H_{52}ClNSn$	$C_{36}H_{41}Cl_6N_2Sn$
F_w	518.7	580.9	833.1
Crystal size (mm)	0.11 × 0.27 × 0.47	0.26 × 0.26 × 0.52	0.13 × 0.37 × 0.44
Colour	Colourless	Colourless	Colourless
Temperature (K)	293	200	200
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P1$	$P2_12_12_1$	$P2_1$
a (Å)	9.53(1)	12.866(5)	14.480(9)
b (Å)	25.51(2)	23.37(2)	21.07(1)
c (Å)	9.217(9)	10.223(5)	12.345(8)
α (°)	97.69(8)		
β (°)	118.47(7)		114.83(4)
γ (°)	84.66(9)		
V (Å^3)	1950(4)	3073(2)	3418(3)
Z	3	4	4
D_{calc} (g cm^{-3})	1.325	1.255	1.619
F(000)	804	1224	1692
μ (cm^{-1})	10.96	9.35	12.46
Transmission factors	0.282–1	0.691–1	0.855–1
No. of data collected	9486	4000	8431
θ_{max} (°)	27.6	27.7	27.6
No. of unique data with $I \geq 3.0\sigma(I)$	5520	3587	6172
R	0.080	0.025	0.048
R_w	0.088	0.032	0.050
Residual electron density (e Å^{-3})	1.83	0.36	1.20

*3.2.11. Men_2PhLSn (**11**)*

A solution of LiL·etherate (1.51 g, 6.04 mmol) in TMEDA (50 ml) was added to a solution of Men_2PhSnI (2.30 g, 3.83 mmol) in TMEDA (40 ml) and the solution was stirred at r.t. for 15 h. Water (1 ml) was added, the solution was dried ($MgSO_4$) and the solvent removed in vacuo. Purification of the residue was achieved by column chromatography (silica gel 60, 70–230 mesh) using a 70:30 solution of hexane–dichloromethane. Crystallisation in hot methanol afforded a white solid (0.83 g, 33%); m.p. 155°C. ^{1}H-NMR ($CDCl_3$): δ 0.38–2.24 (38H, m), 2.47 (3H, s), 2.76 (3H, s), 7.24–7.84 (11H, m). ^{13}C-NMR ($CDCl_3$): δ 16.13, 17.16, 21.74, 21.84, 22.49, 22.77, 27.06, 27.20, 32.58, 33.69, 35.32, 35.54, 35.57, 35.68, 36.94 (J(^{13}C–^{119}Sn) 439 Hz), 37.62 J(^{13}C–^{119}Sn) 407 Hz), 40.80, 43.29, 45.32, 46.32, 46.48, 50.98, 115.34, 125.02, 125.37, 125.95, 126.88, 127.23 (2C), 128.27, 135.01, 135.86, 137.56 (2C), 137.87, 138.67 (J(^{13}C–^{119}Sn) 431 Hz), 147.48 (J(^{13}C–^{119}Sn) 295 Hz), 153.44. ^{119}Sn-NMR ($CHCl_3$): δ −99.1 Anal. Calc. for $C_{38}H_{55}NSn$: C, 70.8; H, 8.6; N, 2.2. Found: C, 70.6; H, 8.6; N, 2.0%.

3.3. X-ray crystallography

Data were collected on a Rigaku AFC6R diffractometer fitted with graphite monochromatised Mo–K_α radiation, $\lambda = 0.71073$ Å. Corrections were made for Lorentz and polarisation effects [23] as well as for absorption employing an empirical method [24]. The structures were solved by Patterson methods [25] and each refined by a full-matrix least-squares procedure based on F [23]. The absolute structures were determined on the basis of the known configuration of the menthyl. For the refinement of **8** all non-hydrogen atoms were refined with anisotropic displacement parameters but for the refinements of **3** and **10** only non-carbon and non-hydrogen atoms were refined anisotropically. The refinements were continued with the application of a weighting scheme of the form $w = 1/[\sigma^2(F_o) + g|F_o|^2]$ where $g = 0.00022$, 0.00018 and 0.019 for **3**, **8** and **10**, respectively. The significant residual electron density peaks (Table 4) in the final difference maps were located in the region of the tin atom in each case. Crystallographic and refinement data are given in Table 4. Diagrams of the molecules were drawn with ORTEP [26] plotted at the 35% (for **3**) and 50% (for **8** and **10**) probability levels.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 141615 for compound **3**, CCDC No. 141614 for compound **8**, and CCDC No. 141616 for compound **10**. Copies of the 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 www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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