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Sterically hindered organotin compounds

II. Synthesis of the organotin halides $(\text{mesityl})_2SnX_nY_{2-n}$, $(\text{mesityl})SnX_nY_{3-n}$ and $R_4Sn_2X_2$ ($R = 2,4,6\text{-}^iPr_3C_6H_2$, $X = Cl$, $Y = Br$). Crystal structure of the ditin species $(R_2BrSn)_2$

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Abstract

Reaction of mesityllithium with $SnCl_4$ (2:1) gives $(\text{mesityl})_2SnCl_2$, while the corresponding reaction using mesitylmagnesium bromide gives a mixture of halogenato-products $(\text{mesityl})_2SnCl_2$, $(\text{mesityl})_2SnBr_2$ and $(\text{mesityl})_2SnClBr$. Reaction of this latter mixture with $SnCl_4$ (1:1) gives the full range of $(\text{mesityl})SnX_nY_{3-n}$ ($X = Cl$, $Y = Br$). In contrast, the more sterically demanding carbanion source $2,4,6\text{-}^iPr_3C_6H_2Li$ reacts with $SnCl_4$ or $SnBr_4$ (1:1) to give the coupled ditin product $(2,4,6\text{-}^iPr_3C_6H_2)_4Sn_2(\text{hal})_2$. The structure of the bromide, $[(2,4,6\text{-}^iPr_3C_6H_2)_4Sn_2Br_2]$ (Sn–Sn) has been determined and shown to consist of molecular units in an approximately staggered conformation, with an Sn–Sn distance of 2.841(1) Å. The molecule is highly sterically congested, leading to non-equivalence of methyl groups in some isopropyl units owing to hindered rotation about C–C and C–Sn bonds.

Introduction

There has been considerable interest in recent years in the use of sterically demanding ligands and their effect on the chemistry of metal-containing compounds. Much of this attention has focused on the ability of bulky ligands to impart kinetic stability to inherently thermodynamically unstable species [1–3], though examples in which the use of bulky ligands yields unexpected reaction products are not uncommon. For example, with reference to the area of organotin chemistry, the use of the supermesityl ligand, $2,4,6\text{-}^tBu_3C_6H_2$, has been found to lead to products in which a proton on one of the C_4H_9 groups is activated and can lead to the formation of $-CH_2Sn\equiv$ linkages [4,5], while reagents such as ^tBuLi

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often act as bases rather than carbanion sources [6]. In this paper we report an unanticipated scrambling of halogens in the preparation of (mesityl)$_2$SnCl$_2$ using (mesityl)MgBr where no such reaction occurs with mesityllithium (also prepared from mesityl bromide; mesityl = 2,4,6-Me$_3$C$_6$H$_2$), and the synthesis of [(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$BrSn]$_2$ from 2,4,6-^{i}Pr$_3$C$_6$H$_2$Li and SnBr$_4$, the organolithium acting as both a base and a carbanion source.

Results and discussion

Mesityllithium and mesitylmagnesium bromide, both prepared *in situ* from mesityl bromide, reacted in 2 : 1 ratio with SnCl$_4$ to give differing products. With mesityllithium in THF the sole product appeared to be (mesityl)$_2$SnCl$_2$, as anticipated, characterised by a ^{119}Sn NMR chemical shift of -51.6 ppm. On the other hand, the Grignard reagent in diethyl ether reacted with SnCl$_4$ under similar conditions to give, after removal of inorganic by-products, a mixture which showed three signals in its ^{119}Sn NMR spectrum at -52.4 (3%), -97.8 (30%) and -148.1 ppm (67%) (percentages based upon NMR integrals). The first of these species appears to be (mesityl)$_2$SnCl$_2$ from the similarity of its ^{119}Sn chemical shift to that of an authentic sample, while the successive incremental upfield shift of the remaining signals is typical of sequential substitution by a heavier halogen. For example, Me$_2$SnX$_2$ gave rise to signals at $+140$ (X = Cl), $+70$ (X = Br) and -159 ppm (X = I) in their tin NMR spectra [7]. Accordingly, we assign the two species mentioned above as (mesityl)$_2$SnClBr (-97.8 ppm) and (mesityl)$_2$SnBr$_2$ (-148.1 ppm). Both the ^{1}H and ^{13}C NMR spectra of the product(s) have a complexity typical of a mixture of products, and the individual resonances cannot be assigned to the components with any certainty. However, elemental analysis of the mixture based on weightings of each component given by the NMR integrals above is consistent with expectation (see Experimental). We previously noted the formation of (Me$_3$Si)$_3$CSnCl$_n$Br$_{n-3}$ from Br$_2$ cleavage of (Me$_3$Si)$_3$CSnPh$_3$ in CCl$_4$ (FeBr$_3$ catalyst) [8], while Cardin *et al.* found that reaction of 2,6-Et$_2$C$_6$H$_3$Li (from BuLi and 2,6-Et$_2$C$_6$H$_3$Br) with SnCl$_2$ gives *cyclo*-(R$_2$Sn)$_3$Sn(R)Br (R = 2,6-Et$_2$C$_6$H$_3$). In this latter case, bromine incorporation in the final product was ascribed to LiBr formed in the initial preparation of 2,6-Et$_2$C$_6$H$_3$Li and carried through to final stages of reaction [9].

When the (mesityl)$_2$SnCl$_n$Br$_{2-n}$ mixture described above is used in a redistribution reaction with SnCl$_4$, the full range of (mesityl)SnCl$_n$Br$_{3-n}$ compounds is observed in the ^{119}Sn NMR spectra of the product (percentages based on NMR integrals):

$$\begin{array}{llllll}
\mathrm{R_2SnCl_nBr_{2-n} + SnCl_4} & \xrightarrow{150^\circ\mathrm{C},\ 3\ \mathrm{h}} & \mathrm{RSnCl_3} + & \mathrm{RSnCl_2Br} + & \mathrm{RSnClBr_2} + & \mathrm{RSnBr_3} \\
\mathrm{R = 2,4,6\text{-}Me_3C_6H_2} & \delta\ ^{119}\mathrm{Sn}: & -85.5 & -150.1 & -219.7 & -294.2\ \mathrm{ppm} \\
 & \%: & 40 & 44 & 14 & 2
\end{array}$$

The resonance associated with (mesityl)SnCl$_3$ has been assigned on the basis of a comparison with the chemical shift of PhSnCl$_3$ (-60.5 ppm) [7]. Again, the upfield shift which accompanies increasing bromine content is consistent with that for other monoorganotin halides (MeSnCl$_3$: $+21$ ppm; MeSnBr$_3$: -165 ppm), and has also been observed in the series [SnCl$_n$Br$_{6-n}$]$^{2-}$ [10]. Furthermore, the additional data available in the monomesityl series allow the internal consistency of the assignments to be tested by the method of pairwise interactions [11]. Thus, assuming tetrahedral geometry throughout and, for the purposes of this analysis, ignoring any contribution from the aryl group which is common to all species, pairwise contributions for Cl–Cl, Br–Br and Cl–Br can be derived from $RSnCl_3$, $RSnBr_3$ and $RSnCl_2Br$ as −28.5, −98.1 and −60.8 ppm respectively. Using these values, the predicted ^{119}Sn NMR chemical shift for $RSnClBr_2$ is −219.7 ppm, exactly as observed. As with the $(mesityl)_2SnCl_nBr_{2-n}$ mixture, elemental analysis based on weightings of each component given by the NMR integrals above is consistent with expectation (see Experimental).

In contrast to the above reactions, the bulkier carbanion source 2,4,6-$^iPr_3C_6H_2Li$ (from 2,4,6-$^iPr_3C_6H_2Br$ and BuLi) reacts in 1:1 ratio with $SnBr_4$ to give the ditin product $[(2,4,6\text{-}^iPr_3C_6H_2)_2BrSn]_2$, characterised by $^1J(^{119}Sn-^{117}Sn) = 5212$ Hz. The corresponding reaction with $SnCl_4$ gives an impure oil, which we assume to be primarily the corresponding $R_4Sn_2Cl_2$ from the similarity in the infrared spectra of the two compounds. This latter compound was obtained in pure (solid) form by Masamune from R_2SnCl_2 and lithium naphthalenide [12], while Weidenbruch *et al.* have recently reported the coupling of $^tBu_2(2,4,6\text{-}^iPr_3C_6H_2)SnCl$ to give $^tBu_4(2,4,6\text{-}^iPr_3C_6H_2)_2Sn_2$ using ^tBuLi [6].

The structure of $[(2,4,6\text{-}^iPr_3C_6H_2)_2BrSn]_2$ is shown in Fig. 1. It consists of discrete molecules, unlike $(Me_2ClSn)_2$ where the diminished steric demands of the ligands allow intermolecular Cl: → Sn bridges to link molecules into a helical band structure [13]. The Sn–Sn bond length [2.841(1) Å] reflects the steric crowding of the molecule, being longer than in $(Me_2ClSn)_2$ [2.780(4), 2.770(2) Å] [13] but shorter than in the more hindered hexaorganoditin $^tBu_4(2,4,6\text{-}^iPr_3C_6H_2)_2Sn_2$ [3.034(1) Å] [6]. The observed bond length is very close to that reported for $[(Me_3Si)_2CH]_4Sn_2Cl_2$ [2.844(1) Å] [14]. The Sn–Br bond [2.551(1), 2.537(1) Å] is intermediate between that seen in $Cp(CO)_2FeSnBr_3$ [2.491(2)–2.508(2); average: 2.501(2) Å] [15] and $[(CO)_5Mn]_4Sn_2Br_2$ [2.576(1) Å] [16].

The steric demands of the ligands in the title ditin manifest themselves in three ways. Firstly, the molecule adopts an approximately staggered conformation with the dihedral angle Br1–Sn1–Sn2–Br2 = 161.6°. This contrasts with the related hexaorganoditin, $Bu_4(2,4,6\text{-}^iPr_3C_6H_2)_2Sn_2$, which contains the same aryl group but which adopts an eclipsed conformation, with the aryl groups disposed in a *syn* fashion [6]. Secondly, packing the organic groups around the tin–tin bond leads to an irregular coordination sphere about each metal, evidenced by two distinct bond angles to carbon [C1–Sn1–Sn2: 135.2(3), C46–Sn2–Sn1: 131.8(3); C16–Sn1–Sn2: 104.6(3), C31–Sn2–Sn1: 105.0(3)°]. Finally, the packing of organic groups is sufficient to prevent free rotation of both the aryl groups about the various Sn–C bonds and ^iPr groups about the C–C link to the aromatic ring. This gives rise to a complex ^1H NMR spectrum (see Ref. 12 for similar comments regarding $R_4Sn_2Cl_2$) in the region associated with the isopropyl groups, which is tabulated in Table 1 and correlates CH and CH_3 environments from a 2D-COSY-90 experiment. Six multiplets of the same intensity are observed for the methine protons, each of which must correspond to two equivalent ^iPr groups of the twelve in the molecule. Of these, three signals (2.72, 2.86, 3.40 ppm) correlate with methyl doublets of integrated intensity 12H (1.13, 1.23, 1.44 ppm respectively) which correspond to free rotation of the ^iPr moiety (*i.e.* equivalent CH_3 groups). The remaining three methine signals (2.50, 3.14, 3.21 ppm) each correlate to two doublets of integrated

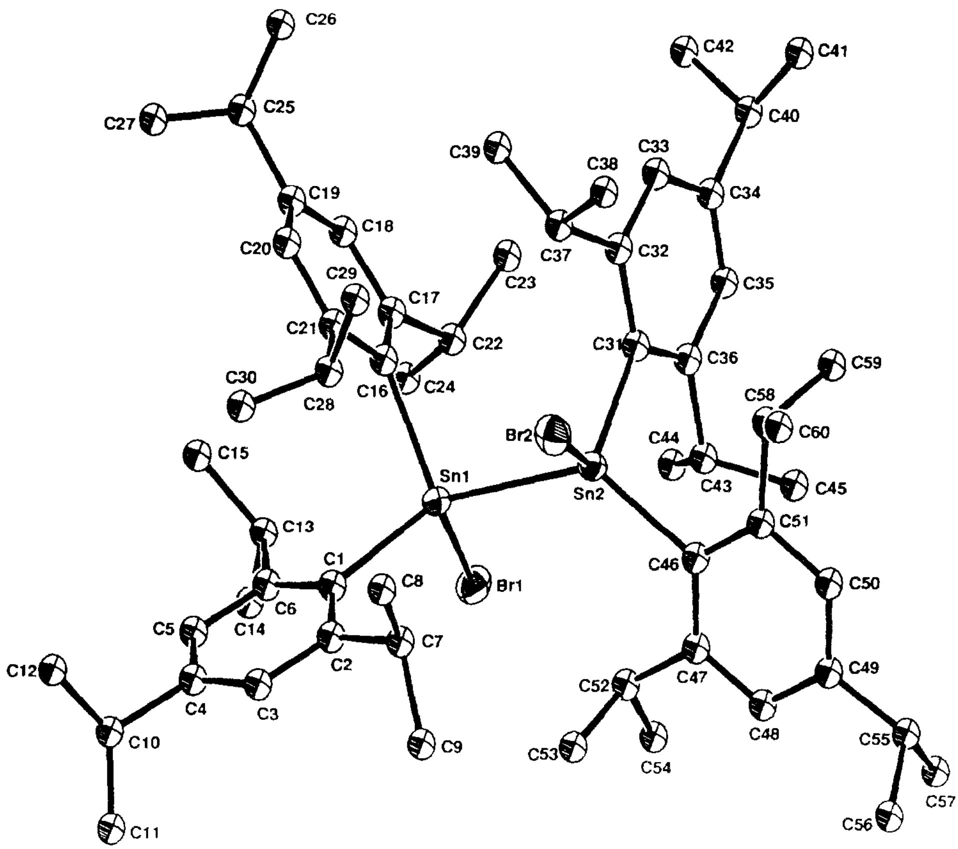

Fig. 1. The asymmetric unit of 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromo-1,2-ditin.

intensity 6H, one of which is at relatively low field (1.27, 1.23, 1.13 ppm, respectively) while the other is more shielded by about 1 ppm (0.25, 0.31, 0.11 ppm, respectively). Thus, six ^{i}Pr groups each show non-equivalent CH_3 units, and within

Table 1

Correlations between ^1H chemical shift values (ppm) for methyl and methine environments for the isopropyl groups of 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromo-1,2-ditin

$\delta[(CH_3)_2CH]$	$\delta[(CH_3)_2CH]$
2.50 (m, 2H)	0.25 (d, 6H); 1.27 (d, 6H)
2.72 (m, 2H)	1.13 (t, 12H) [a]
2.86 (m, 2H)	1.23 (d, 12H) [b]
3.14 (m, 2H)	0.31 (d, 6H); 1.23 (d, 6H) [b]
3.12 (m, 2H)	0.11 (d, 6H); 1.13 (t, 6H) [a]
3.40 (m, 2H)	1.44 (t, 12H) [c]

[a] Two overlapping doublets, total integral 18H. [b] Total integral at this chemical shift is 18H. [c] This signal probably arises from two overlapping doublets of very similar chemical shift, associated with two distinct methyl groups of isopropyl units in restricted environments. Neither methyl experiences any shielding due to nearby ring currents, and thus can be assigned to be iso-propyl groups centred on C7 and C52.

Table 2

Through space distances (Å) between methyl groups and mean aryl ring planes [a]

Carbon	Aryl ring	distance
C15	C16–C21	3.54
C23	C31–C36	3.60
C30	C1–C6	3.48
C39	C16–C21	3.57
C45	C46–C51	3.53
C59	C31–C36	3.81

[a] Distances are C–(mean plane); numbering refers to Fig. 1.

each ^{i}Pr one of the two methyl groups is in a more shielded environment. From the crystallography (Fig. 1), the four exterior ^{i}Pr groups (based on C10, C25, C40 and C55) along with two at C7 and C52 are in relatively unhindered orientations, and correspond to the six freely rotating hydrocarbon fragments. The remaining six ^{i}Pr groups all have one methyl group which is sitting approximately 3.5Å from the centre of a spatially adjacent aromatic ring (Table 2). These CH_3 groups all experience a shielding effect from their position above the centre of the aromatic ring current, and are assignable to the three high field doublets (0.11, 0.25, 0.31 ppm). Restricted rotation about Sn–Sn and Sn–C bonds in $^{t}Bu_4(2,4,6\text{-}^{i}Pr_3C_6H_2)_2Sn_2$ has also been noted [6].

We previously described the use of the corresponding dichloroditin compound in the synthesis of four-membered heterocycles $(R_2SnS)_2$ and $(R_2SnS_{0.5}O_{0.5})_2$ [17]. We believe that reaction of the ditin with S^{2-} (from Na_2S) probably proceeds *via* the three membered thiadistannirane ring Sn_2S, which then relieves ring strain by inserting either sulphur (anaerobic conditions) or oxygen if the reaction is carried out in air. Since this initial report, spectroscopic evidence has appeared for the formation of the thiadistannirane from reaction of methylthiirane with the distannylene $R_2Sn{=}SnR_2$ ($R = 2,4,6\text{-}^{i}Pr_3C_6H_2$) [18], while the stannylene reacts in an analogous fashion with tellurium to give the corresponding telluradistannirane, Sn_2Te [19]. An azadistanniridine R_4Sn_2NR' has also now been reported, from the monomeric stannylene R_2Sn [$R = 2,4,6\text{-}(CF_3)_3C_6H_2$] and $R'N_3$ (R' = mesityl) [20].

Experimental

Spectra were recorded on the following instruments JEOL GX270 (^{1}H, ^{13}C NMR), JEOL GX400 (^{119}Sn NMR). Details of our Mössbauer spectrometer and related procedures are given elsewhere [21]. NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature. ^{119}Sn chemical shifts are relative to Me_4Sn.

All reactions were carried out under dinitrogen using dry solvents.

Synthesis of dimesityltin dichloride

Mesityllithium was prepared from mesityl bromide (5.00 g, 25 mmol) in dry THF by the dropwise addition of n-butyllithium (10.3 ml 2.4 *M* solution in hexane, 25 mmol) at −78°C. After 3 h, tin(IV) chloride (3.20 g, 13 mmol) in dry hexane was added dropwise, and the mixture allowed to warm to room temperature. Stirring was continued for a further 15 h, then 2 h at reflux. After cooling, the solvents were removed *in vacuo*, chloroform added and the solution filtered to remove unwanted inorganic by-products. The solvent was again evaporated to leave an off-white solid, from which the desired compound was obtained in pure form by recrystallisation from ethyl acetate/light petroleum (b.p. 60–80°C) (1.10 g, 21%, m.p. 172–173°C). Anal. Found: C 50.30, H 5.27%. Calcd. for $C_{18}H_{22}Cl_2Sn$: C 50.50, H 5.20%.

^1H NMR: 2.28 s (6H, p-$CH_3C_6H_2$), 2.54 s (12H, o-$CH_3C_6H_2$), 6.93 s (4H, C_6H_2); ^{13}C NMR: 21.08 (p-$CH_3C_6H_2$), 24.68 (o-$CH_3C_6H_2$), 129.55, 139.15, 141.38, 143.53 (o,m,i,p-C_6H_2); ^{119}Sn NMR: −51.6 ppm; ^{119}Sn Mössbauer: IS = 1.33, QS = 2.65 mm s^{-1}.

Synthesis of dimesityltin dihalides

Mesityl Grignard was prepared from mesityl bromide (31.40 g, 158 mmol) and magnesium (3.90 g, 160 mmol) in dry ether. Unchanged magnesium was filtered off through a glass wool plug and the Grignard solution was cooled to −20°C and tin(IV) chloride (19.60 g, 75 mmol) in light dry petroleum (b.p. 60–80°C) added dropwise. The mixture was stirred at room temperature for 15 h and at reflux for a further 2 h. The solution was filtered and the filtrate concentrated to give a light yellow oil. Trituration with light petroleum (b.p. 80–100°C) yielded an off-white solid, which was recrystallised from the same solvent (11.2 g, 30%). Anal. Found: C 42.70, H 4.42%. Calcd. for 3% $C_{18}H_{22}Cl_2Sn$, 30% $C_{18}H_{22}BrClSn$, 67% $C_{18}H_{22}Br_2Sn$, percentages based on NMR integrals: C 43.25%, H 4.44%.

^{119}Sn NMR: −52.4 [(mesityl)$_2$SnCl$_2$], −97.8 [(mesityl)$_2$SnClBr], −148.1 ppm [(mesityl)$_2$SnBr$_2$]; ^{119}Sn Mössbauer: IS = 1.38, QS = 2.52 mm s^{-1}.

Synthesis of mesityltin trihalides

Anhydrous tin(IV) chloride (1.56 g, 6 mmol) was added to the above dimesityltin dihalide mixture (3.00 g, 6 mmol) at −5°C under anaerobic conditions. The mixture was allowed to warm to room temperature, then heated at 150°C for 3 h. Recrystallisation of the resulting solid from light petroleum (b.p. 80–100°C) yielded 3.20 g (70%) of a white solid. Anal. Found: C 28.60, H 2.93%. Calcd. for 41% $C_9H_{11}Cl_3Sn$, 44% $C_9H_{11}BrCl_2Sn$, 14% $C_9H_{11}Br_2ClSn$, 2% $C_9H_{11}Br_3Sn$, percentages based on NMR integrals: C 28.78, H 2.95%.

^{119}Sn NMR: −85.5 [(mesityl)SnCl$_3$], −150.1 [(mesityl)SnCl$_2$Br], −219.7 [(mesityl)SnClBr$_2$], −294.2 ppm [(mesityl)SnBr$_3$]; ^{119}Sn Mössbauer: IS = 1.20, QS = 1.72 mm s^{-1}.

Synthesis of 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromo-1,2-ditin

2,4,6-Tri-isopropylphenyllithium was prepared from 2,4,6-tri-isopropylphenyl bromide (5.00 g, 18 mmol) and ^nBuLi (7.07 ml 2.5 M solution in hexane, 18 mmol) in dry THF at −78°C. The solution was allowed to warm to room temperature, during which time a white precipitate formed and then redissolved. The solution was re-cooled to −78°C, and tin(IV) bromide (7.74 g, 18 mmol) in dry light petroleum (b.p. 60–80°C) added dropwise. The mixture was stirred at room temperature for 15 h and under reflux for a further 2 h. Solvent removal *in vacuo* yielded a brown oil, which was first triturated with acetone, and the solid formed

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	U_{iso} or U_{eq} ^{a}
Sn1	0.18129(7)	0.09039(2)	0.15218(4)	0.0436(5) ^{a}
Sn2	0.31152(7)	0.12140(2)	0.01634(4)	0.0428(4) ^{a}
Br1	−0.03538(11)	0.08346(4)	0.08457(7)	0.0643(8) ^{a}
Br2	0.53182(12)	0.10671(3)	0.06806(8)	0.0658(8) ^{a}
C1	0.1890(10)	0.0369(3)	0.2215(6)	0.050(3)
C2	0.2767(10)	0.0094(3)	0.2085(6)	0.052(3)
C3	0.2802(12)	−0.0230(3)	0.2616(7)	0.068(3)
C4	0.1972(12)	−0.0263(3)	0.3225(8)	0.073(4)
C5	0.1085(12)	0.0008(3)	0.3359(8)	0.074(4)
C6	0.0999(11)	0.0334(3)	0.2848(7)	0.059(3)
C7	0.3741(11)	0.0102(3)	0.1424(7)	0.064(3)
C8	0.5059(12)	0.0157(4)	0.1786(8)	0.084(4)
C9	0.3725(13)	−0.0255(4)	0.0884(8)	0.084(4)
C10	0.2003(16)	−0.0609(5)	0.3812(11)	0.115(5)
C11	0.1546(20)	−0.0945(5)	0.3531(12)	0.156(7)
C12	0.2723(17)	−0.0559(4)	0.4578(9)	0.122(6)
C13	−0.0010(11)	0.0618(3)	0.3024(7)	0.065(3)
C14	−0.1299(12)	0.0444(4)	0.2919(8)	0.081(4)
C15	0.0136(13)	0.0792(4)	0.3898(7)	0.078(4)
C16	0.1923(10)	0.1346(3)	0.2489(6)	0.050(3)
C17	0.1014(10)	0.1630(3)	0.2567(6)	0.053(3)
C18	0.1035(11)	0.1851(3)	0.3302(7)	0.062(3)
C19	0.1933(11)	0.1802(3)	0.3904(7)	0.063(3)
C20	0.2837(11)	0.1538(3)	0.3805(7)	0.062(3)
C21	0.2879(10)	0.1307(3)	0.3099(6)	0.052(3)
C22	0.0028(11)	0.1724(3)	0.1901(7)	0.067(3)
C23	0.0035(13)	0.2138(3)	0.1646(8)	0.081(4)
C24	−0.1248(13)	0.1607(4)	0.2176(8)	0.091(4)
C25	0.1910(14)	0.2053(4)	0.4684(8)	0.084(4)
C26	0.2735(15)	0.2381(4)	0.4598(9)	0.108(5)
C27	0.1812(18)	0.1867(5)	0.5440(10)	0.137(6)
C28	0.3957(10)	0.1031(3)	0.3022(7)	0.056(3)
C29	0.5221(12)	0.1235(3)	0.3008(7)	0.075(4)
C30	0.3988(12)	0.0729(3)	0.3726(7)	0.071(4)
C31	0.2600(10)	0.1819(3)	0.0137(6)	0.046(3)
C32	0.3281(10)	0.2091(3)	0.0640(6)	0.054(3)
C33	0.2978(11)	0.2483(3)	0.0511(7)	0.066(3)
C34	0.2069(11)	0.2586(3)	−0.0067(7)	0.065(3)
C35	0.1447(12)	0.2322(3)	−0.0513(7)	0.072(4)
C36	0.1710(11)	0.1931(3)	−0.0420(7)	0.058(3)
C37	0.4226(11)	0.1997(3)	0.1304(7)	0.060(3)
C38	0.5519(12)	0.2078(4)	0.1016(8)	0.085(4)
C39	0.4008(12)	0.2201(3)	0.2127(7)	0.075(4)
C40	0.1714(13)	0.3011(4)	−0.0177(8)	0.083(4)
C41	0.2807(13)	0.3238(4)	−0.0435(9)	0.096(4)
C42	0.1091(14)	0.3170(4)	0.0548(8)	0.101(5)
C43	0.0859(11)	0.1658(3)	−0.0911(7)	0.067(3)
C44	−0.0493(12)	0.1683(4)	−0.0666(8)	0.087(4)
C45	0.0959(14)	0.1697(4)	−0.1840(8)	0.092(4)
C46	0.3244(9)	0.1035(3)	−0.1129(6)	0.041(2)
C47	0.2399(10)	0.0758(3)	−0.1464(6)	0.047(3)
C48	0.2500(10)	0.0658(3)	−0.2295(6)	0.055(3)
C49	0.3364(11)	0.0824(3)	−0.2799(7)	0.057(3)

Table 3 (continued)

Atom	x	y	z	U_{iso} or U_{eq} ^{a}
C50	0.4136(11)	0.1100(3)	−0.2475(7)	0.057(3)
C51	0.4092(10)	0.1213(3)	−0.1646(6)	0.053(3)
C52	0.1444(10)	0.0570(3)	−0.0940(6)	0.053(3)
C53	0.1882(13)	0.0192(3)	−0.0642(8)	0.081(4)
C54	0.0146(12)	0.0537(4)	−0.1372(7)	0.077(4)
C55	0.3408(12)	0.0722(4)	−0.3733(7)	0.073(4)
C56	0.3893(13)	0.0329(4)	−0.3863(8)	0.089(4)
C57	0.2151(15)	0.0741(5)	−0.4153(10)	0.121(6)
C58	0.4950(11)	0.1539(3)	−0.1341(7)	0.064(3)
C59	0.4652(13)	0.1907(4)	−0.1773(8)	0.086(4)
C60	0.6338(13)	0.1436(4)	−0.1455(9)	0.096(4)

then recrystallised from the same solvent to give a white solid (1.80 g, 17%). Anal. Found: C 59.50, H 7.84%. Calcd. for $C_{60}H_{92}Br_2Sn_2$: C 59.53, H 7.66%.

^{1}H NMR: see Table 1; ^{13}C NMR: 22.54, 22.80, 23.09, 23.81, 23.97, 25.33, 25.66, 26.43, 27.73 (CH_3), 34.19, 37.33, 39.86, 41.81 (Me_2CH), 122.15, 122.93, 123.42, 123.97, 141.58, 145.76, 150.63, 152.38, 153.61, 154.75, 155.20 (C_6H_2); ^{119}Sn NMR: −118.3 ppm [$^1J(^{119}Sn-^{117}Sn)$: 5212 Hz]; ^{119}Sn Mössbauer: IS = 1.54, QS = 2.23 mm s^{-1}; m/e (EI) 605 [P-($^iPr_3C_6H_2$)$_2$SnBr].

The structure of 1,1,2,2-tetra(2,4,6-tri-isopropylphenyl)-1,2-dibromo-1,2-ditin

Crystal data: $C_{60}H_{92}Br_2Sn_2$, $M = 1210.58$, Monoclinic, $P2_1/n$, $a = 10.723(3)$, $b = 35.225(7)$, $c = 16.076(3)$ Å, $\beta = 91.50(2)°$, $Z = 4$, $U = 6070.5$ Å^3, $D_c = 1.32$ g cm^{-3}, λ(Mo–K_α) = 0.71069 Å, μ(Mo–K_α) = 20.68 cm^{-1}, $F(000) = 2448$.

Crystals were grown by slow evaporation of an acetone solution; a crystal of approximate dimensions 0.25 × 0.25 × 0.25 mm was used for data collection. Data were collected in the range $2 < \theta < 22°$ (h $0 \rightarrow 11$, k $0 \rightarrow 36$, l $-17 \rightarrow 17$) at room temperature on a Hilger and Watts Y290 automatic four circle diffractometer. Unit cell dimensions were based on 12 accurately centred reflections with $\theta > 15°$. A monitor reflection measured after every 50 reflections showed no systematic decay in intensity. In all, 4982 unique observed reflections [$I > 3\sigma(I)$] were collected. Data were corrected for Lorentz and polarisation effects. The structure

Table 4

Selected bond lengths (Å) and angles (°)

Sn1–Sn2	2.841(1)	Sn1–Br1	2.551(1)
Sn1–C1	2.191(1)	Sn1–C16	2.202(10)
Sn2–Br2	2.537(1)	Sn2–C31	2.201(10)
Sn2–C46	2.179(9)		
Br1–Sn1–Sn2	99.8(1)	C1–Sn1–Sn2	135.2(3)
C1–Sn1–Br1	99.0(3)	C16–Sn1–Sn2	104.6(3)
C16–Sn1–Br1	113.6(3)	C16–Sn1–C1	104.4(4)
Br2–Sn2–Sn1	98.2(1)	C31–Sn2–Sn1	105.0(3)
C31–Sn2–Br2	115.8(3)	C46–Sn2–Sn1	131.8(3)
C46–Sn2–Br2	99.9(3)	C46–Sn2–C31	106.5(4)

was solved by conventional Patterson and Fourier methods [22,23]. Structure factors were taken from the usual sources [24–26]. In the final cycles of refinement both tin and bromine atoms were treated anisotropically, all other atoms isotropically. Hydrogen atoms were included at calculated positions (C–H: 1.08 Å) with fixed isotropic temperature factors (0.05 $Å^2$). Final $R = 5.62\%$ $R_w = 5.31\%$ [$w = 4.885/\sigma^2(F)$] and 277 variable parameters, max. shift/esd = 0.018, residual electron density maxima and minima 0.27, −0.36 e $Å^{-3}$, respectively.

Final fractional atomic coordinates and isotropic temperature factors are given in Table 3, with selected bond distances and angles in Table 4. The asymmetric unit along with atomic labelling is shown in Fig. 1. Tables of anisotropic temperature factors, hydrogen atom positions and a full list of intramolecular distances and angles have been deposited with the Cambridge Crystallographic Database. A list of observed and calculated structure factors is available from the author.

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