

# Sulphur Substituted Organotin Compounds

## Part 9\*. Crystal and Molecular Structure and Reactions of [(*p*-Chlorophenylthio)methyl]tricyclohexylstannane

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(Received December 27, 1989)

### Abstract

The crystal and molecular structure of [(*p*-chlorophenylthio)methyl]tricyclohexylstannane (**II**) has been determined. In the two independent molecules of monoclinic **II** there are slightly distorted tetrahedral geometries about tin with intramolecular Sn–S distances of 3.29(1) and 3.26(1) Å. Compound **II** reacts with *N*-bromosuccinimide,  $I_2$ ,  $Pb(OAc)_4$  or  $CF_3CO_2H$  to give  $XCH_2SC_6H_4Cl$ -*p* ( $X = Br, I, AcO$  or  $H$ ) and the appropriate tricyclohexyltin species; **II** is less reactive than  $Cy_3SnCH_2SeC_6H_4Cl$ -*p* towards  $I_2$ . Oxidative cleavage of **II** by *m*- $ClC_6H_4CO \cdot O \cdot OH$  provides mainly  $CH_3S(O)C_6H_4Cl$ -*p*. The absorption maximum for the charge transfer complex of **II** and  $(NC)_2C=C(CN)_2$  is reported.

### Introduction

$\alpha$ -(Organothio)alkylstannanes,  $RSCH_2SnR^1_3$  [**1**] have attracted some attention [2–7], with synthesis and properties in solution, including spectra and a number of reactions, having been reported. The most extensively studied compounds are those with  $R^1 = Ph$  (**I**); reactions of **I** ( $R^1 = Ph$ ) can occur at the  $Ph-Sn$  bond, the  $Sn-CH_2$  bond or at the sulphur atom. No structure determination of **I** in the solid state has yet been published.

We now wish to report the crystal and molecular structure of [(*p*-chlorophenylthio)methyl]tricyclohexylstannane,  $Cy_3SnCH_2SC_6H_4Cl$ -*p* (**II**). In addition, a series of reactions of **II** with electrophilic and other reagents are reported.

\*For Part 8, see ref. 1.

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### Results and Discussion

#### Crystal and Molecular Structure of **II**

The data are consistent with the atomic arrangements shown in Fig. 1.

In the unit cell of **II**, there are two independent molecules of almost identical structure, each having a slightly distorted tetrahedral geometry about tin (Fig. 1). Atomic coordinates are listed in Table 1, bond lengths in Table 2, bond angles in Table 3 and torsional angles in Table 4. There are no intermolecular contacts  $< 4.1$  Å.

The C–Sn bond lengths are 2.06(3)–2.22(4) (Cy–Sn) and 2.10(4) ( $CH_2-Sn$ ) Å for one independent molecule and 2.13(3)–2.16(3) and 2.14(3) Å, respectively for the other. These values are within the regions normally found for alkyl–Sn bonds. The bond angles about tin vary between 105.6(13) and 113.6(12)° and 106.1(11) and 113.2(7)°.

The intramolecular tin–sulphur distances are 3.29(1) and 3.26(1) Å which are well within the sum

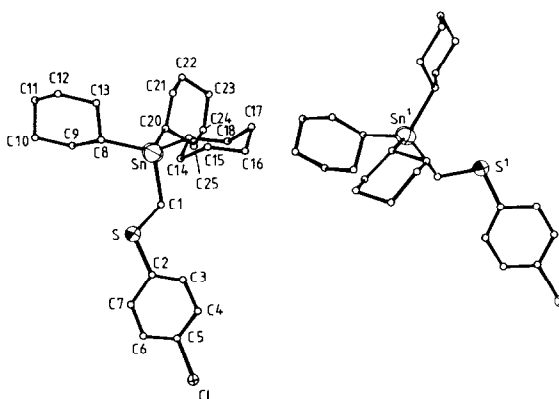


Fig. 1. Molecular structure of **II**.

TABLE 1. Fractional atomic coordinates and isotropic (or equivalent isotropic) temperature factors with e.s.d.s in parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> / <i>U</i> <sub>iso</sub> <sup>a</sup>
Sn	0.23078(12)	−0.22900	0.42758(9)	0.068(2)
Sn(′)	0.23017(12)	0.29067(43)	−0.05807(9)	0.063(2)
S(′)	0.3020(6)	0.5458(12)	−0.1591(4)	0.110(10)
S	0.2965(6)	0.0342(13)	0.5639(4)	0.110(7)
Cl(′)	0.5091(6)	1.1566(12)	−0.1395(4)	0.125(10)
Cl	0.5057(7)	0.6417(13)	0.6425(4)	0.133(10)
C(1′)	0.3122(16)	0.4725(36)	−0.0684(15)	0.09(1)
C(1)	0.3103(19)	−0.0518(46)	0.4799(19)	0.13(1)
C(2′)	0.3649(14)	0.7108(28)	−0.1485(14)	0.059(8)
C(2)	0.3615(14)	0.1999(30)	0.5823(14)	0.063(8)
C(3′)	0.4041(12)	0.7771(49)	−0.0808(11)	0.061(6)
C(3)	0.3681(14)	0.2816(57)	0.6551(13)	0.088(8)
C(4′)	0.4461(14)	0.9123(31)	−0.0779(13)	0.057(7)
C(4)	0.4119(15)	0.4105(33)	0.6724(13)	0.062(8)
C(5′)	0.4528(19)	0.9823(43)	−0.1445(18)	0.10(1)
C(5)	0.4492(17)	0.4678(38)	0.6191(16)	0.08(1)
C(6′)	0.4157(16)	0.9162(36)	−0.2139(15)	0.073(9)
C(6)	0.4457(14)	0.3967(33)	0.5511(14)	0.059(8)
C(7′)	0.3731(13)	0.7822(54)	−0.2157(12)	0.078(7)
C(7)	0.4022(13)	0.2606(42)	0.5364(12)	0.068(8)
C(8)	0.2962(16)	−0.3914(38)	0.3847(15)	0.078(9)
C(8′)	0.2961(15)	0.1162(33)	0.0168(13)	0.058(8)
C(9′)	0.3630(15)	0.1917(31)	0.0793(13)	0.076(9)
C(9)	0.3667(15)	−0.3163(32)	0.3586(14)	0.078(9)
C(10′)	0.4110(16)	0.0654(35)	0.1330(15)	0.09(1)
C(10)	0.4139(16)	−0.4330(35)	0.3238(15)	0.09(1)
C(11)	0.3641(15)	−0.5413(34)	0.2647(14)	0.075(9)
C(11′)	0.3597(17)	−0.0325(37)	0.1687(15)	0.09(1)
C(12′)	0.2978(16)	−0.1108(34)	0.1105(14)	0.087(9)
C(12)	0.3011(17)	−0.6163(37)	0.2914(16)	0.10(1)
C(13)	0.2543(17)	−0.4974(38)	0.3241(15)	0.08(1)
C(13′)	0.2463(19)	0.0127(42)	0.0521(16)	0.10(1)
C(14)	0.168(2)	−0.329(5)	0.502(2)	0.12(1)
C(14′)	0.1440(16)	0.4090(38)	−0.0104(14)	0.068(9)
C(15′)	0.115(2)	0.560(4)	−0.056(2)	0.13(1)
C(15)	0.1046(19)	−0.4372(43)	0.4608(18)	0.11(1)
C(16′)	0.054(2)	0.639(5)	−0.024(2)	0.13(1)
C(16)	0.2110(18)	−0.4222(41)	0.5684(16)	0.10(1)
C(17)	0.1686(19)	−0.5000(42)	0.6214(18)	0.13(1)
C(17′)	0.0764(17)	0.6870(36)	0.0546(14)	0.09(1)
C(18′)	0.1042(18)	0.5400(38)	0.0995(15)	0.10(1)
C(18)	0.115(2)	−0.609(4)	0.573(2)	0.12(1)
C(19)	0.054(2)	−0.504(5)	0.514(2)	0.15(2)
C(19′)	0.1706(18)	0.4461(41)	0.0711(15)	0.10(1)
C(20)	0.142(2)	−0.107(4)	0.335(2)	0.11(1)
C(20′)	0.1739(17)	0.1992(35)	−0.1700(15)	0.08(1)
C(21′)	0.0966(19)	0.1236(48)	−0.1717(18)	0.12(1)
C(21)	0.104(2)	0.017(5)	0.370(2)	0.14(1)
C(22′)	0.055(2)	0.058(5)	−0.253(2)	0.14(1)
C(22)	0.040(2)	0.098(5)	0.304(2)	0.17(2)
C(23)	0.072(2)	0.162(4)	0.247(2)	0.12(1)
C(23′)	0.1121(19)	−0.0646(45)	−0.2739(18)	0.12(1)
C(24′)	0.180(2)	0.015(5)	−0.275(2)	0.14(1)
C(24)	0.103(2)	0.034(4)	0.208(2)	0.12(1)
C(25)	0.178(2)	−0.035(5)	0.274(2)	0.15(2)
C(25′)	0.223(2)	0.075(4)	−0.196(2)	0.12(1)

<sup>a</sup>*U*<sub>eq</sub> calculated as  $\frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

TABLE 2. Bond lengths (Å) for **II** with e.s.d.s in parentheses

Sn—C(1)	2.10(4)	Sn—C(8)	2.06(3)
Sn—C(14)	2.12(4)	Sn—C(20)	2.22(4)
Sn(')—C(1')	2.14(3)	Sn(')—C(8')	2.13(3)
Sn(')—C(14')	2.16(3)	Sn(')—C(20')	2.15(3)
S(')—C(1')	1.70(3)	S(')—C(2')	1.76(3)
S—C(1)	1.74(4)	S—C(2)	1.78(3)
Cl(')—C(5')	1.76(4)	Cl—C(5)	1.76(4)
C(2')—C(3')	1.36(4)	C(2')—C(7')	1.39(4)
C(2)—C(3)	1.45(4)	C(2)—C(7)	1.32(4)
C(3')—C(4')	1.35(5)	C(3)—C(4)	1.32(5)
C(4')—C(5')	1.36(5)	C(4)—C(5)	1.38(4)
C(5')—C(6')	1.37(5)	C(5)—C(6)	1.35(4)
C(6')—C(7')	1.35(5)	C(6)—C(7)	1.37(5)
C(8)—C(9)	1.56(4)	C(8)—C(13)	1.46(5)
C(8')—C(9')	1.54(4)	C(8')—C(13')	1.48(5)
C(9')—C(10')	1.54(4)	C(9)—C(10)	1.52(4)
C(10')—C(11')	1.48(4)	C(10)—C(11)	1.50(4)
C(11)—C(12)	1.46(4)	C(11')—C(12')	1.46(4)
C(12')—C(13')	1.59(5)	C(12)—C(13)	1.50(5)
C(14)—C(15)	1.48(6)	C(14)—C(16)	1.46(5)
C(14')—C(15')	1.53(5)	C(14')—C(19')	1.45(4)
C(15')—C(16')	1.50(5)	C(15)—C(19)	1.56(5)
C(16')—C(17')	1.43(4)	C(16)—C(17)	1.50(5)
C(17)—C(18)	1.44(5)	C(17')—C(18')	1.49(5)
C(18')—C(19')	1.59(5)	C(18)—C(19)	1.58(5)
C(20)—C(21)	1.46(6)	C(20)—C(25)	1.51(5)
C(20')—C(21')	1.49(5)	C(20')—C(25')	1.51(5)
C(21')—C(22')	1.56(5)	C(21)—C(22)	1.58(6)
C(22')—C(23')	1.55(6)	C(22)—C(23)	1.40(5)
C(23)—C(24)	1.46(5)	C(23')—C(24')	1.38(5)
C(24')—C(25')	1.51(5)	C(24)—C(25)	1.64(5)

of the van der Waal's radii (4.05 Å) but much greater than the sum of the covalent radii (2.44 Å). Values for covalent Sn—S bond lengths have been reported [8], e.g. in  $\text{Ph}_3\text{SnSC}_6\text{H}_4\text{Bu}^t\text{-}p$  [8a] and  $\text{SCH}_2\text{CH}_2\text{SCH}_2\text{SSnSCH}_2\text{CH}_2\text{SCH}_2\text{S}$  (**III**) [8b], values obtained were 2.413(3) and 2.42 Å, respectively. The intramolecular Sn...S distances in  $\text{ClPh}_2\text{SnCH}_2\text{CH}_2\text{-CH}_2\text{SC}_6\text{H}_4\text{Me-}p$  (**IV**) [9a],  $(\text{ClMe}_2\text{SnCH}_2\text{CH}_2\text{CH}_2)_2\text{S}$  (**V**) [9b] and **III** [8b] were found to be 3.195(4), 3.079(4)–3.118(4) and 3.13 Å, respectively; these values are only 0.1–0.2 Å less than the Sn—S distances found in **II**.

In compounds **IV** and **V**, the geometry about tin provides clear evidence for Sn...S intramolecular associations. The small values for the S...Sn—C<sub>1</sub> angles (28.0(10) and 28.2(8)°) do not provide any support for Sn...S interaction in **II**; the average bond angles about tin are those expected for tetrahedral tin, however there are no obvious factors for the slight opening of some C—Sn—C bond angles (Table 3). 'Normal' Sn—C and S—C bond lengths coupled with 'typical' C—S—C bond angles will, of necessity, place the tin and sulphur atoms *c.* 3.1–3.4 Å apart.

The cyclohexyl rings adopt chair conformations with the tin atom occupying the equatorial positions as shown by the torsional angles (Table 4).

The bond angles at sulphur in **II** are 105.4(15) and 105.7(14)° with the S—C bond lengths being 1.74(4) and 1.70(3) (Sn—C<sub>alkyl</sub>) and 1.76(3) and 1.78(3) (Sn—C<sub>aryl</sub>) Å. For comparison, the S—C bond lengths in pentacoordinate **IV** were found to be 1.749(17) (S—C<sub>alkyl</sub>) and 1.799(13) (S—C<sub>aryl</sub>) Å: relevant data for  $\text{Ph}_3\text{SnOCOC}_6\text{H}_4\text{SCH}_3\text{-}p$  (**VI**) are S—C bond lengths 1.799(5) (S—C<sub>alkyl</sub>) and 1.762(3) (S—C<sub>aryl</sub>) Å with the C—S—C bond angle = 104.2(2)° [10]. It is of interest to note that in **IV** in which there is S—Sn coordination, S—C<sub>alkyl</sub> is slightly shorter than S—C<sub>aryl</sub>, whereas in **VI** in which there is no S...C interaction (and in  $\text{CH}_3\text{SPh}$  in the gas phase [11]) the reverse is found.

The gas-phase, electron diffraction study of  $\text{CH}_3\text{SPh}$  indicated S—C<sub>alkyl</sub> and S—C<sub>aryl</sub> bond lengths of 1.803(13) and 1.749(12) Å with a CSC bond angle of 105.6(2)° [11]. Of interest, the alkyl-carbon in gaseous  $\text{CH}_3\text{SPh}$  was calculated to be out of the plane containing the phenyl ring and the S atom, the dihedral angle in  $\text{CH}_3\text{SPh}$  being 45(10)°. (In **II**, the S, C<sub>1</sub> and Sn atoms are all out of the plane of the aryl ring.) The structure of  $\text{CH}_3\text{SPh}$  was also investigated in the liquid state using dipole moments and birefringence in a electric field [11, 12], the dihedral angle being calculated to be between 23–40°.

From photoelectron spectral (and also theoretical) studies on alkyl aryl sulphides, indications have been found [13] for two rotamers; (i) a planar form with the C<sub>alkyl</sub> in the plane containing the aryl ring and the S atom and (ii) a perpendicular form in which the C<sub>alkyl</sub> is out of this plane. Greater steric hindrance by R and RSAr leads to a greater proportion of the less-conjugated conformer (the perpendicular form) [14]. Compound **II** in the solid clearly does not exist in the 'planar' form, and neither does **VI**.

#### Interaction with $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ or $\text{I}_2$

Tetracyanoethylene (a  $\pi$ -acceptor) forms charge-transfer complexes with arenes, including aryl sulphides [15–18]. Values for  $\lambda_{\text{max}}$  for complexes with alkyl aryl sulphides and with  $\text{Ph}_3\text{SnCH}_2\text{SAr}$  compounds [2] have been reported. The  $\lambda_{\text{max}}$  value for the TCNE complex with **II** is listed in Table 5, along with values for related species. Substitution of H by  $\text{R}_3\text{Sn}$  in  $\text{CH}_3\text{SC}_6\text{H}_4\text{Cl-}p$  leads to longer wavelength absorptions for the charge-transfer complexes with TCNE, due to the increasing electron release by the  $\text{R}_3\text{Sn}$  groups. Of interest, the  $\text{Cy}_3\text{Sn}$  group appears a stronger electron releasing group than is  $\text{Ph}_3\text{Sn}$ . The ionization potential of **II** was calculated from the empirical equation, eqn. (1).

$$(1/\lambda_{\text{max}}) (\text{cm}^{-1}) = 7331 IP - 41\,830 \quad (1)$$

Iodine (a  $\sigma$ -acceptor) also forms complexes with sulphides [18, 21, 22]. A deep yellow–brown colouration ( $\lambda_{\text{max}} \sim 355$  nm) developed on addition

TABLE 3. Valency angles (°) for **II** with e.s.d.s in parentheses

C(1)–Sn–C(8)	105.6(13)	C(1)–Sn–C(14)	113.4(14)
C(1)–Sn–C(20)	105.6(14)	C(8)–Sn–C(14)	113.6(14)
C(8)–Sn–C(20)	112.7(12)	C(14)–Sn–C(20)	105.9(14)
C(1')–Sn(')–C(8')	106.1(11)	C(1')–Sn(')–C(14')	104.9(12)
C(1')–Sn(')–C(20')	109.8(11)	C(8')–Sn(')–C(14')	113.2(10)
C(8')–Sn(')–C(20')	113.1(11)	C(14')–Sn(')–C(20')	109.3(11)
C(1')–S(')–C(2')	105.7(14)	C(1)–S–C(2)	105.4(15)
Sn(')–C(1')–S(')	115.4(15)	Sn–C(1)–S	117.5(18)
S(')–C(2')–C(3')	126.0(21)	S(')–C(2')–C(7')	116.7(21)
C(3')–C(2')–C(7')	117.3(26)	S–C(2)–C(3)	116.2(21)
S–C(2)–C(7)	127.6(21)	C(3)–C(2)–C(7)	116.2(26)
C(2')–C(3')–C(4')	122.2(24)	C(2)–C(3)–C(4)	120.8(24)
C(3')–C(4')–C(5')	119.7(24)	C(3)–C(4)–C(5)	118.4(24)
Cl(')–C(5')–C(4')	119.1(24)	Cl(')–C(5')–C(6')	121.3(25)
C(4')–C(5')–C(6')	119.6(30)	Cl–C(5)–C(4)	117.7(22)
Cl–C(5)–C(6)	118.9(23)	C(4)–C(5)–C(6)	123.4(28)
C(5')–C(6')–C(7')	119.8(26)	C(5)–C(6)–C(7)	116.4(24)
C(2')–C(7')–C(6')	121.3(25)	C(2)–C(7)–C(6)	124.7(25)
Sn–C(8)–C(9)	113.6(20)	Sn–C(8)–C(13)	117.5(20)
C(9)–C(8)–C(13)	108.4(22)	Sn(')–C(8')–C(9')	111.6(18)
Sn(')–C(8')–C(13')	112.9(19)	C(9')–C(8')–C(13')	110.9(20)
C(8')–C(9')–C(10')	111.6(22)	C(8)–C(9)–C(10)	114.6(23)
C(9')–C(10')–C(11')	111.0(23)	C(9)–C(10)–C(11)	113.6(22)
C(10)–C(11)–C(12)	112.9(22)	C(10')–C(11')–C(12')	111.6(22)
C(11')–C(12')–C(13')	111.9(25)	C(11)–C(12)–C(13)	111.9(26)
C(8)–C(13)–C(12)	118.4(25)	C(8')–C(13')–C(12')	111.5(24)
Sn–C(14)–C(15)	111.7(22)	Sn–C(14)–C(16)	118.4(24)
C(15)–C(14)–C(16)	104.6(31)	Sn(')–C(14')–C(15')	110.1(19)
Sn(')–C(14')–C(19')	114.6(20)	C(15')–C(14')–C(19')	109.8(27)
C(14')–C(15')–C(16')	110.1(27)	C(14)–C(15)–C(19)	112.3(28)
C(15')–C(16')–C(17')	117.1(28)	C(14)–C(16)–C(17)	120.4(29)
C(16)–C(17)–C(18)	104.8(26)	C(16')–C(17')–C(18')	105.9(27)
C(17')–C(18')–C(19')	114.0(24)	C(17)–C(18)–C(19)	106.0(30)
C(15)–C(19)–C(18)	102.9(26)	C(14')–C(19')–C(18')	110.5(24)
Sn–C(20)–C(21)	108.8(21)	Sn–C(20)–C(25)	112.4(24)
C(21)–C(20)–C(25)	110.1(32)	Sn(')–C(20')–C(21')	112.2(19)
Sn(')–C(20')–C(25')	111.9(19)	C(21')–C(20')–C(25')	106.9(27)
C(20')–C(21')–C(22')	112.4(26)	C(20)–C(21)–C(22)	107.5(29)
C(21')–C(22')–C(23')	106.5(27)	C(21)–C(22)–C(23)	111.8(31)
C(22)–C(23)–C(24)	108.8(32)	C(22')–C(23')–C(24')	107.1(32)
C(23')–C(24')–C(25')	113.0(29)	C(23)–C(24)–C(25)	104.3(26)
C(20)–C(25)–C(24)	105.0(28)	C(20')–C(25')–C(24')	109.3(27)

of  $I_2$  to **II** in  $CH_2Cl_2$  solution; in comparison, the value of  $\lambda_{max}$  for the  $I_2CH_3SC_6H_4Cl-p$  complex in a non-polar solvent is 337 nm [22]. The complex between  $I_2$  and **II** is not stable, reaction occurs readily to give  $Cy_3SnI$  and  $ICH_2SC_6H_4Cl-p$  (**VII**). The product **VII** ( $\delta CH_2 = 4.46$  ppm) on standing in the reaction solution is slowly converted to  $CH_2(SC_6H_4Cl-p)_2$  ( $\delta CH_2 = 4.18$  ppm). From a competitive reaction between **II** and  $Cy_3SnCH_2SeC_6H_4Cl-p$  for a deficit of iodine in  $CCl_4$ ,  $Cy_3SnCH_2SeC_6H_4Cl-p$  was found to be 3.2 times more reactive than **II**. This was based on relative yields of the two products,  $ICH_2SeC_6H_4Cl-p$  and  $ICH_2SC_6H_4Cl-p$ . The relative reactivities of those tin compounds follows the donor abilities of S and Se, for example the formation

constants for complexes  $CH_3SeC_6H_4Cl-p:I_2$  and  $CH_3SC_6H_4Cl-p:I_2$  at 25 °C in heptane were calculated to be 29 and 4.3 l/mole, respectively [18b].

During the course of the reaction between **II** and  $I_2$ ,  $\delta H$   $CH_2$  shifted to 2.21 (from 2.07); a shift in  $\delta H$  for  $CH_3$  in  $CH_3SPh$  has also been reported to occur on complexation with  $I_2$  (to 2.53 from 2.46 ppm) [18b].

#### Other Reactions

A number of reactions of **I** ( $R = \text{aryl}$ ,  $R^1 = \text{Ph}$ ) with electrophiles and oxidants have been previously reported; reaction occurred at both or either of the different carbon–tin bonds present in **I** as well as at the sulphur atom [2–7]. Cyclohexyl–tin bonds are

TABLE 4. Selected torsional angles

Molecule 1			Molecule 2		
(1)	C(8)–C(9)–C(10)–C(11)	47.0(24)	(1)	C(8')–C(9')–C(10')–C(11')	–56.0(24)
(2)	C(13)–C(8)–C(9)–C(10)	–47.1(25)	(2)	C(9')–C(10')–C(11')–C(12')	58.0(25)
(3)	C(9)–C(8)–C(13)–C(12)	49.0(26)	(3)	C(10')–C(11')–C(12')–C(13')	–56.2(26)
(4)	C(11)–C(12)–C(13)–C(8)	–53.8(28)	(4)	C(11')–C(12')–C(13')–C(8')	53.7(26)
(5)	C(10)–C(11)–C(12)–C(13)	50.4(26)	(5)	C(9')–C(8')–C(13')–C(12')	–51.3(24)
(6)	C(9)–C(10)–C(11)–C(12)	–49.5(25)	(6)	C(13')–C(8')–C(9')–C(10')	53.6(24)
(1)	C(14)–C(16)–C(17)–C(18)	61.2(32)	(1)	C(14')–C(15')–C(16')–C(17')	59.5(29)
(2)	C(16)–C(17)–C(18)–C(19)	–65.6(29)	(2)	C(15')–C(16')–C(17')–C(18')	–57.5(31)
(3)	C(17)–C(18)–C(19)–C(15)	70.5(30)	(3)	C(16')–C(17')–C(18')–C(19')	53.5(28)
(4)	C(14)–C(15)–C(19)–C(18)	–65.4(30)	(4)	C(17')–C(18')–C(19')–C(14')	–55.4(25)
(5)	C(16)–C(14)–C(15)–C(19)	54.3(29)	(5)	C(15')–C(14')–C(19')–C(18')	52.8(23)
(6)	C(15)–C(14)–C(16)–C(17)	–52.8(30)	(6)	C(19')–C(14')–C(15')–C(16')	–54.9(26)
(1)	C(20)–C(21)–C(22)–C(23)	–58.5(34)	(1)	C(20')–C(21')–C(22')–C(23')	58.9(30)
(2)	C(21)–C(22)–C(23)–C(24)	65.9(33)	(2)	C(21')–C(22')–C(23')–C(24')	–60.4(32)
(3)	C(22)–C(23)–C(24)–C(25)	–68.4(32)	(3)	C(22')–C(23')–C(24')–C(25')	65.7(32)
(4)	C(23)–C(24)–C(25)–C(20)	66.2(31)	(4)	C(23')–C(24')–C(25')–C(20')	–65.1(33)
(5)	C(21)–C(20)–C(25)–C(24)	–63.5(31)	(5)	C(21')–C(20')–C(25')–C(24')	56.3(29)
(6)	C(20)–C(25)–C(24)–C(23)	66.2(31)	(6)	C(25')–C(20')–C(24')–C(22')	–57.4(29)
Sn–C(8)–C(9)–C(10)	–177.7(29)		Sn'–C(8')–C(9')–C(10')	–179.6(26)	
Sn–C(8)–C(13)–C(12)	179.5(35)		Sn'–C(8')–C(13')–C(12')	–177.4(29)	
Sn–C(14)–C(15)–C(19)	–176.5(33)		Sn'–C(14')–C(19')–C(18')	177.4(25)	
Sn–C(14)–C(16)–C(17)	–177.9(36)		Sn'–C(14')–C(15')–C(16')	178.5(28)	
Sn–C(20)–C(25)–C(24)	175.0(33)		Sn'–C(20')–C(25')–C(24')	179.5(32)	
Sn–C(20)–C(21)–C(22)	–178.9(34)		Sn'–C(20')–C(21')–C(22')	179.6(34)	

TABLE 5. Charge-transfer absorption maxima for (NC)<sub>2</sub>C=C(CN)<sub>2</sub> complexes in CH<sub>2</sub>Cl<sub>2</sub> solution

Compound	$\lambda_{\max}$ (nm)	$I_p$ <sup>a</sup>
CH <sub>3</sub> SPh	572 <sup>b</sup>	8.10 <sup>c</sup> , 8.07 <sup>d</sup>
CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	572 <sup>b</sup>	8.09 <sup>c</sup> , 8.07 <sup>d</sup>
Ph <sub>3</sub> SnCH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	598 <sup>b</sup>	7.99 <sup>b</sup>
Cy <sub>3</sub> SnCH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	621 <sup>e</sup>	7.90 <sup>e</sup>
Cy <sub>3</sub> SnCH <sub>2</sub> SeC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	641 <sup>f</sup>	7.83 <sup>f</sup>

<sup>a</sup> Ionization potentials, either directly measured or calculated from  $(\lambda_{\max})^{-1} = 7331 I_p - 41\,830$ . <sup>b</sup> Ref. 2. <sup>c</sup> Ref. 17. <sup>d</sup> Ref. 19. <sup>e</sup> This study. <sup>f</sup> Ref. 20.

less prone to cleavage than are phenyl–tin bonds and it was considered that any reaction of **II** would involve the Sn–CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* moiety. This has been borne out, as shown by the results listed in Table 6. Thus **II** appears to be a good transfer agent of the CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* group.

The reaction of **II** with *N*-bromosuccinimide (NBS) produced BrCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* (**VIII**). Reactions of NBS with organotin compounds have been previously reported [25]; with aryl–tin species, electrophilic aromatic substitutions are said to occur, in contrast to the free-radical reactions with alkyl–tin compounds. A further possibility with **II** is an initial

electrophilic attack by NBS at S (Scheme 1). An additional product detected in the NBS reaction was CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* ( $\delta CH_3$  2.43). Ylides (similar to **IX**) have also been postulated to occur in reactions of **I** (R = Me, R<sup>1</sup> = Bu) with MeI [7] and of **I** (R = Ar, R<sup>1</sup> = Ph) with *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCl [2].

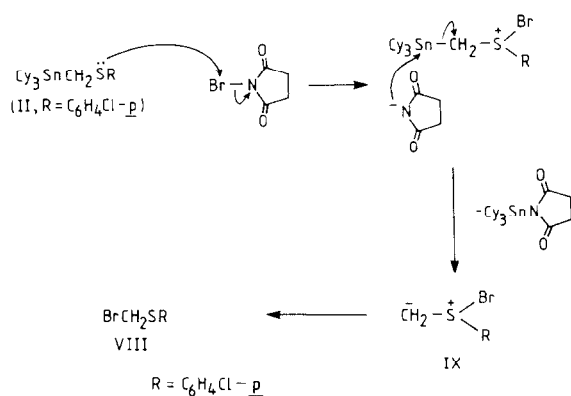
Reaction of the Me<sub>3</sub>Si analogue of **II**, viz. Me<sub>3</sub>SiCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* (**X**), with NBS in CCl<sub>4</sub> at 0 °C was recently reported to provide **VIII** but only in the presence of a strong acid, such as CF<sub>3</sub>SO<sub>3</sub>H or CF<sub>3</sub>CO<sub>2</sub>H [26, 27]. (In the absence of a strong acid, the product obtained was Me<sub>3</sub>SiCHXSC<sub>6</sub>H<sub>4</sub>Cl-*p* (**XI**, X = Br).) *N*-Chlorosuccinimide (NCS) reacted similarly with **X**. The role of the strong acid in the reaction between (**X**) and the *N*-halosuccinimide (NXS) was to protonate NXS and to provide a more reactive species. Carbon–tin bonds are considerably more reactive than are carbon–silicon bonds; clearly the Sn–CH<sub>2</sub>(SC<sub>6</sub>H<sub>4</sub>Cl-*p*) bond is sufficiently reactive to be cleaved by NBS alone. Ishibashi *et al.* considered a similar mechanism to Scheme 1 for reaction of **X** with protonated NXS [26, 27].

Strong acids, such as CF<sub>3</sub>CO<sub>2</sub>H, readily cleave **II** to give CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p*; in contrast **XI** (X = Cl) is inert to CF<sub>3</sub>CO<sub>2</sub>H.

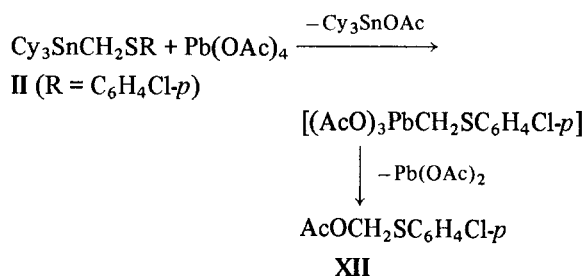
The reaction of **II** with Pb(OAc)<sub>4</sub> provides AcOCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* (**XII**), probably via labile (AcO)<sub>3</sub>–PbCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* (Scheme 2). Alkyl–lead triacetates

TABLE 6. Products of equimolar reactions (0.15–0.25 M) of II

Reagent	Conditions	Products	
		Sulphur-containing products	Others
I <sub>2</sub>	CCl <sub>4</sub> /4 d r.t.	ICH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>a</sup> [ $\delta$ H: 4.46(s, 2H, CH <sub>2</sub> ), 7.34(brs, 4H, C <sub>6</sub> H <sub>4</sub> )]	Cy <sub>3</sub> SnI [ $\delta$ H: 1.20–2.00(m)]; $\delta$ <sup>119</sup> Sn + 65.6
Br <sub>2</sub>	CCl <sub>4</sub> /2 d r.t.	BrCH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>b</sup> [ $\delta$ H: 4.72(s, 2H, CH <sub>2</sub> ), 7.32(d, 2H), 7.41(d, 2H) aryl]	Cy <sub>3</sub> SnBr [ $\delta$ H: 1.10–2.00(m)]
NBS	CD <sub>2</sub> Cl <sub>2</sub> r.t.	BrCH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>b</sup> (95%) [ $\delta$ H: 4.81(s, 2H, CH <sub>2</sub> ), 7.35(d, 2H), 7.41(d, 2H) aryl] CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> ( $\delta$ CH <sub>3</sub> 2.43) (5%)	Cy <sub>3</sub> SnNCOCH <sub>2</sub> CH <sub>2</sub> CO [ $\delta$ H: 1.20–2.00(m, 33H, Cy), 2.60(s, 4H, CH <sub>2</sub> )]
Pb(OAc) <sub>4</sub>	CDCl <sub>3</sub> /5 d r.t.	AcOCH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>c</sup> [ $\delta$ H: 2.02(s, 3H, CH <sub>3</sub> ), 5.36(s, 2H, CH <sub>2</sub> ), 7.38(d, 2H), 7.48(d, 2H) aryl]	Cy <sub>3</sub> SnOAc [ $\delta$ H: 1.20–2.00(m, 33H, Cy); 2.07(s, 3H, CH <sub>3</sub> )] Pb(OAc) <sub>2</sub> [ $\delta$ H: 2.07(s)]
CF <sub>3</sub> CO <sub>2</sub> H (excess)	CCl <sub>4</sub> /r.t.	CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>d</sup> [ $\delta$ H: 2.40(s, 3H, CH <sub>3</sub> ), 7.12(d, 2H), 7.20(d, 2H) aryl]	Cy <sub>3</sub> SnO <sub>2</sub> CCF <sub>3</sub> [ $\delta$ H: 1.20–2.0(m)]
MeI (5-fold excess)	CCl <sub>4</sub> /reflux	CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>e, d</sup> [ $\delta$ H: 2.39(s, 3H, CH <sub>3</sub> )]	
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> /CO·O·OH	CCl <sub>4</sub> /r.t.	CH <sub>3</sub> S(O)C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>f</sup> (80%) [ $\delta$ H: 2.72(s, 3H, CH <sub>3</sub> ), 7.47(d, 2H), 7.62(d, 2H) aryl] Cy <sub>3</sub> SnCH <sub>2</sub> S(O)C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (20%) [ $\delta$ H CH <sub>2</sub> 2.57 J <sup>119</sup> Sn– <sup>1</sup> H 30 Hz] <sup>g</sup>	Cy <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Cl- <i>m</i> [ $\delta$ H: 1.20–2.00(m)] <sup>g</sup>
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> /CO·O·OH	CD <sub>2</sub> Cl <sub>2</sub> /r.t.	CH <sub>3</sub> S(O)C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> <sup>f</sup> (62%) [ $\delta$ CH <sub>2</sub> : 2.73] Cy <sub>3</sub> SnCH <sub>2</sub> S(O)C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (26%) [ $\delta$ CH <sub>2</sub> 2.58 J <sup>119</sup> Sn– <sup>1</sup> H 33 Hz] <sup>g</sup> <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (12%) [ $\delta$ CH <sub>2</sub> 5.72] <sup>g</sup>	Cy <sub>3</sub> SnO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Cl- <i>m</i> [ $\delta$ H: 1.20–2.10(m)] <sup>g</sup>
Cl <sub>2</sub> Pt(COD)	CD <sub>2</sub> Cl <sub>2</sub> /7 d r.t.	no reaction	

<sup>a</sup>Literature value  $\delta$ CH<sub>2</sub> = 4.46 for ICH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p* [5].<sup>b</sup>Literature value  $\delta$ CH<sub>2</sub> = 4.67 for BrCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* in CCl<sub>4</sub> [5].<sup>c</sup>Literature values for CF<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* [ $\delta$ H 5.53(2H, s, CH<sub>2</sub>) 7.32(4H, s)] [27]. <sup>d</sup>Literature value for CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>Cl-*p* [ $\delta$ CH<sub>3</sub> 2.43] [23]. <sup>e</sup>Only partial reaction (25% yield). <sup>f</sup>Literature value for CH<sub>3</sub>S(O)Ph in CDCl<sub>3</sub> [ $\delta$ CH<sub>3</sub> 2.73] [24]. <sup>g</sup>Aryl absorptions not resolved.

Scheme 1.



Scheme 2.

have been reported to be unisolatable [28]. Exchange reactions of Pb(OAc)<sub>4</sub> with organotin species have been used to generate vinyl-, aryl- and heteroaryl-

lead triacetates [29]. These particular organolead derivatives are more thermally stable than are the alkyl analogues; Pinhey and co-workers used them *in situ* to arylate and to vinylate  $\beta$ -diketones. Attempts to use the combination  $\text{Pb}(\text{OAc})_4$  and **II** in this study to alkylate 2-methylcyclohexa-1,3-dione (**XIII**) failed; the only sulphur-containing product isolated was **XII**, with **XIII** being completely recovered.

Ishibashi *et al.* reported the formation of  $\text{CF}_3\text{CO}_2\text{-CH}_2\text{SC}_6\text{H}_4\text{Cl-}p$  [ $\delta\text{H}$ : 5.53(2H, s,  $\text{CH}_2$ ) and 7.32(4H, s, aryl)] from  $\text{Me}_3\text{SiCH}_2\text{S}(\text{O})\text{C}_6\text{H}_4\text{Cl-}p$  and  $(\text{CF}_3\text{-CO})_2\text{O}$  or  $\text{CF}_3\text{CO}_2\text{H}$ . Other routes to  $\alpha$ -acyloxyalkyl sulphides,  $\text{RCO}_2\text{CH}_2\text{SAr}$ , include (i) the anionic oxidation of  $\text{Me}_3\text{SiCH}_2\text{SAr}$  [30] or  $\text{CH}_3\text{SAr}$  in  $\text{HOAc}$  [31], (ii)  $\text{PhCO}\cdot\text{O}\cdot\text{OBu}^t$  oxidation of  $\text{CH}_3\text{SAr}$  [32] and (iii) the reaction of  $\text{CH}_3\text{S}(\text{O})\text{Ar}$  with  $(\text{RCO})_2\text{O}$  (the Pummerer reaction) [33].

Reaction of  $m\text{-ClC}_6\text{H}_4\text{CO}\cdot\text{O}\cdot\text{OH}$  with **II** in  $\text{CCl}_4$  provides mainly  $\text{CH}_3\text{S}(\text{O})\text{C}_6\text{H}_4\text{Cl-}p$  ( $\delta\text{CH}_3$  2.70) and a little  $\text{Cy}_3\text{SnCH}_2\text{S}(\text{O})\text{C}_6\text{H}_4\text{Cl-}p$  ( $\delta\text{CH}_2$  2.55,  $J^{119}\text{Sn-}^1\text{H}$  33 Hz) (in a ratio of c. 5:1). The latter compound was not isolated but could be detected in solution. When the reaction was performed in  $\text{CD}_2\text{Cl}_2$ , an additional product was  $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{CH}_2\text{SC}_6\text{H}_4\text{Cl-}p$  ( $\delta\text{CH}_2$  5.61).

## Experimental

Melting points (m.p.) were measured on a Kofler hotstage and are uncorrected.  $^1\text{H}$  NMR spectra were obtained on a Perkin-Elmer R34 (220 MHz) spectrometer and  $^{119}\text{Sn}$  NMR spectra on a Jeol FX90 instrument;  $\delta$   $^{119}\text{Sn}$  relative to  $\text{Me}_4\text{Sn}$ .

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer. Mass spectra were obtained using an AEI MS 30 spectrometer,  $M$  of tin-containing peaks was based on  $^{120}\text{Sn}$  and of chlorine containing peaks on  $^{35}\text{Cl}$ .

The compound,  $\text{Cy}_3\text{SnCH}_2\text{I}$ , was obtained from  $\text{Cy}_3\text{SnCl}$ ,  $\text{CH}_2\text{I}_2$  and a zinc-copper couple by a published procedure [34]. The compound  $\text{Cy}_3\text{SnCH}_2\text{SC}_6\text{H}_4\text{Cl-}p$  was prepared from  $\text{Cy}_3\text{SnCH}_2\text{I}$  and  $\text{NaSC}_6\text{H}_4\text{Cl-}p$  in  $\text{EtOH}$  solution.  $\text{Cy}_3\text{SnCH}_2\text{SC}_6\text{H}_4\text{Cl-}p$ , m.p. 56–58 °C. *Anal.* Found: C, 57.2; H, 7.4. Calc. for  $\text{C}_{25}\text{H}_{39}\text{ClSSn}$ : C, 57.1; H, 7.4%.  $\delta\text{H}$  ( $\text{CCl}_4$ ; 220 MHz): 1.10–2.00 (m, 33H, Cy), 2.10 (s, 2H,  $J^{119}\text{Sn-}^1\text{H}$  40 Hz,  $\text{CH}_2$ ); 7.16 (s, br, 4H, aryl).  $\delta^{119}\text{Sn}$  ( $\text{CDCl}_3$ ), 67.8 ppm.  $m/z$  (20 eV) (%), fragment): 526(1,  $M$ ), 443(100,  $M - \text{Cy}^+$ ), 369(20,  $\text{Cy}_3\text{Sn}^+$ ). Mössbauer spectrum:  $IS$   $\delta$  1.41 mm  $\text{s}^{-1}$  (relative to  $\text{BaSnO}_3$ ), 1.68 mm  $\text{s}^{-1}$  at 77 K.

Compounds  $\text{Cy}_3\text{SnCH}_2\text{SeC}_6\text{H}_4\text{Cl-}p$  [20] and dichloro(cycloocta-1,5-diene)platinum [35] were samples obtained in other studies. All other reagents were purified commercial samples.

## Reactions of II

Equimolar solutions of **II** and the reagent were mixed at room temperature. The progress of the reaction were monitored by  $^1\text{H}$  NMR spectroscopy. Data are given in Table 5.

Interactions with  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$  were carried out as previously described [2].

### Competitive reaction between II and

#### $\text{Cy}_3\text{SnCH}_2\text{SeC}_6\text{H}_4\text{Cl-}p$

To a solution of **II** (0.0375 g,  $7.28 \times 10^{-5}$  mol) and  $\text{Cy}_3\text{SnCH}_2\text{SeC}_6\text{H}_4\text{Cl-}p$  (0.0266 g,  $4.65 \times 10^{-5}$  mol) in  $\text{CDCl}_3$  (1 ml), was added  $\text{I}_2$  (0.0089 g,  $3.51 \times 10^{-5}$  mol). The solution was left until colourless; the relative yields of  $\text{ICH}_2\text{SeC}_6\text{H}_4\text{Cl-}p$  ( $\delta\text{CH}_2$  4.25) and  $\text{ICH}_2\text{SC}_6\text{H}_4\text{Cl-}p$  ( $\delta\text{CH}_2$  4.50) were estimated by  $^1\text{H}$  NMR to be 2.1:1.

## Crystal Structure Determination of II

### Crystal data

$\text{C}_{25}\text{H}_{39}\text{ClSSn}$ ,  $M = 515.19$  monoclinic, space group  $P2_1$ ,  $a = 17.577(24)$ ,  $b = 8.427(10)$ ,  $c = 17.915(19)$  Å,  $\beta = 104.5(10)^\circ$ ,  $V = 2569(5)$  Å<sup>3</sup>,  $Z = 4$  (two independent molecules in the asymmetric unit),  $D_c = 1.36$  g  $\text{cm}^{-3}$ ,  $D_m = 1.32$  g  $\text{cm}^{-3}$ ,  $F(000) = 1088$ ,  $T =$  room temperature.

### Data collection and processing

A colourless crystal of approximate dimensions  $1.0 \times 0.17 \times 0.17$  mm was used for data collection. The cell dimensions were obtained from setting angles of 14 independent reflexions with  $16 < 2\theta < 21$  on a Nicolet P<sub>3</sub> automated diffractometer using monochromated  $\text{Mo K}\alpha$  radiation. A total of 3992 unique intensities was measured with  $\theta < 50^\circ$  as  $\theta$ - $2\theta$  scans. A total of 2314 reflexions had  $F > 6(F)$ . Range of  $hkl$ :  $0 \leq h \leq 20$ ,  $0 \leq k \leq 9$ ,  $-20 \leq l \leq 20$ . Corrections were made for Lorentz and polarization effects, but no corrections were applied for absorption. Two reference reflexions, monitored periodically, showed no significant variation in intensity.

### Structure analysis and refinement

The approximate position of the tin atoms were calculated using a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located from successive difference Fourier maps using SHELX 76. All hydrogen atoms were located, but given ideal geometry. Atomic scattering factors were obtained from SHELX 76 [36] and the weighting scheme adopted was  $w = 2.1647/\sigma^2(F_o)$ . Due to the large number of refinable parameters, refinement of the parameters of each crystallographically independent molecule was attempted separately and alternatively. Limitation of core memory precluded full matrix refinement on the entire structure though, and only tin, sulphur and chlorine atoms were given

anisotropic temperature factors. The final  $R$  and  $R_w$  values were 0.0590 and 0.0475, respectively, and the largest parameter shift/standard deviation was 0.005. Final  $\Delta\rho_{\max} = 0.20$  and  $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$ . Molecular geometries were generated by the GX package [37] the final positional parameters are given in Table 1, bond distances, Table 2, and angles in Table 3. The coordination about tin together with atomic labelling is shown in Fig. 1.

## Supplementary Material

Additional material, deposited with the Cambridge Crystallographic Data Centre, comprises lists of anisotropic thermal parameters, H atom positions and torsional angles.

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