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Sulphur Substituted Organotin Compounds
Part 9*. Crystal and Molecular Structure and Reactions of [(*p*-Chlorophenylthio)methyl] tricyclohexylstannane

PHILIP J. COX

School of Pharmacy, Robert Gordon's Institute of Technology, Schoolhill, Aberdeen AB1 1FR, Scotland (U.K.)

SOLANGE M. S. V. DOIDGE-HARRISON, IAN W. NOWELL

School of Applied Sciences, Robert Gordon's Institute of Technology, St. Andrews Street, Aberdeen AB1 1HG, Scotland (U.K.)

R. ALAN HOWIE, ANDREW P. RANDALL and JAMES L. WARDELL**

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland (U.K.)

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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

α-(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.

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

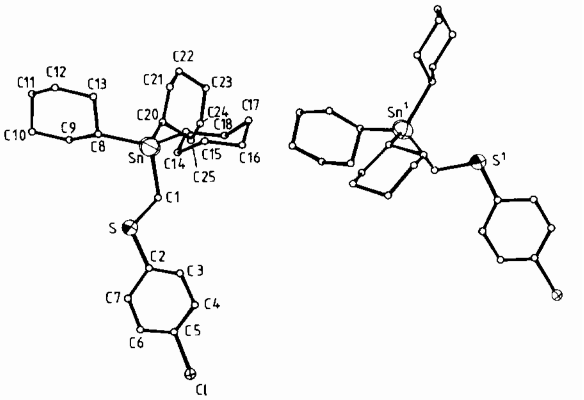

Fig. 1. Molecular structure of II.

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*For Part 8, see ref. 1.

**Author to whom correspondence should be addressed.

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

	x/a	y/b	z/c	U_{eq}/U_{iso} [a]
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)

[a] U_{eq} calculated as $\frac{1}{3}\Sigma\Sigma U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

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 $Ph_3SnSC_6H_4Bu^t$-*p* [8a] and $SCH_2CH_2SCH_2SSnSCH_2CH_2SCH_2S$ (**III**) [8b], values obtained were 2.413(3) and 2.42 Å, respectively. The intramolecular Sn---S distances in $ClPh_2SnCH_2CH_2CH_2SC_6H_4Me$-*p* (**IV**) [9a], $(ClMe_2SnCH_2CH_2CH_2)_2S$ (**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_1 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_{alkyl}) and 1.76(3) and 1.78(3) (Sn–C_{aryl}) Å. For comparison, the S–C bond lengths in pentacoordinate **IV** were found to be 1.749(17) (S–C_{alkyl}) and 1.799(13) (S–C_{aryl}) Å: relevant data for $Ph_3SnOCOC_6H_4SCH_3$-*p* (**VI**) are S–C bond lengths 1.799(5) (S–C_{alkyl}) and 1.762(3) (S–C_{aryl}) 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_{alkyl} is slightly shorter than S–C_{aryl}, whereas in **VI** in which there is no S...C interaction (and in CH_3SPh in the gas phase [11]) the reverse is found.

The gas-phase, electron diffraction study of CH_3SPh indicated S–C_{alkyl} and S–C_{aryl} 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 CH_3SPh was calculated to be out of the plane containing the phenyl ring and the S atom, the dihedral angle in CH_3SPh being 45(10)°. (In **II**, the S, C_1 and Sn atoms are all out of the plane of the aryl ring.) The structure of CH_3SPh 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_{alkyl} in the plane containing the aryl ring and the S atom and (ii) a perpendicular form in which the C_{alkyl} 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 $(NC)_2C{=}C(CN)_2$ or I_2

Tetracyanoethylene (a π-acceptor) forms charge-transfer complexes with arenes, including aryl sulphides [15–18]. Values for λ_{max} for complexes with alkyl aryl sulphides and with Ph_3SnCH_2SAr compounds [2] have been reported. The λ_{max} value for the TCNE complex with **II** is listed in Table 5, along with values for related species. Substitution of H by R_3Sn in $CH_3SC_6H_4Cl$-*p* leads to longer wavelength absorptions for the charge-transfer complexes with TCNE, due to the increasing electron release by the R_3Sn groups. Of interest, the Cy_3Sn group appears a stronger electron releasing group than is Ph_3Sn. The ionization potential of **II** was calculated from the empirical equation, eqn. (1).

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

Iodine (a σ-acceptor) also forms complexes with sulphides [18, 21, 22]. A deep yellow–brown colouration ($\lambda_{max} \sim 355$ 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(22)	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 λ_{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 $CH_2(SC_6H_4Cl\text{-}p)_2$ ($\delta CH_2 = 4.18$ 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 $CH_3SeC_6H_4Cl\text{-}p{:}I_2$ and $CH_3SC_6H_4Cl\text{-}p{:}I_2$ 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, δH CH_2 shifted to 2.21 (from 2.07); a shift in δH 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 = aryl, $R^1 = Ph$) 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 $(NC)_2C{=}C(CN)_2$ complexes in CH_2Cl_2 solution

Compound	λ_{max} (nm)	*Ip* [a]
CH_3SPh	572[b]	8.10[c], 8.07[d]
$CH_3SC_6H_4Cl$-*p*	572[b]	8.09[c], 8.07[d]
$Ph_3SnCH_2SC_6H_4Cl$-*p*	598[b]	7.99[b]
$Cy_3SnCH_2SC_6H_4Cl$-*p*	621[e]	7.90[e]
$Cy_3SnCH_2SeC_6H_4Cl$-*p*	641[f]	7.83[f]

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

less prone to cleavage than are phenyl–tin bonds and it was considered that any reaction of **II** would involve the Sn–$CH_2SC_6H_4Cl$-*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 $CH_2SC_6H_4Cl$-*p* group.

The reaction of **II** with *N*-bromosuccinimide (NBS) produced $BrCH_2SC_6H_4Cl$-*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 $CH_3SC_6H_4Cl$-*p* (δCH_3 2.43). Ylides (similar to **IX**) have also been postulated to occur in reactions of **I** (R = Me, R^1 = Bu) with MeI [7] and of **I** (R = Ar, R^1 = Ph) with *o*-$O_2NC_6H_4SCl$ [2].

Reaction of the Me_3Si analogue of **II**, viz. $Me_3SiCH_2SC_6H_4Cl$-*p* (**X**), with NBS in CCl_4 at 0 °C was recently reported to provide **VIII** but only in the presence of a strong acid, such as CF_3SO_3H or CF_3CO_2H [26, 27]. (In the absence of a strong acid, the product obtained was $Me_3SiCHXSC_6H_4Cl$-*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–$CH_2(SC_6H_4Cl$-*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].

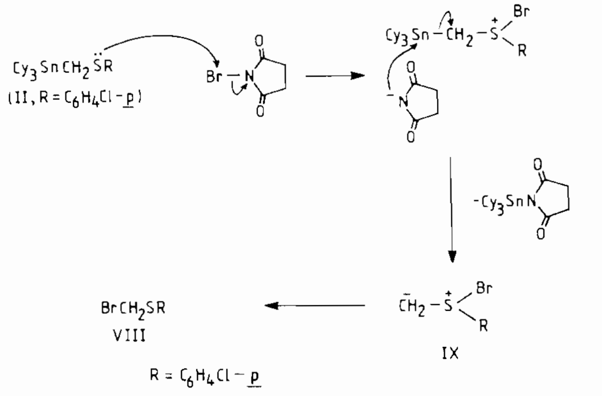
Strong acids, such as CF_3CO_2H, readily cleave **II** to give $CH_3SC_6H_4Cl$-*p*; in contrast **XI** (X = Cl) is inert to CF_3CO_2H.

The reaction of **II** with $Pb(OAc)_4$ provides $AcOCH_2SC_6H_4Cl$-*p* (**XII**), probably via labile $(AcO)_3PbCH_2SC_6H_4Cl$-*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_2	CCl_4/4 d r.t.	$ICH_2SC_6H_4Cl$-*p* [a] [δH; 4.46(s, 2H, CH_2), 7.34(brs, 4H, C_6H_4)]	Cy_3SnI [δH: 1.20–2.00(m)]; δ^{119}Sn + 65.6
Br_2	CCl_4/2 d r.t.	$BrCH_2SC_6H_4Cl$-*p* [b] [δH: 4.72(s, 2H, CH_2), 7.32(d, 2H), 7.41(d, 2H) aryl]	Cy_3SnBr [δH: 1.10–2.00(m)]
NBS	CD_2Cl_2 r.t.	$BrCH_2SC_6H_4Cl$-*p* [b] (95%) [δH: 4.81(s, 2H, CH_2), 7.35(d, 2H), 7.41(d, 2H) aryl] $CH_3SC_6H_4Cl$-*p* (δCH_3 2.43) (5%)	$Cy_3\overline{SnNCOCH_2CH_2CO}$ [δH: 1.20–2.00(m, 33H, Cy), 2.60(s, 4H, CH_2)]
$Pb(OAc)_4$	$CDCl_3$/5 d r.t.	$AcOCH_2SC_6H_4Cl$-*p* [c] [δH: 2.02(s, 3H, CH_3), 5.36(s, 2H, CH_2), 7.38(d, 2H), 7.48(d, 2H) aryl]	Cy_3SnOAc [δH: 1.20–2.00(m, 33H, Cy); 2.07(s, 3H, CH_3)] $Pb(OAc)_2$ [δH: 2.07(s)]
CF_3CO_2H (excess)	CCl_4/r.t.	$CH_3SC_6H_4Cl$-*p* [d] [δH: 2.40(s, 3H, CH_3), 7.12(d, 2H), 7.20(d, 2H) aryl]	$Cy_3SnO_2CCF_3$ [δH: 1.20–2.0(m)]
MeI (5-fold excess)	CCl_4/reflux	$CH_3SC_6H_4Cl$-*p* [e, d] [δH: 2.39(s, 3H, CH_3)]	
m-ClC_6H_4/ CO·O·OH	CCl_4/r.t.	$CH_3S(O)C_6H_4Cl$-*p* [f] (80%) [δH: 2.72(s, 3H, CH_3), 7.47(d, 2H), 7.62(d, 2H) aryl] $Cy_3SnCH_2S(O)C_6H_4Cl$-*p* (20%) [δH CH_2 2.57 J ^{119}Sn–^{1}H 30 Hz] [g]	$Cy_3SnO_2CC_6H_4Cl$-*m* [δH: 1.20–2.00(m)] [g]
m-ClC_6H_4/ CO·O·OH	CD_2Cl_2/r.t.	$CH_3S(O)C_6H_4Cl$-*p* [f] (62%) [δCH_2: 2.73] $Cy_3SnCH_2S(O)C_6H_4Cl$-*p* (26%) [δCH_2 2.58 J ^{119}Sn–^{1}H 33 Hz] [g] *m*-$ClC_6H_4CO_2CH_2SC_6H_4Cl$-*p* (12%) [δ$CH_2$ 5.72] [g]	$Cy_3SnO_2CC_6H_4Cl$-*m* [δH: 1.20–2.10(m)] [g]
$Cl_2Pt(COD)$	CD_2Cl_2/7 d r.t.	no reaction	

[a] Literature value δCH_2 = 4.46 for $ICH_2SC_6H_4Me$-*p* [5]. [b] Literature value δCH_2 = 4.67 for $BrCH_2SC_6H_4Cl$-*p* in CCl_4 [5]. [c] Literature values for $CF_3CO_2CH_2SC_6H_4Cl$-*p* [δH 5.53(2H, s, CH_2) 7.32(4H, s)] [27]. [d] Literature value for $CH_3SC_6H_4Cl$-*p* [δCH_3 2.43] [23]. [e] Only partial reaction (25% yield). [f] Literature value for $CH_3S(O)Ph$ in $CDCl_3$ [δCH_3 2.73] [24]. [g] Aryl absorptions not resolved.



Scheme 1.

$$\begin{tikzcd} Cy_3SnCH_2SR + Pb(OAc)_4 \arrow[r, "-Cy_3SnOAc"] & {} \\ & {[(AcO)_3PbCH_2SC_6H_4Cl\text{-}p]} \arrow[d, "-Pb(OAc)_2"] \\ & AcOCH_2SC_6H_4Cl\text{-}p \end{tikzcd}$$

II ($R = C_6H_4Cl$-*p*)

XII

Scheme 2.

have been reported to be unisolatable [28]. Exchange reactions of $Pb(OAc)_4$ 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 β-diketones. Attempts to use the combination $Pb(OAc)_4$ 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 $CF_3CO_2CH_2SC_6H_4Cl$-*p* [δH: 5.53(2H, s, CH_2) and 7.32(4H, s, aryl)] from $Me_3SiCH_2S(O)C_6H_4Cl$-*p* and $(CF_3CO)_2O$ or CF_3CO_2H. Other routes to α-acyloxyalkyl sulphides, RCO_2CH_2SAr, include (i) the aniodic oxidation of Me_3SiCH_2SAr [30] or CH_3SAr in HOAc [31], (ii) $PhCO{\cdot}O{\cdot}OBu^t$ oxidation of CH_3SAr [32] and (iii) the reaction of $CH_3S(O)Ar$ with $(RCO)_2O$ (the Pummerer reaction) [33].

Reaction of *m*-$ClC_6H_4CO{\cdot}O{\cdot}OH$ with **II** in CCl_4 provides mainly $CH_3S(O)C_6H_4Cl$-*p* (δCH_3 2.70) and a little $Cy_3SnCH_2S(O)C_6H_4Cl$-*p* (δCH_2 2.55, $J\,^{119}Sn-^1H$ 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 CD_2Cl_2, an additional product was *m*-$ClC_6H_4CO_2CH_2SC_6H_4Cl$-*p* (δ$CH_2$ 5.61).

Experimental

Melting points (m.p.) were measured on a Kofler hotstage and are uncorrected. ^1H NMR spectra were obtained on a Perkin-Elmer R34 (220 MHz) spectrometer and ^{119}Sn NMR spectra on a Jeol FX90 instrument; δ ^{119}Sn relative to Me_4Sn.

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}Sn and of chlorine containing peaks on ^{35}Cl.

The compound, Cy_3SnCH_2I, was obtained from Cy_3SnCl, CH_2I_2 and a zinc–copper couple by a published procedure [34]. The compound $Cy_3SnCH_2SC_6H_4Cl$-*p* was prepared from Cy_3SnCH_2I and $NaSC_6H_4Cl$-*p* in EtOH solution. $Cy_3SnCH_2SC_6H_4Cl$-*p*, m.p. 56–58 °C. *Anal.* Found: C, 57.2; H, 7.4. Calc. for $C_{25}H_{39}ClSSn$: C, 57.1; H, 7.4%. δH (CCl_4; 220 MHz): 1.10–2.00 (m, 33H, Cy), 2.10 (s, 2H, $J\,^{119}Sn-^1H$ 40 Hz, CH_2); 7.16 (s, br, 4H, aryl). δ ^{119}Sn ($CDCl_3$), 67.8 ppm. *m/z* (20 eV) (%, fragment): 526(1, *M*), 443(100, $M - Cy^+$), 369(20, Cy_3Sn^+). Mössbauer spectrum: *IS* δ 1.41 mm s^{-1} (relative to $BaSnO_3$), 1.68 mm s^{-1} at 77 K.

Compounds $Cy_3SnCH_2SeC_6H_4Cl$-*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 ^1H NMR spectroscopy. Data are given in Table 5.

Interactions with $(NC)_2C{=}C(CN)_2$ were carried out as previously described [2].

Competitive reaction between II and $Cy_3SnCH_2SeC_6H_4Cl$-p

To a solution of **II** (0.0375 g, 7.28×10^{-5} mol) and $Cy_3SnCH_2SeC_6H_4Cl$-*p* (0.0266 g, 4.65×10^{-5} mol) in $CDCl_3$ (1 ml), was added I_2 (0.0089 g, 3.51×10^{-5} mol). The solution was left until colourless; the relative yields of $ICH_2SeC_6H_4Cl$-*p* (δCH_2 4.25) and $ICH_2SC_6H_4Cl$-*p* (δCH_2 4.50) were estimated by ^1H NMR to be 2.1:1.

Crystal Structure Determination of II

Crystal data

$C_{25}H_{39}ClSSn$, $M = 515.19$ monoclinic, space group $P2_1$, $a = 17.577(24)$, $b = 8.427(10)$, $c = 17.915(19)$ Å, $\beta = 104.5(10)°$, $V = 2569(5)$ Å^3, $Z = 4$ (two independent molecules in the asymmetric unit), $D_c = 1.36$ g cm^{-3}, $D_m = 1.32$ g 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_3 automated diffractometer using monochromated Mo Kα radiation. A total of 3992 unique intensities was measured with $\theta < 50°$ as θ–2θ scans. A total of 2314 reflexions had $F > 6\,(F)$. Range of *hkl*: $0 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 9$, $-20 \leqslant l \leqslant 20$. 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 $\Delta\rho_{min} = -0.26$ e Å^{-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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