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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXII *. STRUCTURAL AND TIN-119 MÖSSBAUER STUDIES OF SOME FIVE-COORDINATE TRIORGANOTIN ANIONS

PHILIP G. HARRISON *, KIERAN MOLLOY, ROBIN C. PHILLIPS,
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (Great Britain)

PETER J. SMITH and ALAN J. CROWE
International Tin Research Institute, Fraser Road, Greenford, Perivale, Middlesex (Great Britain)

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Summary

The structures of two complexes, $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2^-]^-$ and $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$, have been determined by X-ray diffraction. Both materials are monoclinic, space group $P2_{1/c}$. Unit cell data for $[Ph_3PCH_2Ph]^+$ $[Bu_3SnCl_2]^-$ are *a* 9.8521(6), *b* 16.9142(4), *c* 22.3517(7) Å, *β* 91.4235(9)°; and for $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ *a* 34.9760(3), *b* 11.1290(5), *c* 24.2410(2) Å, *β* 108.56(2)°, and both consist of the component ionic species. The organotin anions each have trigonal bipyramidal geometry with equatorial organic groups and axial halogens. In the $[Ph_3SnCl_2]^-$ anion the two Sn—Cl bond distances are the same (2.58(1) and 2.60(1) Å), but in $[Bu_3SnCl_2]^-$, as in $[Me_3SnCl_2]^-$, they are substantially different (2.573(7) and 2.689(6) Å). The Sn—C bond distances also vary: $[Ph_3SnCl_2]^-$ 2.15(4), 2.16(3) and 2.25(5); $[Bu_3SnCl_2]^-$ 2.21(1), 2.20(2) and 2.29(2) Å. Tin-119 Mössbauer data for these and several other similar complexes are also reported.

Introduction

A problem frequently encountered in the biocidal applications of triorganotin compounds is that of sufficient aqueous solubility. One solution to this is to incorporate the triorganotin residue into an ion such as an $[R_3SnX_2]^-$ anion

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* For part XXI see ref. 1.

(X = halogen). This is, however, by no means completely satisfactory since the stability constant of the complex is dependent on the nature of the halogen and also the particular gegenion. Thus, whilst no difficulty is encountered in the formation of $[Me_3SnX_2]^-$ (X = Cl, Br, I) anions using tetraalkylammonium halides and trimethyltin halide [2], no reaction can be observed between the same tetraalkylammonium halides and tributyltin halides or with tetramethylammonium fluoride and tributyltin fluoride. The tributyldichlorostannate(IV) anion can, however, be stabilised by the much more bulky organophosphonium or -arsonium cations, and in this paper we report the properties of several such complexes as well as the structures of two.

Experimental

Preparation of the $[R_3SnCl_2]^-$ salts.

The triorganodichlorostannate(IV) salts were obtained in high yields by mixing equimolar amounts of the appropriate triorganotin chloride and tetraorganophosphonium chloride in methanol or isopropanol, and allowing the solution to crystallise at room temperature. The white crystalline complexes were all stable in air except for $[Ph_3PCH_2Ph]^+[(PhCH_2)_3SnCl_2]^-$, which decomposed suddenly on standing for 2—3 weeks in a stoppered bottle. Melting point and analytical data are given in Table 1. Tributyltin bromide or iodide did not form tributyldihalostannate(IV) anions with benzyltriphenylphosphonium bromide or iodide, and only the starting materials were recovered. Similarly the attempted reactions of various tetraalkylammonium chlorides, $R_3R'N^+ Cl^-$ (R = R' = Me or Et; R = Me or Et, R' = CH_2Ph), with tributyltin chloride, and of tetramethylammonium fluoride with tributyltin fluoride in methanol, also returned the

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Analysis (Found (calcd.) (%))					M.p. (°C)
	C	H	Cl	Sn	P	
$[Ph_3PCH_2Ph][Me_3SnCl_2]$	57.2 (57.1)	5.3 (5.3)	12.2 (12.1)	20.1 (20.2)	5.0 (5.3)	202—203
$[Ph_3PCH_2Ph][Et_3SnCl_2]$	59.0 (59.0)	5.9 (5.9)	11.5 (11.3)	18.8 (18.9)	4.9 (4.9)	189—190
$[Ph_3PCH_2Ph][Pr_3SnCl_2]$	60.5 (60.7)	6.5 (6.4)	10.3 (10.6)	17.6 (17.7)	4.3 (4.6)	117—120
$[Ph_3PCH_2Ph][Bu_3SnCl_2]$	62.1 (62.2)	6.9 (6.9)	10.3 (9.9)	16.5 (16.7)	3.8 (4.3)	115—118
$[Ph_4P][Bu_3SnCl_2]$	61.4 (61.7)	6.8 (6.8)	10.1 (10.1)	17.8 (17.0)	4.4 (4.4)	85—88
$[Bu_4P][Bu_3SnCl_2]$	54.5 (54.2)	10.3 (10.2)	11.9 (11.5)	18.3 (19.2)	5.4 (5.3)	69—70
$[Ph_3PCH_2Ph][(PhCH_2)_3SnCl_2]$	67.3 (67.6)	6.0 (5.3)	8.5 (8.7)	13.8 (14.6)	3.5 (3.8)	73—75
$[Ph_3PCH_2Ph][Ph_3SnCl_2]$	62.1 (62.2)	6.9 (6.9)	10.3 (9.9)	16.5 (16.7)	3.8 (4.3)	205—207 [a]

[a] Quoted as 205—207°C [10].

reactants. The arsonium salt $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ was obtained by the recrystallisation of the initial product from the reaction of $Ph_3AsCHCOPh$ and Ph_3SnCl [3].

Crystal structure determination of $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$

Monoclinic crystals of the material were obtained by recrystallisation from benzene (Found: C, 60.9; H, 4.5. $C_{44}H_{37}AsCl_2OSn$ calcd.: C, 61.05; H, 4.3%). A crystal of approximate dimensions 0.4 × 0.35 × 0.4 mm was selected and mounted directly onto a fine glass fibre.

Crystal data: $C_{44}H_{37}AsCl_2OSn$, $M = 846.813$, Monoclinic, a 34.9760(3), b 11.1290(5), c 24.2410(2) Å, β 108.56(2)°, U 8945.09 Å^3, $D_c = 1.416$, $Z = 4$, $F(000) = 3264$, Mo-K_α radiation λ 0.71069 Å, μ(Mo-K_α) 7.49 cm^{-1}; Space group $P2_{1/c}$ by systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$).

Data collection and cell measurements. The space group and initial cell parameters were obtained from oscillation and zero- and first-layer Weissenberg photographs obtained using a Leeds equi-inclination Weissenberg camera. The cell parameters were refined and the intensity data collected using Mo-K_α radiation using a Hilger and Watts four-circle diffractometer Y290. Reference reflections were counted every 100 reflections, and the diffractometer orientation was checked every 200 reflections. Data were collected up to θ 25°. All the reflections were brought to the same relative intensity, and those with $I < 3\sigma(I)$ were considered as unobserved and discarded, reducing the total number of reflections to 1912. Corrections were made for Lorentz and polarisation effects, but none was applied for absorption due to the low value of μ.

Structure determination and refinement. The positional coordinates of the tin and arsenic atoms were obtained from a three-dimensional Patterson synthesis, and were subsequently used to phase an initial structure factor calculation. Refinement of these positions produced the positions of the two chlorine atoms, and after several cycles of blocked-matrix least-squares refinement the positions of all but one of the non-hydrogen light atoms were obtained giving an R-value at this stage of 0.128. Four further cycles with the tin, arsenic and chlorine atoms varying anisotropically afforded the position of the remaining light atom. Four cycles of blocked-matrix refinement with all atoms varying anisotropically gave a final R-value of 0.105.

All calculations were performed using the X-ray 70 suite of programmes [4], and the atomic scattering factors used were those for neutral atoms and the chloride anion [5]. The final atomic positional parameters and anisotropic thermal parameters are listed in Tables 2 and 3, respectively. Atomic numbering is shown in Fig. 1, whilst intramolecular bond distance and angle data are listed in Table 4.

Crystal structure determination of $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$

Crystals suitable for intensity measurements were obtained by recrystallisation from methanol, and one of approximate dimensions 0.4 × 0.4 × 0.4 mm was selected and mounted onto a fine glass fibre.

Crystal data: $C_{37}H_{49}Cl_2PSn$, $M = 714.42$, Monoclinic, a 9.8521(6), b 16.9142(4), c 22.3517(7) Å, β 91.4235(9)°, V 3723.58 Å^3, $Z = 4$, $F(000) = 1470$, Mo-K_α radiation λ 0.71069 Å, μ(Mo-K_α) 11.0 cm^{-1}, Space group $P2_{1/c}$ by

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES FOR $[Ph_3AsCH_2CO_2Ph]^+[Ph_3SnCl_2]^-$ (with estimated standard deviations in parentheses)

Atom	*x/a*	*y/b*	*z/c*
Sn	0.11729(8)	0.17594(31)	0.02042(13)
Cl(1)	0.1262(3)	−0.0562(10)	0.0219(6)
Cl(2)	0.1113(3)	0.4071(10)	0.0178(6)
C(1)	0.099(1)	0.173(4)	−0.073(2)
C(2)	0.123(2)	0.156(5)	−0.104(2)
C(3)	0.102(2)	0.167(6)	−0.174(2)
C(4)	0.066(2)	0.165(9)	−0.198(4)
C(5)	0.055(2)	0.186(8)	−0.169(3)
C(6)	0.067(2)	0.175(6)	−0.109(3)
C(7)	0.073(1)	0.181(6)	0.071(2)
C(8)	0.048(1)	0.061(6)	0.057(2)
C(9)	0.019(1)	0.052(6)	0.092(2)
C(10)	0.020(2)	0.168(6)	0.131(3)
C(11)	0.043(3)	0.239(7)	0.130(3)
C(12)	0.068(2)	0.263(6)	0.104(2)
C(13)	0.181(1)	0.193(4)	0.068(2)
C(14)	0.199(1)	0.119(4)	0.120(2)
C(15)	0.243(1)	0.128(6)	0.148(2)
C(16)	0.267(1)	0.212(4)	0.130(3)
C(17)	0.252(2)	0.286(5)	0.081(3)
C(18)	0.206(2)	0.276(5)	0.050(4)
C(19)	0.341(1)	0.051(4)	0.300(2)
C(20)	0.347(1)	0.064(5)	0.245(2)
C(21)	0.165(2)	0.464(5)	0.297(3)
C(22)	0.182(2)	0.362(7)	0.291(2)
C(23)	0.191(2)	0.357(4)	0.241(4)
C(24)	0.176(1)	0.444(5)	0.186(2)
C(25)	0.351(1)	0.322(4)	0.315(2)
C(26)	0.381(1)	0.409(5)	0.323(2)
C(27)	0.372(2)	0.514(4)	0.290(2)
C(28)	0.165(2)	0.036(5)	0.251(2)
C(29)	0.307(2)	0.449(5)	0.237(2)
C(30)	0.311(1)	0.350(4)	0.269(2)
C(31)	0.417(1)	0.149(4)	0.393(2)
C(32)	0.437(1)	0.201(4)	0.446(2)
C(33)	0.477(2)	0.175(6)	0.473(3)
C(34)	0.496(1)	0.118(6)	0.442(2)
C(35)	0.478(2)	0.071(7)	0.387(3)
C(36)	0.440(2)	0.089(5)	0.365(2)
C(37)	0.339(1)	0.161(4)	0.419(1)
C(38)	0.290(2)	0.157(3)	0.395(2)
C(39)	0.271(1)	0.125(3)	0.436(2)
C(40)	0.227(2)	0.127(5)	0.410(2)
C(41)	0.206(2)	0.091(5)	0.452(3)
C(42)	0.274(1)	0.438(5)	0.489(3)
C(43)	0.236(2)	0.436(5)	0.470(2)
C(44)	0.208(1)	0.407(5)	0.507(2)
O(1)	0.269(1)	0.179(3)	0.344(1)
As	0.3592(12)	0.1736(5)	0.3548(2)

systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$).

Data collection and cell measurements. The intensity data collection and cell measurement procedure was identical with that used for $[Ph_3AsCH_2COPh]^+$-$[Ph_3SnCl_2]^-$ above, yielding a total number of reflections of 3928. Again, correc-

(continued on p. 427)

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS FOR $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ (with estimated standard deviations in parentheses) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	4.9(2)	5.9(2)	6.8(2)	−0.2(2)	1.5(1)	−0.1(2)	C(22)	11(5)	12.5(6)	5.5(5)	2(4)	−1(3)	4(4)
Cl(1)	6.8(9)	5.8(8)	10.8(10)	−0.0(7)	3.7(7)	−0.4(7)	C(23)	8.5(4)	4(4)	28(9)	4(3)	7(6)	7(5)
Cl(2)	5.7(8)	5.2(7)	10.5(10)	0.2(6)	−0.7(7)	−0.6(8)	C(24)	4(3)	10.5(4)	12(4)	1(3)	3(3)	−2(4)
C(1)	3(2)	9(3)	8(3)	3(2)	6(2)	−1(3)	C(25)	5(3)	5(2)	6(3)	0(3)	2(2)	−0(3)
C(2)	17(6)	13(5)	10(4)	13(4)	7(4)	5(4)	C(26)	11(4)	12(5)	3(2)	−1(4)	2(3)	1(3)
C(3)	25(8)	10(4)	10(4)	3(6)	15(5)	−1(4)	C(27)	16(5)	8(4)	3(3)	1(3)	5(3)	2(3)
C(4)	7(5)	47(10)	17(9)	3(8)	5(6)	−7(1)	C(28)	13(5)	8(4)	3(3)	−6(4)	0(3)	−0(3)
C(5)	16(7)	24(10)	6(4)	4(7)	−2(4)	−8(5)	C(29)	11(5)	5(3)	11(5)	−3(3)	1.5(3)	2(3)
C(6)	12(6)	13(5)	13(5)	5(5)	0(4)	−3(6)	C(30)	11.5(4)	7(4)	5(3)	−0(3)	2(3)	1(3)
C(7)	4(3)	15(6)	10(4)	2(3)	1(3)	10(5)	C(31)	4(3)	7.5(4)	8(3)	−1(3)	2(3)	4(3)
C(8)	4(3)	22(6)	8(3)	1(4)	−2(2)	6(4)	C(32)	8(4)	7(3)	5(3)	0(3)	2(3)	−2(3)
C(9)	4(3)	20(7)	10(4)	−2(4)	3(3)	7(4)	C(33)	4(4)	13(5)	12.5(5)	1.5(4)	−1(3)	1(5)
C(10)	9(6)	28(12)	6(4)	7(7)	6(7)	4(7)	C(34)	4(4)	13.5(5)	7(4)	1(3)	3(3)	1.5(3)
C(11)	16(10)	16(7)	12(6)	6(6)	11(6)	4(5)	C(35)	4(4)	22(8)	12(5)	1(5)	2(4)	−5(5)
C(12)	7(4)	17(6)	8(4)	4(4)	3(3)	−7(4)	C(36)	7(4)	14(5)	13(5)	6(4)	3(4)	−4(4)
C(13)	5(3)	6(3)	5(2)	0(2)	−0.5(2)	−2(2)	C(37)	2(2)	8(3)	6(2)	−4(2)	1(2)	0.5(2)
C(14)	11(4)	7(3)	7(3)	1(3)	5(3)	−3(3)	C(38)	22(6)	0.5(2)	7(3)	−0.5(3)	7(4)	0.5(2)
C(15)	4(3)	19(6)	5(3)	0.5(3)	−3(2)	−2(3)	C(39)	6(3)	5(3)	5(3)	−0(2)	2(2)	−1(2)
C(16)	7(4)	5(3)	20(6)	−1(3)	9(4)	−0(4)	C(40)	12(6)	13(5)	12(4)	1(4)	8(5)	−1.5(4)
C(17)	9(4)	7.5(4)	16(6)	1(3)	6(4)	0(4)	C(41)	11(5)	10(4)	12(5)	1(4)	2(4)	2(4)
C(18)	17(6)	8(4)	11(4)	0(4)	8(4)	1(3)	C(42)	2(3)	11(4)	15(4)	−1(3)	4(3)	1.5(4)
C(19)	3(3)	5(3)	8.5(3)	−0(2)	1(2)	−1(2)	C(43)	18(7)	11(5)	10(4)	−4(5)	10(5)	2(4)
C(20)	8.5(4)	15(5)	5(3)	−0(3)	0(3)	3(3)	C(44)	12(4)	9(4)	4(3)	−1(3)	−0(3)	−1(3)
C(21)	9(4)	8(4)	12(4)	0(4)	−3(3)	3(4)	O(1)	6(2)	14(3)	6(2)	−3(2)	0(1)	3(2)
							As	4.7(2)	6.1(3)	6.1(2)	0.0(2)	0.8(2)	0.3(2)

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[a] U_{ij} are of the form $\exp - 2\pi^2 \times 10^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)$.

TABLE 4

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (degrees) IN $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ (with estimated standard deviations in parentheses)

Distances				Angles			
Sn—Cl(1)	2.60(1)	C(19)—C(20)	1.41(7)	Cl(1)—Sn—Cl(2)	177.5(4)	C(19)—As—C(25)	108(2)
Sn—Cl(2)	2.58(1)	C(20)—C(21)	1.47(8)	C(1)—Sn—C(7)	123(1)	C(25)—As—C(31)	110(2)
Sn—C(1)	2.15(4)	C(21)—C(22)	1.29(9)	C(1)—Sn—C(13)	118(1)	C(19)—As—C(31)	108(2)
Sn—C(7)	2.25(5)	C(22)—C(23)	1.36(12)	C(7)—Sn—C(13)	118(1)	C(37)—As—C(19)	113(2)
Sn—C(13)	2.16(3)	C(23)—C(24)	1.58(9)	Cl(1)—Sn—C(1)	89(1)	C(37)—As—C(25)	116(2)
		C(24)—C(19)	1.43(6)	Cl(1)—Sn—C(7)	96(2)	C(37)—As—C(31)	102(2)
C(1)—C(2)	1.32(8)	C(25)—C(26)	1.40(7)	Cl(1)—Sn—C(13)	89(1)		
C(2)—C(3)	1.61(6)	C(26)—C(27)	1.39(7)	Cl(2)—Sn—C(1)	90(1)	C(19)—C(20)—C(21)	118(5)
C(3)—C(4)	1.25(11)	C(27)—C(28)	1.39(6)	Cl(2)—Sn—C(7)	86(2)	C(20)—C(21)—C(22)	129(6)
C(4)—C(5)	1.06(14)	C(28)—C(29)	1.32(7)	Cl(2)—Sn—C(13)	89(1)	C(21)—C(22)—C(23)	112(6)
C(5)—C(6)	1.37(8)	C(29)—C(30)	1.33(7)			C(22)—C(23)—C(24)	128(5)
C(6)—C(1)	1.16(6)	C(30)—C(25)	1.50(5)	C(1)—C(2)—C(3)	114(5)	C(23)—C(24)—C(19)	111(5)
C(7)—C(8)	1.57(8)	C(31)—C(32)	1.36(6)	C(2)—C(3)—C(4)	122(8)	C(24)—C(19)—C(18)	120(4)
C(8)—C(9)	1.52(8)	C(32)—C(33)	1.37(7)	C(3)—C(4)—C(5)	93(9)	C(25)—C(26)—C(27)	118(4)
C(9)—C(10)	1.58(12)	C(33)—C(34)	1.32(9)	C(4)—C(5)—C(6)	128(9)	C(26)—C(27)—C(28)	123(5)
C(10)—C(11)	1.15(13)	C(34)—C(35)	1.38(8)	C(5)—C(6)—C(1)	134(7)	C(27)—C(28)—C(29)	119(5)
C(11)—C(12)	1.23(12)	C(35)—C(36)	1.28(8)	C(6)—C(1)—C(2)	102(5)	C(28)—C(29)—C(30)	123(5)
C(12)—C(7)	1.27(9)	C(36)—C(31)	1.37(8)	C(7)—C(8)—C(9)	111(5)	C(29)—C(30)—C(25)	119(4)
C(13)—C(14)	1.45(5)	C(37)—C(38)	1.61(7)	C(8)—C(9)—C(10)	113(6)	C(30)—C(25)—C(26)	116(4)
C(14)—C(15)	1.45(5)	C(38)—O(1)	1.25(5)	C(9)—C(10)—C(11)	115(8)	C(31)—C(32)—C(33)	118(5)
C(16)—C(17)	1.39(8)	C(38)—C(39)	1.40(8)	C(10)—C(11)—C(12)	141(9)	C(32)—C(33)—C(34)	117(4)
C(17)—C(18)	1.55(9)	C(39)—C(40)	1.47(7)	C(11)—C(12)—C(13)	115(7)	C(33)—C(34)—C(35)	125(5)
		C(40)—C(41)	1.46(10)	C(12)—C(7)—C(8)	124(5)	C(34)—C(35)—C(36)	115(7)
As—C(19)	1.86(4)	C(41)—C(42)	1.41(8)	C(13)—C(14)—C(15)	118(4)	C(35)—C(36)—C(31)	124(5)
As—C(25)	1.89(4)	C(42)—C(43)	1.27(9)	C(14)—C(15)—C(16)	122(4)	C(36)—C(31)—C(32)	119(4)
As—C(31)	1.96(3)	C(43)—C(44)	1.56(10)	C(15)—C(16)—C(17)	123(6)		
As—C(37)	1.92(4)	C(44)—C(39)	1.39(5)	C(16)—C(17)—C(18)	115(5)	As—C(37)—C(38)	109(3)
				C(17)—C(18)—C(13)	123(4)	C(37)—C(38)—O(1)	124(5)
				C(18)—C(13)—C(14)	118(4)	C(37)—C(38)—C(39)	116(6)
						O(1)—C(38)—C(39)	120(5)
						C(39)—C(40)—C(41)	113(4)
						C(40)—C(41)—C(42)	125(5)
						C(41)—C(42)—C(43)	118(6)
						C(42)—C(43)—C(44)	126(5)
						C(43)—C(44)—C(39)	112(4)
						C(44)—C(39)—C(40)	125(5)

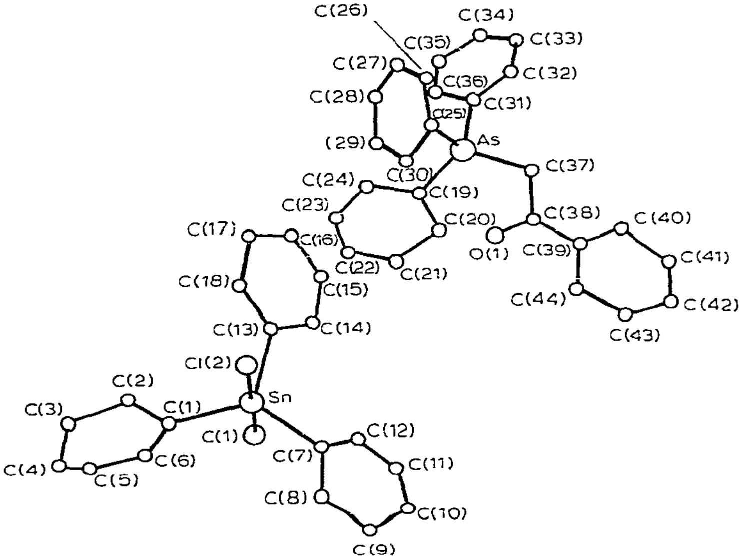

Fig. 1. Atomic numbering in $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$.

tions were made for Lorentz and polarisation effects, but none for absorption.

Structure determination and refinement. A three-dimensional Patterson synthesis was used to obtain the positional parameters of the tin atom, which were used to phase the initial structure factor calculation. These parameters were refined by one cycle of full-matrix isotropic least-squares before a difference Fourier synthesis was employed to locate the positions of the two chlorine atoms, the phosphorus and the four carbon atoms bonded to phosphorus. Following one cycle of full-matrix isotropic least-squares refinement of these atoms, a second difference Fourier synthesis located the positions of eighteen further carbon atoms, three bonded to tin and the rest belonging to the phosphonium cation. After two further cycles of full-matrix isotropic least-squares refinement, the three carbon atoms bonded to the tin were rejected because of their high thermal parameters. A third difference Fourier synthesis then afforded the positions of the six outstanding atoms in the phosphonium cation and six carbon atoms belonging to the anion. Refinement by two cycles of full matrix least-squares with the tin atom varying anisotropically resulted in the rejection of the six carbon atoms of the anion again because of high thermal parameters. After twelve further cycles of least-squares refinement, the positions of the carbon atoms of the anion could still not be located satisfactorily. Refinement of the $[Cl_3SnC_2]$ skeleton alone during this refinement sequence resulted in a drifting of the carbon atoms along a mean path through their respective n-butyl chains to an average Sn—C distance of 2.55 Å, and therefore the positions of the three carbon atoms bonded to tin were then fixed at their values determined after the second difference Fourier synthesis, whilst the remaining atoms were refined by four cycles of full-matrix anisotropic least-squares to a convergent *R*-value of 0.104.

Calculations in this case were performed using the CRYSTALS suite of program

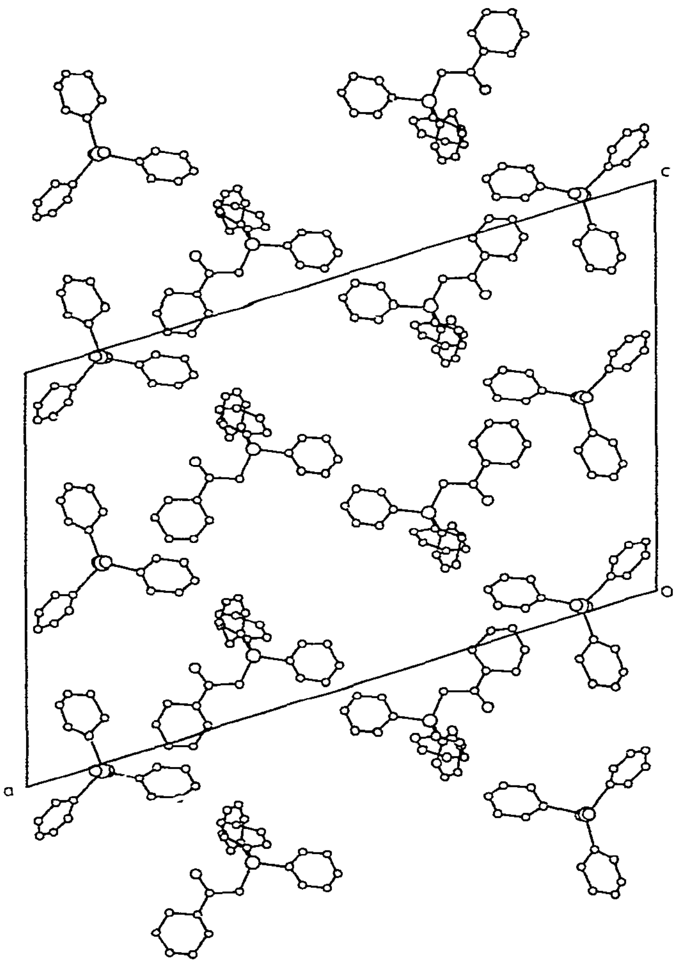

Fig. 2. Projection of the unit cell of $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ onto the *ac* plane.

mes, and the atomic scattering factors used were as above [4,5]. The final atomic positional parameters and anisotropic thermal parameters are listed in Tables 5 and 6, respectively. Atomic numbering is shown in Fig. 3, whilst intramolecular bond distance and angle data are listed in Table 7.

Mössbauer spectra. Our Mössbauer spectrometer has been described elsewhere [6]. Spectra were recorded as finely powdered samples at 77 K vs. $Ca^{119m}SnO_3$ (The Radiochemical Centre, Amersham). Data reduction was accomplished by fitting to Lorentzian line shapes employing usual least-squares methods. The data are listed in Table 8, and a typical spectrum is illustrated in Fig. 5. Isomer shifts are quoted with respect to SnO_2.

Discussion

As can clearly be seen from Fig. 2 and 4, both $[Ph_3AsCH_2COPh]^+[Ph_3SnCl_2]^-$ and $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ consist of stacks of non-interacting cations and

TABLE 5

FINAL FRACTIONAL COORDINATES FOR $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ (with estimated standard deviations in parentheses).

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.4358(2)	0.1670(1)	−0.1680(1)	C(13)	0.875(3)	0.171(2)	0.085(1)
P(1)	0.8789(5)	0.3381(4)	−0.0013(2)	C(14)	0.764(2)	0.400(1)	0.038(1)
Cl(1)	0.4791(7)	0.2226(4)	0.4169(3)	C(15)	0.720(2)	0.377(2)	0.095(1)
Cl(2)	0.3919(8)	0.4387(5)	0.2510(3)	C(16)	0.630(2)	0.428(2)	0.126(1)
C(1)	0.040(2)	0.335(1)	0.039(1)	C(17)	0.592(3)	0.499(2)	0.101(1)
C(2)	0.061(2)	0.380(1)	0.090(1)	C(18)	0.362(2)	0.022(1)	0.454(1)
C(3)	0.186(3)	0.377(2)	0.119(1)	C(19)	0.722(2)	0.473(1)	0.014(1)
C(4)	0.285(3)	0.331(2)	0.096(1)	C(20)	0.901(2)	0.124(1)	0.423(1)
C(5)	0.265(3)	0.287(2)	0.042(2)	C(21)	0.022(2)	0.096(1)	0.406(1)
C(6)	0.143(2)	0.287(2)	0.014(1)	C(22)	0.031(3)	0.067(2)	0.348(1)
C(7)	0.817(2)	0.262(1)	0.490(1)	C(23)	0.920(3)	0.062(2)	0.308(1)
C(8)	0.774(3)	0.198(1)	0.045(1)	C(24)	0.794(3)	0.090(2)	0.328(1)
C(9)	0.641(3)	0.190(2)	0.055(1)	C(25)	0.782(2)	0.122(1)	0.385(1)
C(10)	0.595(3)	0.150(2)	0.106(2)	C(26)	0.269(2)	0.380(1)	0.386(1)
C(11)	0.689(4)	0.122(2)	0.150(2)	C(27)	0.650(3)	0.372(2)	0.342(1)
C(12)	0.833(4)	0.128(2)	0.139(1)	C(28)	0.394(3)	0.232(2)	0.266(1)

anions. The geometry at the arsenic atom in the $[Ph_3AsCH_2COPh]^+$ cation is slightly distorted tetrahedral. All four of the As—C bonds, including the unique As—alkyl bond distance, are of very similar length (1.86(4)—1.96(3) Å, mean 1.925 Å), and are comparable with other As—C bond distances. The geometry about the As—CH_2—C group also appears to be regularly tetrahedral, with an

(continued on p. 432)

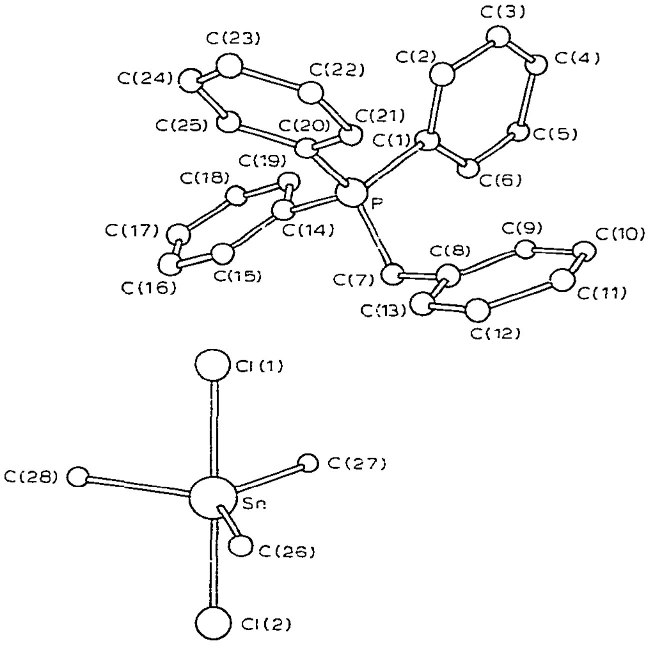

Fig. 3. Atomic numbering in $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$.

TABLE 6

FINAL ANISOTROPIC THERMAL PARAMETERS FOR $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ (with estimated standard deviations in parentheses) [a, b]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	7.5(1)	8.4(1)	5.9(1)	0.0(1)	−0.4(1)	−0.6(1)	C(13)	10(2)	8(2)	9(2)	1(2)	−1(2)	0(2)
P(1)	5.4(3)	6.0(3)	5.1(3)	−0.4(3)	0.0(2)	−0.1(3)	C(14)	6(1)	7(1)	5(1)	−1(1)	0(1)	−1(1)
Cl(1)	9.2(5)	8.3(5)	8.0(4)	1.3(4)	0.1(4)	0.1(4)	C(15)	8(2)	8(2)	7(2)	−1(1)	1(1)	−1(1)
Cl(2)	11.9(6)	10.7(6)	6.6(4)	1.0(4)	−0.9(4)	1.9(5)	C(16)	6(2)	10(2)	9(2)	−3(2)	1(1)	−2(2)
C(1)	5(1)	6(1)	6(1)	1(1)	−0.5(9)	0(1)	C(17)	6(2)	9(2)	12(2)	−3(2)	−1(2)	0(2)
C(2)	7(1)	6(1)	6(1)	0(1)	−1(1)	1(1)	C(18)	6(1)	8(2)	8(2)	2(1)	−1(1)	−1(1)
C(3)	6(2)	9(2)	8(2)	1(1)	−1(1)	0(1)	C(19)	6(1)	7(2)	7(1)	0(1)	−1(1)	0(1)
C(4)	6(2)	11(2)	10(2)	3(2)	−1(1)	−2(2)	C(20)	8(2)	6(1)	5(1)	0(1)	0(1)	1(1)
C(5)	6(2)	13(3)	10(2)	3(2)	0(1)	1(2)	C(21)	7(2)	8(2)	6(1)	0(1)	2(1)	1(1)
C(6)	6(2)	10(2)	7(2)	1(1)	0(1)	2(1)	C(22)	10(2)	8(2)	8(2)	1(1)	3(2)	2(2)
C(7)	8(2)	5(1)	6(1)	0(1)	0(1)	1(1)	C(23)	12(2)	9(2)	6(2)	1(1)	−1(2)	0(2)
C(8)	9(2)	6(1)	5(1)	0(1)	−1(1)	−1(1)	C(24)	10(2)	9(2)	6(2)	1(1)	0(1)	0(2)
C(9)	8(2)	8(2)	7(2)	1(1)	1(1)	−1(1)	C(25)	8(2)	7(2)	6(1)	−1(1)	0(2)	0(1)
C(10)	10(2)	15(1)	12(3)	2(2)	0(2)	−3(2)							
C(11)	16(3)	10(3)	12(3)	2(2)	2(2)	−2(2)							
C(12)	16(3)	10(2)	10(2)	3(2)	−2(2)	−1(2)							

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[a] U_{ij} are of the form $\exp - 2\pi^2 \times 10^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)$. [b] Atoms C(26), C(27) and C(28) were not allowed to refine anisotropically, and had final isotropic thermal paramaters (U_{iso}) of 0.177, 0.182 and 0.187, respectively.

TABLE 7

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (degrees) IN $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ (with estimated standard deviations in parentheses)

Bond distances				Bond angles (°)			
Sn(1)—Cl(1)	2.689(6)	C(14)—C(15)	1.41(5)	Cl(1)—Sn(1)—Cl(2)	179.2(2)	C(7)—C(8)—C(9)	119(3)
Sn(1)—Cl(2)	2.573(7)	C(15)—C(16)	1.44(3)	Cl(1)—Sn(1)—C(26)	88.2(2)	C(7)—C(8)—C(13)	118(2)
Sn(1)—C(26)	2.210(8)	C(16)—C(17)	1.38(3)	Cl(1)—Sn(1)—C(27)	90.2(6)	C(9)—C(8)—C(13)	123(3)
Sn(1)—C(27)	2.220(20)	C(17)—C(18)	1.37(3)	Cl(1)—Sn(1)—C(28)	87.5(5)	C(8)—C(9)—C(10)	122(3)
Sn(1)—C(28)	2.286(22)	C(18)—C(19)	1.38(3)	Cl(2)—Sn(1)—C(26)	91.3(3)	C(9)—C(10)—C(11)	119(2)
		C(19)—C(14)	1.40(4)	Cl(2)—Sn(1)—C(27)	90.3(6)	C(10)—C(11)—C(12)	120(2)
P(1)—C(1)	1.81(3)			Cl(2)—Sn(1)—C(28)	92.5(6)	C(11)—C(12)—C(13)	118(2)
P(1)—C(7)	1.80_5(4)	C(20)—C(21)	1.35(4)	C(26)—Sn(1)—C(27)	124.0(5)	C(12)—C(13)—C(8)	118(2)
P(1)—C(14)	1.78_5(4)	C(21)—C(22)	1.39(3)	C(26)—Sn(1)—C(28)	119.7(6)		
P(1)—C(20)	1.82(3)	C(22)—C(23)	1.39(2)	C(27)—Sn(1)—C(28)	116.1(7)	P(1)—C(14)—C(15)	120(2)
		C(23)—C(24)	1.41(2)			P(1)—C(14)—C(19)	121(2)
C(1)—C(2)	1.38(4)	C(24)—C(25)	1.39(2)	C(1)—P(1)—C(7)	108(2)	C(15)—C(14)—C(19)	119(2)
C(2)—C(3)	1.38(4)	C(25)—C(20)	1.44(4)	C(1)—P(1)—C(14)	109(2)	C(14)—C(15)—C(16)	119(2)
C(3)—C(4)	1.36(3)			C(1)—P(1)—C(20)	110(2)	C(15)—C(16)—C(17)	119(2)
C(4)—C(5)	1.43(3)			C(7)—P(1)—C(14)	113(2)	C(16)—C(17)—C(18)	122(2)
C(5)—C(6)	1.34(3)			C(7)—P(1)—C(10)	106(2)	C(17)—C(18)—C(19)	120(2)
C(6)—C(1)	1.42(4)			C(14)—P(1)—C(20)	110(2)	C(18)—C(19)—C(14)	121(2)
C(7)—C(8)	1.49(5)			P(1)—C(1)—C(2)	120(2)	P(1)—C(20)—C(21)	122(2)
C(8)—C(9)	1.34(4)			P(1)—C(1)—C(6)	117(2)	P(1)—C(20)—C(25)	117(2)
C(9)—C(10)	1.41(4)			C(2)—C(1)—C(6)	123(2)	C(21)—C(20)—C(25)	122(2)
C(10)—C(11)	1.42(4)			C(1)—C(2)—C(3)	119(3)	C(20)—C(21)—C(22)	118(2)
C(11)—C(12)	1.44(3)			C(2)—C(3)—C(4)	119(3)	C(21)—C(22)—C(23)	123(1)
C(12)—C(13)	1.47(4)			C(4)—C(4)—C(5)	122(3)	C(22)—C(23)—C(24)	118(1)
C(13)—C(8)	1.39(4)			C(4)—C(5)—C(6)	120(2)	C(23)—C(24)—C(25)	120(1)
				C(5)—C(6)—C(1)	118(2)	C(24)—C(25)—C(20)	118(2)
				P(1)—C(7)—C(8)	116(3)		

TABLE 8

TIN-119 MÖSSBAUER DATA FOR THE COMPLEXES

Complex	δ [a]	Δ [a]	Γ_+ [a]	Γ_- [a]	I_+/I_- [b]
$[Ph_3PCH_2Ph][Me_3SnCl_2]$	1.43	3.38	0.887	0.983	0.990
$[Ph_3PCH_2Ph][Et_3SnCl_2]$	1.56	3.46	0.919	0.869	0.951
$[Ph_3PCH_2Ph][Pr_3SnCl_2]$	1.55	3.42	0.863	0.830	0.940
$[Ph_3PCH_2Ph][Bu_3SnCl_2]$	1.50	3.41	0.812	0.843	1.034
$[Ph_3PCH_2Ph][Ph_3SnCl_2]$	1.34	2.89	0.593	0.585	0.962
$[Ph_3PCH_2Ph][(PhCH_2)_3SnCl_2]$	1.59	3.13	0.852	0.845	1.126
$[Ph_4P][Bu_3SnCl_2]$	1.55	3.44	0.871	0.862	0.988
$[Bu_4P][Bu_3SnCl_2]$	1.54	3.44	0.845	0.824	0.997
$[Ph_3AsCH_2COPh][Ph_3SnCl_2]$ [c]	1.43	2.88			

[a] mm s^{-1}. The positive and negative signs refer to the peaks at higher and lower velocity, respectively. [b] Area ratio of higher velocity peak to lower velocity peak. [c] Ref. 3.

As—C—C bond angle of 109.8(26)°. The (As)C—C(O) bond is slightly longer (1.61 Å) than is usually found for C—C(O) bonds in simple aldehydes or ketones (1.516 Å) [7], and the carbonyl bond distance is lengthened slightly (1.25(5) Å) compared to that in simple carbonyl compounds (1.23 Å). The four atoms of the C—C(=O)—C group are almost coplanar, the largest deviation from the mean plane being 0.003 Å, and the phenyl ring bonded to this group is only slightly twisted (1.7°) from planarity with it.

Similarly, the bond parameters for the $[Ph_3PCH_2Ph^+]$ cation are in no way unexceptional, with only slight distortion from tetrahedral geometry at phosphorus. Again the P—alkyl bond distance ($1.80_5(4)$ Å) is intermediate in the

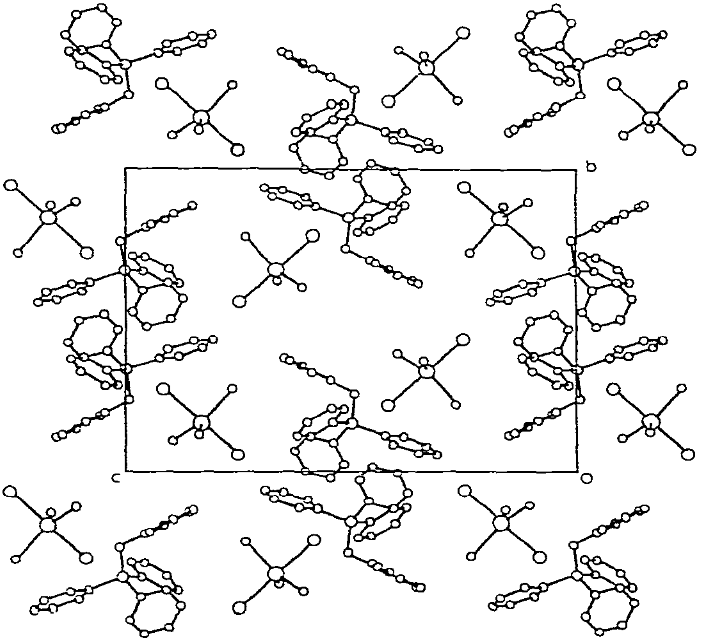

Fig. 4. Projection of the unit cell of $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ onto the *bc* plane.

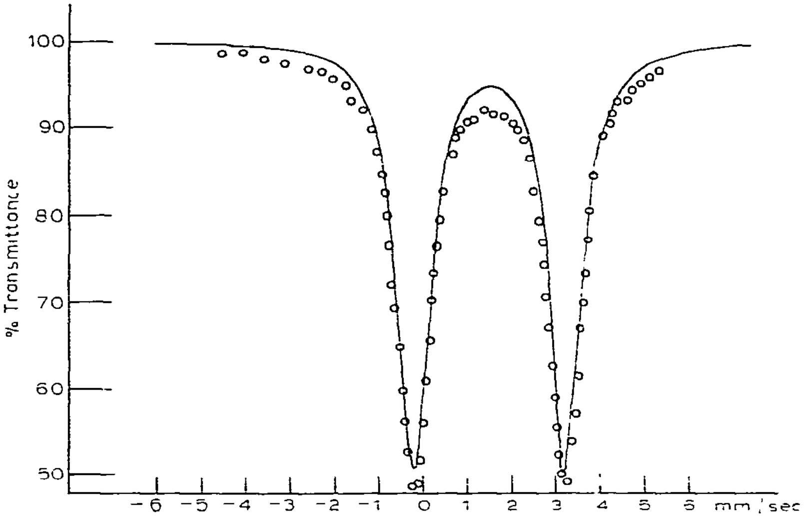

Fig. 5. Tin-119 Mössbauer spectrum of $[Ph_3PCH_2Ph]^+[Bu_3SnCl_2]^-$ at 77 K (the solid line represents the curve-fitted Lorentzian line shapes).

range of the P—C distances (mean $1.80_5(4)$ Å). The Ph_3P—C—C(Ph) bond angle is opened to 116(3)° and the phenyl group bonded to carbon twisted almost orthogonally to the (Ph_3)P—C—C(Ph) plane presumably to minimise steric interation of the phenyl groups.

Both the $[Ph_3SnCl_2]^-$ and the $[Bu_3SnCl_2]^-$ anions exhibit trigonal bipyramidal geometry at the tin atom, with the usual equatorial arrangement of organic groups and the chlorine atoms occupying axial positions. The "local" $[C_3SnCl_2]$ skeleton in both approximates to D_{3h}, although in the butyl derivative the two Sn—Cl distances are quite dissimilar (2.573(7) and 2.689(6) Å) as has also been observed in the $[Me_3SnCl_2]^-$ anion [8] (2.572(4) and 2.696(3) Å). The two distances in the $[Ph_3SnCl_2]^-$ anion are, however, very similar (2.58(1) and 2.60(1) Å). An analogous inequality in M—X_{axial} bond distances has also been observed in $Me_3SnONC_6H_{10}$ [9], where planar Me_3Sn units are unsymmetrically bridged by oxygen atoms. The mean Sn—C bond distances in both anions are relatively long (2.21(2) and 2.19(4) Å) (cf. the $[Me_3SnCl_2]^-$ anion: mean Sn—C distance 2.12(1) Å [8]), and, in both anions, one Sn—C bond is significantly longer than the other two. The three phenyl groups in the $[Ph_3SnCl_2]^-$ anion are twisted with respect to each other, probably due to the steric bulk of the rings. The angles of twist of each ring with respect to the SnC_3 plane are 60.45° (ring C(1)—C(6)), 9.49° (ring C(7)—C(12)) and 52.66° (ring C(13)—C(18)).

The tin-119 Mössbauer spectrum of each of the complexes consisted of a quadrupole split doublet resonance of which that illustrated in Fig. 5 is typical. The isomer shifts of the triphenyltin derivatives are somewhat lower (~1.4 mm s^{-1}) than those of the analogous trialkyltin derivatives (~1.5 mm s^{-1}), but all are typical for triorganotin compounds. Similarly, the values of the quadrupole splittings (~3.4 mm s^{-1} for the alkyl derivatives, ~2.9 mm s^{-1} for the phenyl derivatives) are fully consistent with a *trans*-R_3SnCl_2 stereochemistry.

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