bisects the angles N1—Co—N1*a* and N3—Co—C3*a*. With the exception of N1*a* and N3*a*, only the atoms on the crystallographically unique half of the molecule are labelled and will be used to describe the structure. (1) is an octahedral complex with two axially coordinated tetrafluoroborate ligands and four equatorial pyrazole ligands. Selected bond lengths and angles are given in Table 2. The Co—F bond lengths of 2·190 (3) Å in (1) are only slightly longer than the 2·05 (2) and 2·04 (1) Å found in CoF_2 (Stout & Reed, 1954). The Co—F1—B1 bond angle of 151·9 (6)° falls within the wide range (126–180°) observed for monodentate BF_4^- ligands. The coordination of the BF_4^- ligand results in the expected elongation of the B1—F1 bond to 1·422 Å compared with the average bond length ($B—F_{ave}$ = 1·363 Å) of the non-coordinated F atoms. Bond angles within the BF_4^- ligand are unexceptional, ranging from 105·6 (8) to 115·8 (9)°. These data suggest that the tetrafluoroborate anions in (1) can be described as 'normal' (Tomlinson, Bonamico, Dessy, Fares & Scaramuzza, 1972) BF_4^- ligands. An alternative description of the complex as a BF_3 adduct of a cobalt fluoride (Burch, Calabrese & Ittel, 1988) appears inappropriate in this case. The remaining bond lengths and angles about Co show only small deviations from an idealized octahedron. The planes of the pyrazole rings are twisted out of the equatorial plane of the octahedron to minimize steric interactions, but these ligands exhibit no unusual bond lengths or angles.

In conclusion, (1) provides another example of the ability of the tetrafluoroborate anion to act as a ligand to transition metals. Concerning our original intent in carrying out the reaction leading to the formation of (1), we note that the facile hydrolysis of the tris(pyrazolyl)borate ligand in the presence of only small amounts of water may prove a troublesome feature of this increasingly popular class of tridentate ligands.

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Structure of Chlorodiphenyl[3-(*p*-tolylthio)propyl]tin

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Abstract. $[Sn(Cl)(C_6H_5)_2(C_{10}H_{13}S)]$, $M_r = 473{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}943\,(11)$, $b = 10{\cdot}268\,(11)$, $c = 23{\cdot}201\,(12)$ Å, $V = 2130{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}96$ mm^{-1}, $F(000) = 952$, $T = 293$ K, $R = 0{\cdot}0646$ for 2405 observed reflexions. The Sn atom is in a dis-

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torted trigonal bipyramidal environment and is displaced 0·272 (1) Å towards the Cl atom from the equatorial plane of three C atoms. The Cl and S atoms are axial. The intramolecular Sn···S distance is 3·195 (4) Å representing a bond order of 0·22.

Introduction. Reactivities of Ph—Sn bonds in $Ph_3Sn(CH_2)_nS(O)_mAr$ compounds ($n > 2$, $m = 0$, 1 or 2) in cleavage reactions with halogens depend on the particular $(CH_2)_nS(O)_mAr$ group (Wardell & Wigzell, 1981). Nucleophilic assistance in the transition state of the cleavage step by the S, SO or SO_2 groups was invoked to account for the differences in reactivities. This is despite sulfides, as soft bases, being generally poor donors towards tin halides (hard acids). To support the reactivity data, evidence was required that S in $XPh_2Sn(CH_2)_mSAr$ could act as an intramolecular donor. Thus, a crystal structure determination of $ClPh_2SnCH_2CH_2CH_2SC_6H_4Me$-*p* was undertaken.

Experimental. The title compound was prepared in *ca* 70% yield by reaction of $Ph_3SnCH_2CH_2CH_2SC_6H_4Me$-*p* with $MgCl_2$ in EtOH (Wardell & Wigzell, 1982). A colourless crystal, 0·4 × 0·4 × 0·5 mm, was used. The cell dimensions were obtained from setting angles of 12 independent reflexions with $2\theta \simeq 20°$ on a Nicolet *P*3 automated diffractometer using monochromated Mo $K\alpha$ radiation. The intensities of 3226 unique reflections with $2\theta \leq 50°$ were measured from ω–2θ scans and 2405 had $F > 5\sigma F$; h 0–12, k 0–14, l 0–26. The data were corrected for Lorentz and polarization effects; absorption was ignored. Two reference reflexions, monitored periodically, showed no significant variation in intensities.

The structure was determined by the heavy-atom method (Patterson function) which revealed the approximate position of the Sn atom. The remaining non-H atoms were located from successive difference syntheses using *SHELX76* (Sheldrick, 1976). All H atoms were located but given ideal geometry with C—H = 1·00 (2) Å and allowed to ride on attached C atoms. Full-matrix least-squares calculations on F with anisotropic thermal parameters for the Sn, Cl, S and C atoms and a common isotropic thermal parameter for the H atoms converged at $R = 0·0646$, $wR = 0·0673$. Refinement with all coordinates inverted converged at $R = 0·0653$, $wR = 0·0683$, confirming the original absolute configuration (Hamilton, 1965). Atomic scattering factors and anomalous-dispersion terms from *SHELX76*. Final $w = 2·4704/[\sigma^2(F) + 0·001000F^2]$, $\Delta/\sigma < 0·1$, final $\Delta\rho_{max} = 0·6$, $\Delta\rho_{min} = -0·5$ e Å^{-3}. Molecular geometries were generated by the *GX* package (Mallinson & Muir, 1985).

Discussion. The structure of the title compound is shown in Fig. 1. Final atomic parameters are listed in Table 1 and bond lengths and angles in Table 2.* The S atom is coordinated to tin to give a pentacoordinated Sn atom in the discrete monomeric five-membered ring chelate complex. The Sn—S bond length is 3·195 (4) Å; this is slightly longer than those in $(ClMe_2SnCH_2CH_2CH_2)_2S$ [3·097 (4) and 3·118 (4) Å] (Jurkschat *et al.*, 1988). The weaker Sn···S interaction in $ClPh_2SnCH_2CH_2CH_2SC_6H_4Me$-*p* reflects the weaker donor ability of alkyl aryl sulfides compared with dialkyl sulfides. The sum of the covalent radii for Sn and S is 2·44 Å while the sum of the van der Waals radii is 3·9 Å. Tin–sulfur distances in $SCH_2CH_2SCH_2SSnSCH_2CH_2SCH_2S$ (Sn—S and Sn···S = 2·42 and 3·13 Å) reflect a typical single-bond length and a weaker coordinate-bond length (Drager, 1976). Formal bond orders for Sn–element(E) coordinations have been calculated (Drager, 1976) from the coordinate-bond length [d(Sn···E)] and the typical single-bond length [d(Sn—E)$_{av.}$], *viz.* bond order = [d(Sn—E)$_{av.}$] + 1 − [d(Sn···E)].

On the basis of an average value for an Sn—S single-bond length of 2·42 Å, the formal bond order for Sn···S in the title compound is 0·22.

An analogous calculation for $Me_2SnClCH_2CH_2CH_2PPhBu^t$ provided a formal Sn···P bond order of 0·44 (Weichmann, Meunier-Piret & Van Meerssche, 1986) compared to values of 0·6 to 0·7 for triorganotin halide complexes involving an intra- or intermolecular Sn···N or Sn···O coordination. As expected, higher values are found for O and N donors (both hard bases) than for S and P donors (soft bases) towards a hard acid.

The structure of $ClPh_2SnCH_2CH_2CH_2SC_6H_4Me$-*p* is best described as a distorted trigonal bipyramid with S and Cl atoms axial. The displacement of the

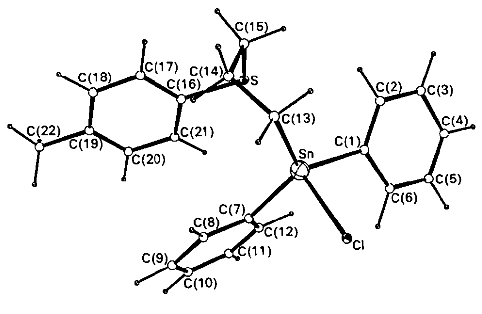

Fig. 1. The atomic arrangement in the molecule.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52714 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic values of the anisotropic temperature factor coefficients* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Sn	0·69158 (9)	0·21143 (8)	0·39026 (3)	0·045
S	1·0001 (4)	0·0593 (4)	0·3737 (2)	0·073
Cl	0·4781 (4)	0·3508 (4)	0·4124 (2)	0·065
C(1)	0·6167 (16)	0·0409 (12)	0·4353 (5)	0·051
C(2)	0·701 (2)	−0·015 (1)	0·477 (1)	0·070
C(3)	0·647 (2)	−0·120 (2)	0·508 (1)	0·091
C(4)	0·493 (3)	−0·164 (2)	0·494 (1)	0·101
C(5)	0·415 (3)	−0·105 (2)	0·452 (1)	0·093
C(6)	0·4726 (17)	−0·0011 (15)	0·4237 (6)	0·065
C(7)	0·6654 (11)	0·1967 (14)	0·2995 (5)	0·049
C(8)	0·7059 (16)	0·2963 (14)	0·2634 (5)	0·059
C(9)	0·6926 (18)	0·2826 (15)	0·2039 (6)	0·070
C(10)	0·6397 (18)	0·1665 (18)	0·1820 (6)	0·076
C(11)	0·6026 (17)	0·0661 (17)	0·2169 (7)	0·069
C(12)	0·6142 (16)	0·0797 (14)	0·2756 (6)	0·058
C(13)	0·8550 (15)	0·3378 (17)	0·4298 (7)	0·071
C(14)	1·0176 (15)	0·3127 (17)	0·4118 (7)	0·076
C(15)	1·0734 (16)	0·1734 (20)	0·4221 (6)	0·084
C(16)	1·0740 (13)	0·1077 (13)	0·3048 (6)	0·055
C(17)	1·1982 (16)	0·1845 (13)	0·2996 (6)	0·060
C(18)	1·2481 (17)	0·2187 (17)	0·2443 (7)	0·070
C(19)	1·177 (2)	0·171 (1)	0·196 (1)	0·073
C(20)	1·0559 (16)	0·0973 (16)	0·2014 (7)	0·068
C(21)	1·000 (2)	0·063 (2)	0·256 (1)	0·078
C(22)	1·236 (2)	0·207 (2)	0·136 (1)	0·109

Table 2. *Bond lengths* (Å) *and valency angles* (°) *with e.s.d.'s in parentheses*

Sn—Cl	2·442 (4)	Sn—C(1)	2·145 (12)
Sn—C(7)	2·119 (10)	Sn—C(13)	2·161 (15)
S—C(15)	1·749 (17)	S—C(16)	1·799 (13)
C(1)—C(2)	1·366 (18)	C(1)—C(6)	1·381 (19)
C(2)—C(3)	1·39 (2)	C(3)—C(4)	1·48 (3)
C(4)—C(5)	1·33 (3)	C(5)—C(6)	1·36 (3)
C(7)—C(8)	1·377 (17)	C(7)—C(12)	1·397 (18)
C(8)—C(9)	1·390 (17)	C(9)—C(10)	1·38 (3)
C(10)—C(11)	1·35 (3)	C(11)—C(12)	1·370 (18)
C(13)—C(14)	1·532 (18)	C(14)—C(15)	1·54 (3)
C(16)—C(17)	1·370 (17)	C(16)—C(21)	1·39 (3)
C(17)—C(18)	1·394 (19)	C(18)—C(19)	1·38 (3)
C(19)—C(20)	1·33 (3)	C(19)—C(22)	1·54 (3)
C(20)—C(21)	1·41 (3)		

Cl—Sn—C(1)	97·5 (4)	Cl—Sn—C(7)	99·6 (3)
Cl—Sn—C(13)	95·1 (4)	C(1)—Sn—C(7)	112·8 (5)
C(1)—Sn—C(13)	119·8 (5)	C(7)—Sn—C(13)	122·6 (5)
C(15)—S—C(16)	104·5 (7)	Sn—C(1)—C(2)	121·2 (10)
Sn—C(1)—C(6)	116·9 (9)	C(2)—C(1)—C(6)	121·5 (12)
C(1)—C(2)—C(3)	120·3 (15)	C(2)—C(3)—C(4)	116·1 (15)
C(3)—C(4)—C(5)	121·1 (16)	C(4)—C(5)—C(6)	120·5 (18)
C(1)—C(6)—C(5)	120·3 (14)	Sn—C(7)—C(8)	121·6 (9)
Sn—C(7)—C(12)	120·0 (9)	C(8)—C(7)—C(12)	118·3 (10)
C(7)—C(8)—C(9)	120·7 (12)	C(8)—C(9)—C(10)	118·9 (12)
C(9)—C(10)—C(11)	121·3 (13)	C(10)—C(11)—C(12)	119·8 (14)
C(7)—C(12)—C(11)	121·0 (12)	Sn—C(13)—C(14)	115·1 (10)
C(13)—C(14)—C(15)	114·8 (12)	S—C(15)—C(14)	113·6 (10)
S—C(16)—C(17)	122·4 (10)	S—C(16)—C(21)	117·4 (10)
C(17)—C(16)—C(21)	120·3 (12)	C(16)—C(17)—C(18)	119·1 (12)
C(17)—C)18)—C(19)	120·7 (14)	C(18)—C(19)—C(20)	119·8 (14)
C(18)—C(19)—C(22)	119·8 (14)	C(20)—C(19)—C(22)	120·3 (14)
C(19)—C(20)—C(21)	121·3 (14)	C(16)—C(21)—C(20)	118·8 (14)

Sn atom from the equatorial plane [C(1), C(7), C(13)] is 0·272 (1) Å, compared to the ideal tetrahedral value of 0·74 Å, based on average Sn—C bond lengths of 2·41 Å. This represents a 63% displacement towards a trigonal bipyramidal array. The sum of the equatorial C—Sn—C bond angles is 356·2 (5)° and the axial angle Cl—Sn—S is 171·1 (2)°. The C—Sn···S angles are 76·1 (4), 86·0 (4) and 86·6 (3)°. The C(7)—Sn—C(13) bond angle [122·6 (5)°] indicates a widening to allow the S···Sn interaction.

The Sn—Cl bond length [2·442 (4) Å] is at the lower end of the range usually found for other pentacoordinate tin complexes, *e.g.* 2·494 (2) Å in ClMe$_2$SnCH$_2$CH$_2$PPhBu^t (Weichmann *et al.*, 1986), 2·449 (1) Å in ClPhBuSnSC(S)NEt$_2$ (Weir & Kumar Das, 1985) and 2·475 (2) Å in (Ph$_3$SNCl)$_2$-(OPPh$_2$CH$_2$)$_2$ (Pelizzi & Pelizzi, 1980) but considerably shorter than in N(CH$_2$CH$_2$CH$_2$)$_3$SnCl, 2·613 (7) Å (Jurkschat, Tzschach, Meunier-Piret & Van Meerssche, 1985). In tetrahedral four-coordinate triorganotin chlorides, Sn—Cl bond lengths are shorter, *e.g.* 2·3538 (14) and 2·3557 (14) Å in Ph$_3$SnCl (Tse, Lee & Gabe, 1986) and 2·380 (3) Å in [(Me$_3$Si)$_3$CH]$_3$SnCl (Gymane, Lappert, Miles, Carty & Taylor, 1977).

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