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μ-Ethane-1,2-diylbis(diphenylphosphine oxide)-κ^2O:O'-bis[dibenzyldichlorotin(IV)]: a centrosymmetric complex containing trigonal-bipyramidal tin(IV), linked into chains of rings by C—H···*π*(arene) hydrogen bonds

E. Mothi Mohamed,[a] Krishnaswamy Panchanatheswaran,[a] John N. Low[b]‡ and Christopher Glidewell[c]*

[a]Department of Chemistry, Bharathidasan University, Tiruchirappalli, Tamil Nadu 620 024, India, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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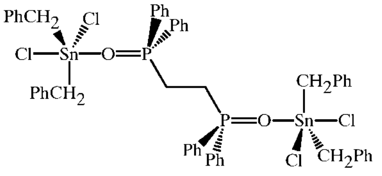
The title compound, $[Sn_2Cl_4(C_7H_7)_4(C_{26}H_{24}O_2P_2)]$, (I), was isolated from the reaction of 1,2-bis(diphenylphosphino)ethane with dibenzyltin(IV) dichloride in the presence of air. The molecules of (I) lie across centres of inversion in space group *C*2/*c* and contain five-coordinate Sn atoms. The molecules are linked into chains of rings by a single C—H···*π*(arene) hydrogen bond.

Comment

The interaction of chelating bisphosphines with tin(IV) halides has been the subject of several investigations. Reaction of both simple phosphines and 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$, with SnX_4 (X = Cl or Br) gave products characterized on the basis of spectral data only as 1:1 adducts containing six-coordinate tin (Reutov *et al.*, 1988). On the other hand, the reaction of the same bisphosphine with Me_2SnCl_2 in the presence of air gave a 1:1 adduct characterized by X-ray diffraction as a continuous-chain polymer containing the oxidized ligand $Ph_2P(O)CH_2CH_2P(O)Ph_2$ bridging pairs of six-coordinate Sn atoms (Pettinari *et al.*, 2001). The analogous product from Ph_2SnCl_2 was assigned a similar structure, but in the absence of air, no reaction was observed with R_2SnCl_2 (R = Me or Ph). We have now investigated the reaction of 1,2-bis(diphenylphosphino)ethane with dibenzyltin(IV) dichloride, $(PhCH_2)_2SnCl_2$, and report here the molecular and supramolecular structure of the product, (I), a 2:1 complex containing the oxidized ligand $Ph_2P(O)CH_2CH_2P(O)Ph_2$ bridging pairs of five-coordinate Sn atoms. The oxidation of the bisphosphine can be readily diagnosed both from the IR absorption characteristics of P═O bonds and from the ^{31}P NMR spectrum.



(I)

Complex (I) is centrosymmetric; it lies across a centre of inversion in space group *C*2/*c*, chosen for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Accordingly, the P—C—C—P fragment of the phosphine oxide ligand has a *trans*-planar conformation. The five-coordinate Sn atom has a trigonal-bipyramidal configuration, with the O atom and one of the chloro ligands (Cl1) in axial sites, and the other chloro ligand and the two benzyl ligands in equatorial sites (Fig. 1); the interbond angles are close to idealized values (Table 1). The axial Sn—Cl bond is longer than the equatorial Sn—Cl bond by ~0.12 Å, and the P—O—Sn fragment is nearly linear. The remaining bond lengths and angles show no unusual values.

The complexes are linked by a single C—H···*π*(arene) hydrogen bond (Table 2), in which the same benzyl group provides both the donor and the acceptor. Benzyl atom C3 in the reference complex centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ acts as a hydrogen-bond donor, *via* atom H3*A*, to the C31–C36 ring at $(1 - x, y, \frac{1}{2} - z)$, which forms part of the complex centred at $(\frac{1}{2}, \frac{1}{2}, 0)$. Propagation of this interaction by the space group then generates a chain of rings running parallel to the [001] direction (Fig. 2).

Since no coordination of unoxidized bisphosphine was observed in the absence of air by Pettinari *et al.* (2001), it seems probable that the bulk of the oxidation occurs before

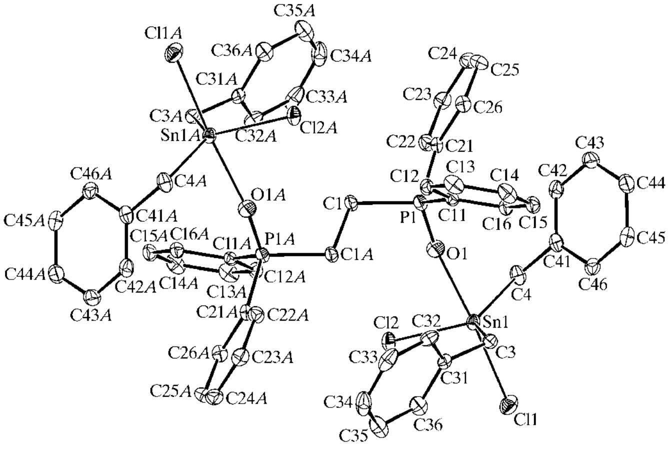


Figure 1
A view of complex (I), showing the atom-labelling scheme. Atoms labelled with the suffix '*A*' are at the symmetry position $(1 - x, 1 - y, 1 - z)$. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, H atoms have been omitted.

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‡ Postal address: Department of Electrical Engineering and Physics, University of Dundee, Dundee DD1 4HN, Scotland.

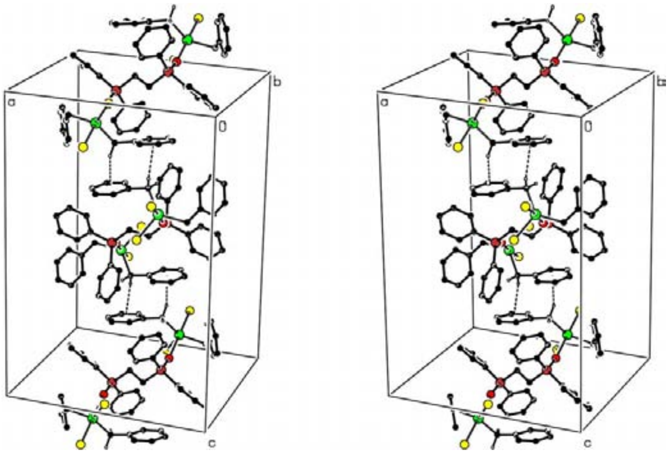

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along the [001] direction. For clarity, H atoms other than those bonded to the C atom involved in the motif shown have been omitted.

the formation of the final product; however, the detailed mechanism of this process remains unknown.

Experimental

For the synthesis of (I), a dilute solution of dibenzyltin(IV) chloride [prepared according to Sisido *et al.* (1961)] in chloroform was added dropwise to an equimolar quantity of 1,2-bis(diphenylphosphino)-ethane, also in chloroform solution, and the mixture was stirred overnight. After removal of the solvent *in vacuo*, a pale yellow solid was obtained; vapour diffusion of light petroleum into a solution of this solid in benzene gave colourless crystals of (I) suitable for single-crystal X-ray diffraction (m.p. 445–447 K). IR (KBr disk): 1191 and 1153 cm^{-1} [ν(P═O)]; ^{1}H NMR (CDCl$_3$): δ 2.26 (*br*, 4H, 2 × CH$_2$P), 2.93 (*s* with Sn satellites, $^2J_{\text{Sn–H}}$ = 93.6 Hz, 8H, 4 × CH$_2$Ph), 6.85–6.98 (*m*, 20H, 4 × Ph), 7.18–7.55 (*m*, 20H, 4 × Ph); ^{31}P NMR (CDCl$_3$): δ 38.7; ^{119}Sn NMR (CDCl$_3$): δ −137.5.

Crystal data

$[Sn_2Cl_4(C_7H_7)_4(C_{26}H_{24}O_2P_2)]$
M_r = 1174.12
Monoclinic, $C2/c$
a = 15.0100 (5) Å
b = 14.7055 (6) Å
c = 22.6909 (6) Å
β = 91.571 (2)°
V = 5006.7 (3) Å^3
Z = 4
D_x = 1.558 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5716 reflections
θ = 3.2–27.5°
μ = 1.32 mm^{-1}
T = 120 (2) K
Needle, colourless
0.20 × 0.07 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min}$ = 0.731, $T_{\max}$ = 0.940
31 842 measured reflections
5716 independent reflections
3778 reflections with $I > 2\sigma(I)$
R_{int} = 0.082
$\theta_{\max}$ = 27.5°
$h = -19 \rightarrow 19$
$k = -18 \rightarrow 19$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.083
S = 0.96
5716 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.20 e Å^{-3}
$\Delta\rho_{\min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—Cl1	2.4788 (10)	Sn1—C3	2.132 (3)
Sn1—Cl2	2.3597 (8)	Sn1—C4	2.137 (4)
Sn1—O1	2.242 (2)	P1—O1	1.467 (3)
Cl2—Sn1—C3	116.68 (9)	O1—Sn1—Cl1	175.87 (6)
Cl2—Sn1—C4	114.37 (9)	P1—O1—Sn1	164.8 (2)
C3—Sn1—C4	128.0 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1 is the centroid of the C31–C36 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3A⋯$Cg1^{\text{i}}$	0.99	2.67	3.466 (3)	137

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Crystals of (I) are monoclinic and the systematic absences permitted $C2/c$ and Cc as possible space groups; $C2/c$ was selected and confirmed by the subsequent analysis. All H atoms were located from difference maps and treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH$_2$).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1706). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2004). C**60**, m172–m173 E. Mothi Mohamed *et al.* • $[Sn_2Cl_4(C_7H_7)_4(C_{26}H_{24}O_2P_2)]$ **m173**