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Triphenylphosphine oxide adducts of diphenylantimony(V) and diorganotin(IV) Lewis acids: structures of $SnPh_2Cl_2\cdot OPPh_3$, $SnPh_2Cl_2\cdot 2OPPh_3$, $SnPh_2Br_2\cdot OPPh_3$ and $SbPh_2Cl_3\cdot OPPh_3$

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Abstract

1:1 and 1:2 adducts of diphenyltin dichloride with triphenylphosphine oxide can be isolated in the solid state but the preparative conditions necessary to isolate an adduct of specific stoichiometry are difficult to define; none of acid: base ratio, choice of solvent or reaction temperature are significant factors. Adventitious crystal seeding probably has a dominant role. Both the 1:1 and 1:2 adducts of $SnPh_2Cl_2$, but only the 1:1 adduct of $SnPh_2Br_2$, were isolated. 1:1 and 1:2 adducts of both $SnMe_2Cl_2$ and $SnBu^n_2Cl_2$ were readily isolated whereas only 1:2 adducts were obtained with $SnPh_2(NCS)_2$ and $SnBu^n_2(NCS)_2$. $SbPh_2Cl_3$ readily forms a 1:1 adduct with triphenylphosphine oxide and the same adduct is obtained from the reaction of the phosphine oxide with $SbPhCl_2$. Crystallographic data are reported for $SnPh_2Cl_2\cdot OPPh_3$, $SnPh_2Cl_2\cdot 2OPPh_3$, $SnPh_2Br_2\cdot OPPh_3$ and $SbPh_2Cl_3\cdot OPPh_3$. Both $SnPh_2Cl_2\cdot OPPh_3$ and $SnPh_2Br_2\cdot OPPh_3$ have tin in trigonal bipyramidal environments. ^{119}Sn Mössbauer quadrupole splitting data are consistent with the same trigonal bipyramidal geometry for tin in $SnMe_2Cl_2\cdot OPPh_3$ whereas the data for the butyl analogue suggest the presence of six-coordinated tin as a result of intermolecular Sn–Cl interactions. A notable feature of all of the adducts subjected to crystallographic studies is the presence of intramolecular π-interactions involving phenyl groups of the phosphine oxide and phenyl groups bonded to the metal. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Organotin; Organoantimony; Adduct; Mössbauer

1. Introduction

Triphenylphosphine oxide has been extensively employed as a ligand for many p-, d-, and f-block metals. Its use has extended to organotin(IV) chemistry where the structures of its adducts have been investigated by Mössbauer, NMR and IR spectroscopy, dipole measurements, and X-ray crystallography [1–11]. Equilibrium studies between diorganotin dihalides and triphenylphosphine oxide in various solvents have been investigated by NMR spectroscopy and calorimetry [6–9]. Crystallographic data are available for $SnPh_2Cl_2\cdot OPPh_3$ [12] $SnPh_3(NO_3)\cdot OPPh_3$ [10], $SnPh_2(NO_3)_2\cdot OPPh_3$ [11] and for the diphosphine oxide adducts $SnPh_3Cl\cdot(OPPh_2)CH_2CH_2(OPPh_2)$ [13] and $(SnPh_3Cl)_2\cdot(OPPh_2)CH_2CH_2(OPPh_2)$ [14].

Triphenylphosphine oxide is an interesting ligand in organotin chemistry insofar as it is one of the few donor ligands which apparently facilitates the isolation of both 1:1 and 1:2 adducts of diorganotin(IV) dihalides. However, in this respect there is a degree of controversy. Although the 1:1 adducts are the predominant solution species, it was the 1:2 adduct of diphenyltin(IV) dichloride with triphenylphosphine oxide which was initially reported in the solid state [1]. Later groups however failed to isolate this adduct, the 1:1 adduct being the product of all preparative attempts [2,3]. On the other hand, 1:2 adduct formation is apparently favoured by $SnMe_2Cl_2$, $SnBu^n_2Cl_2$ and $SnPhMeCl_2$ in the solid state even though in these instances also it is the 1:1 adduct which dominates in solution [3,4]. An objective of the present work was to establish the precise conditions that are necessary to isolate 1:1 and 1:2 adducts of diphenyltin dichloride with triphenylphosphine oxide and if possible to determine the struc-

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ture of the 1:2 adduct. With structural data already available for the 1:1 adduct [12], crystallographic data would then be available, for the first time, for both a five- and six-coordinated diorganotin dihalide adduct containing the same acid–base pair. Furthermore, we were interested in comparing structural parameters for these adducts with those for the adduct $SbPh_2Cl_3\cdot OPPh_3$ for the following reason: The crystal structure determination of $SbPh_2Cl_3\cdot H_2O$ [15] revealed a surprisingly weak antimony–water interaction compared to the tin–water interactions in aqua adducts of dimethyltin dichloride, which would tend to suggest that dimethyltin dichloride is a stronger Lewis acid than diphenylantimony trichloride. This would indeed be a surprising result. However, in apparent contradiction with the above crystallographic observations for aqua adducts, a comparison of the ν(P=O) stretching frequency data for $SbPh_2Cl_3\cdot OPPh_3$ and $SnPh_2Cl_2\cdot 2OPPh_3$ suggests that the former contains the stronger acid–base interaction.

2. Experimental

2.1. Instrumentation

Elemental carbon, hydrogen and nitrogen analyses were determined using a Perkin–Elmer 2400 elemental analyser. Infrared spectra were recorded as Nujol mulls between cesium iodide plates on a Perkin–Elmer FT 1000 Infrared spectrometer. X-ray diffraction data were collected at room temperature on an Enraf Nonius CAD4 diffractometer. ^{119}Sn Mössbauer spectra were recorded on a constant acceleration spectrometer supplied by J&P Engineering (Reading). The spectra were recorded with the sample at liquid nitrogen temperature and a $^{119}CaSnO_3$ source at room temperature. Spectra were fitted using the program PEAKFIT from Jandel Scientific. Chemical shifts are quoted relative to $BaSnO_3$.

Table 1
Analytical data for $SnR_2X_2\cdot n OPPh_3$ and $SbR_2X_3\cdot n OPPh_3$

R	M	X	n	Analyses [a]		
				%C	%H	%N
Me	Sn	Cl	1	48.25 (48.19)	4.16 (4.22)	– –
Me	Sn	Cl	2	58.96 (58.74)	4.78 (4.64)	– –
Bu^n	Sn	Cl	1	53.49 (53.61)	5.20 (5.67)	– –
Bu^n	Sn	Cl	2	60.93 (61.38)	6.01 (5.58)	– –
Ph	Sn	Cl	1	57.89 (57.88)	3.80 (4.02)	– –
Ph	Sn	Cl	2	63.87 (63.98)	4.32 (4.44)	– –
Bu^n	Sn	NCS	2	60.82 (60.98)	4.68 (5.30)	2.93 (3.09)
Ph	Sn	NCS	2	62.79 (63.47)	3.72 (4.23)	2.87 (2.96)
Ph	Sn	Br	1	50.58 (50.65)	3.80 (3.52)	– –
Ph	Sb	Cl	1	54.12 (54.50)	3.83 (3.78)	– –

[a] Found (Calc.).

2.2. Starting materials

Tin starting materials were purchased from Aldrich Chemical Company. Triphenylphosphine oxide and diphenyltin dichloride were used without further purification. Dimethyltin dichloride was sublimed before use. Dibutyltin dichloride was recrystallized from 60:80 petroleum ether. Diphenyltin dibromide, diphenyltin diisothiocyanate, dibutyltin diisothiocyanate, diphenylantimony trichloride and phenylantimony dichloride were prepared by literature methods [16–19].

2.3. Synthesis of $SnPh_2Cl_2\cdot OPPh_3$, $SnPh_2Cl_2\cdot 2OPPh_3$ and $SnPh_2Br_2\cdot OPPh_3$

Preparations of these adducts were undertaken during two phases of the study which were separated by approximately 6 months. During the first phase, only the 1:2 adduct of diphenyltin dichloride could be prepared whereas during the second phase only the 1:1 adduct could be isolated.

The 1:2 adduct of diphenyltin dichloride was typically prepared as follows: An ethanolic solution of diphenyltin dichloride (1 mmol in 50 cm^3) was added dropwise to an ethanolic solution of triphenylphosphine oxide (2 mmol in 50 cm^3) at room temperature. A microcrystalline complex precipitated rapidly from solution and was isolated by filtration and dried under vacuum. Analytical data are in Table 1. Using the same procedure but employing chloroform, toluene or tetrahydrofuran as solvent invariably resulted in the formation of an identical adduct. The same 1:2 adduct was also obtained from refluxing solvents. Good quality crystals, one of which was selected for the crystallographic study, were obtained from a hot toluene solution of the adduct.

During this same phase of the work, attempts were made to isolate the 1:1 adduct of diphenyltin dichloride. Typically, a solution of the phosphine oxide was added dropwise to a solution of the tin Lewis acid. A wide range of solvents was employed, both dried and undried, and reactions were carried out at room temperature, approximately −8°C, and under refluxing conditions. Reactions were also carried out both in the open atmosphere and under nitrogen. All reactions resulted in the precipitation of the 1:2 adduct exclusively. In a further bid to obtain the 1:1 adduct, as much as a ten-fold excess of the Lewis acid was employed in preparative reactions but not even then was the desired adduct obtained.

When the second phase of the work began, renewed emphasis was placed on the isolation of the 1:1 adduct of diphenyltin dichloride. The first preparative effort resulted in the successful isolation of the 1:1 adduct using the following procedure: A solution of triphenylphosphine oxide in methanol (1 mmol in ca. 30 cm^3) was added to a solution of diphenyltin dichloride in methanol (1 mmol in ca. 20 cm^3). A white powder precipitated from solution which was isolated by filtration and dried under vacuum. Analytical data are in Table 1. Good quality crystals of the 1:1 adduct were obtained from the filtrate after approximately twelve hours and one of these was selected for a crystallographic study.

Following the successful isolation of the 1:1 adduct, all efforts to isolate the 1:2 adduct met with failure, the sole product of reaction invariably being the 1:1 adduct. Furthermore, a sample of the 1:2 adduct, obtained from the earlier phase of the work was crystallised from toluene (as had been done in the earlier phase to obtain suitable crystals for crystallography) but now it was the 1:1 adduct which crystallised from solution.

$SnPh_2Br_2 \cdot OPPh_3$ was prepared using the method described for the preparation of $SnPh_2Cl_2 \cdot OPPh_3$. Analytical data are in Table 1. All efforts at obtaining a 1:2 adduct were unsuccessful. A crystal of the 1:1 adduct, grown from methanol, was selected for a crystallographic study.

2.4. Synthesis of $SnMe_2Cl_2 \cdot OPPh_3$ and $SnMe_2Cl_2 \cdot 2OPPh_3$

The 1:1 adduct was prepared by slowly adding a dichloromethane solution of the phosphine oxide (1 mmol in ca. 30 cm^3) to a dichloromethane solution of $SnMe_2Cl_2$ (1 mmol in ca. 30 cm^3). The resulting white precipitate was isolated by filtration and dried under vacuum. Analytical data are in Table 1.

The 1:2 adduct was prepared by adding a dichloromethane solution of $SnMe_2Cl_2$ (1 mmol in ca. 30 cm^3) to a dichloromethane solution of the phosphine oxide (2 mmol in ca. 30 cm^3). The resulting white precipitate was isolated by filtration and dried under vacuum. Analytical data are in Table 1.

2.5. Synthesis of $SnBu^n_2Cl_2 \cdot OPPh_3$ and $SnBu^n_2Cl_2 \cdot 2OPPh_3$

The general procedures were as outlined for the preparation of the dimethyltin dichloride 1:1 and 1:2 adducts. Hot ethanol was the solvent employed in the preparation of the 1:1 adduct while cold ethanol was employed for the preparation of the 1:2 adduct. Analytical data are in Table 1.

2.6. Synthesis of $SnBu^n_2(NCS)_2 \cdot 2OPPh_3$ and $SnPh_2(NCS)_2 \cdot 2OPPh_3$

These adducts were prepared using the procedure outlined for the preparation of $SnMe_2Cl_2 \cdot 2OPPh_3$ using acetonitrile and toluene as solvents for the preparation of the dibutyl- and diphenyltin adducts, respectively. Analytical data are in Table 1. All efforts at synthesising 1:1 adducts were unsuccessful.

2.7. Synthesis of $SbPh_2Cl_3 \cdot OPPh_3$

A toluene solution of triphenylphosphine oxide (1 mmol in ca. 30 cm^3) was added to a toluene solution of $SbPh_2Cl_3$ (1 mmol in ca. 30 cm^3). After approximately 30 min, a white precipitate had formed which was isolated by filtration and dried under vacuum. Analytical data are in Table 1.

Although crystals of reasonable quality were obtained from the toluene filtrate, better quality crystals of the diphenylantimony adduct were obtained from a preparation starting with $SbPhCl_2$. 1 mmol solid $SbPhCl_2$ was added to a toluene solution of the phosphine oxide (1 mmol in ca. 40 cm^3). A white precipitate formed immediately. This solid, which was isolated by filtration, contained chlorine and antimony but almost no carbon. The filtrate, on standing for several days, yielded good quality crystals of $SbPh_2Cl_3 \cdot OPPh_3$. One such crystal was selected for a crystallographic study.

2.8. X-ray crystallography

Crystal data are in Table 2. The structures were solved by direct methods, SHELXS-97 [20], and refined by full matrix least squares using SHELXL-97 [21]. SHELX operations were rendered paperless using OSCAIL which was also used to obtain the drawings [22]. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a Pentium PC.

3. Discussion

The first objective of the present work was to resolve the controversy regarding the stoichiometry of the triphenylphosphine oxide adduct of diphenyltin dichloride. It is clear that the conditions employed in the first

Table 2
Crystallographic data

	$SnPh_2Cl_2{\cdot}OPPh_3$	$SnPh_2Cl_2{\cdot}2OPPh_3$	$SnPh_2Br_2{\cdot}OPPh_3$	$SbPh_2Cl_3{\cdot}OPPh_3$
Empirical formula	$C_{30}H_{25}Cl_2OPSn$	$C_{48}H_{40}Cl_2O_2P_2Sn$	$C_{30}H_{25}Br_2OPSn$	$C_{30}H_{25}Cl_3OPSb$
Formula weight	622.06	450.17	710.98	660.57
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions				
a (Å)	8.9264(7)	11.7160(10)	8.9911(11)	10.981(2)
b (Å)	10.590(2)	12.1450(10)	10.7393(13)	20.352(5)
c (Å)	15.475(2)	17.3740(9)	15.5943(18)	12.991(2)
α (°)	96.240(10)	90	96.852(10)	90
β (°)	99.870(10)	104.540(10)	99.759(10)	101.01(2)
γ (°)	105.870(10)	90	105.240(10)	90
Volume (Å^3)	1367.5(3)	2393.0(3)	1410.4(3)	2849.9(10)
Z	2	2	2	4
D_{calc} (Mg m^{-3})	1.511	1.250	1.674	1.540
Absorption coefficient (mm^{-1})	1.209	0.746	3.816	1.327
F(000)	624	916	696	1320
Crystal size (mm)	$0.25\times0.3\times0.25$	$0.3\times0.41\times0.21$	$0.2\times0.15\times0.25$	$0.52\times0.45\times0.42$
Theta range for data collection (°)	2.03–27.97	2.07–31.96	2.21–25.97	2.00–27.98
Index ranges	$0\leq h\leq 11$; $-13\leq k\leq 13$; $-20\leq l\leq 20$	$0\leq h\leq 7$; $0\leq k\leq 18$; $-25\leq l\leq 25$	$0\leq h\leq 11$; $-13\leq k\leq 12$; $-19\leq l\leq 18$	$0\leq h\leq 14$; $0\leq k\leq 26$; $-17\leq l\leq 16$
Reflections collected	7227	5201	6069	7475
Independent reflections	6591 [$R_{int}=0.0197$]	4738 [$R_{int}=0.0130$]	5520 [$R_{int}=0.0204$]	6871 [$R_{int}=0.0359$]
Reflections observed ($>2\sigma$)	5719	4152	3437	5332
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6591/0/316	4738/0/250	5520/0/316	6871/0/325
Goodness-of-fit on F^2	1.108	1.344	0.952	1.027
Final R [a] indices [$I>2\sigma(I)$]	$R_1=0.0316$, $wR_2=0.1004$	$R_1=0.0687$, $wR_2=0.2765$	$R_1=0.0500$, $wR_2=0.1173$	$R_1=0.0644$, $wR_2=0.1534$
R [a] indices (all data)	$R_1=0.0397$, $wR_2=0.1165$	$R_1=0.0726$, $wR_2=0.2827$	$R_1=0.0922$, $wR_2=0.1306$	$R_1=0.0779$, $wR_2=0.1610$
Largest difference peak and hole (e Å^{-3})	1.140 and −0.816	3.015 and −0.359	1.107 and −2.127	2.869 and −2.635

[a] $R_1=(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. $wR_2=[\Sigma_w(|F_o^2-F_c^2|)^2/\Sigma_w(|F_o^2|)^2]^{1/2}$ $w=1/[(\sigma(F_o)^2+(aP)^2]$; the value of aP was obtained from structure refinement.

report [1] of the diphenyltin dichloride adduct favoured 1:2 stoichiometry (analytical data clearly establish the stoichiometry). However, later efforts apparently using the same conditions invariably led to the exclusive isolation of the 1:1 adduct [2,3]. In the initial studies in this laboratory, reactions were carried out using 1:2 acid:base ratios in the hope of isolating the 1:2 adduct. A range of solvents was employed, including chloroform, which was the solvent employed in the earlier work that yielded the 1:2 adduct [1]. Elemental analytical data for products of these reactions were always consistent with 1:2 adduct formation. Identical 1:2 adducts were obtained from all solvents. Slow cooling of either a hot toluene or a hot ethanolic solution containing the acid–base reactants in a 1:2 molar ratio resulted in the formation of the crystalline 1:2 adduct. Best quality crystals were obtained from toluene, one of which was selected for a crystallographic study. The study confirmed the 1:2 stoichiometry of the adduct.

Having successfully established the existence of the 1:2 adduct, further work was directed towards the isolation of the 1:1 adduct. At that time all efforts at isolating a 1:1 adduct failed, the 1:2 adduct invariably being the isolated product (see Section 2). However, after an intervening six month period, further work was commenced and quite remarkably, it was no longer possible to reproduce the 1:2 adduct (for this reason Mössbauer data were not obtained for the 1:2 adduct), which was the sole product of the earlier work. All efforts now resulted in the formation of the 1:1 adduct. It proved possible to grow crystals of this adduct, even employing the conditions that were previously employed to grow crystals of the 1:2 adduct. A crystallographic study confirmed the 1:1 stoichiometry.

It is frequently the case that, while a 1:1 adduct is predominately, or indeed solely, the adduct which exists in solution, the 1:2 adduct is invariably the one which is isolated in the solid state. This is often attributed to the

1:2 adduct having the more favourable lattice energy. It would appear that very similar lattice energies for $SnPh_2Cl_2{\cdot}OPPh_3$ and $SnPh_2Cl_2{\cdot}2OPPh_3$ contributes to the uncertainty of isolating an adduct with a specific stoichiometry. The situation is highly reminiscent of the problem that is frequently encountered in the synthesis of polymorphic materials. Difficulty in isolating a specific polymorph when a compound is known to exist in two or more solid state modifications is frequently encountered. The persistence of a modification first encountered in a particular laboratory is well documented. This phenomenon, which is clearly applicable to the 1:1 and 1:2 adducts as indicated above, is not well understood but it is speculated that particles in the environment at the time of synthesis preferentially seed the growth of a specific phase.

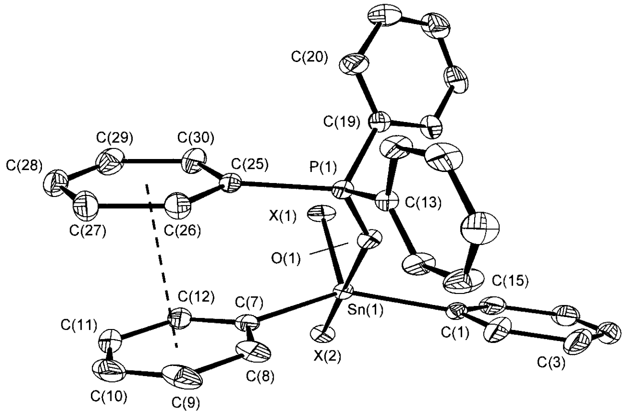

Fig. 1. The atomic labelling scheme for the asymmetric unit of $SnPh_2X_2{\cdot}OPPh_3$ Dashed line connects aromatic rings involved in π-interactions. Close ring contacts are as follows, for X = Cl (Br): C(7)–C(25), 3.71 (3.73); C(8)–C(26), 3.73 (4.06); C(9)–C(27), 4.02 (4.29); C(11)–C(29), 4.28 (3.99); C(12)–C(30) 4.01 (3.71) Å.

Table 3
Selected bond lengths (Å) and bond angles (°) for $SnPh_2X_2{\cdot}OPPh_3$ (X = Cl, Br)

	$SnPh_2Cl_2{\cdot}OPPh_3$	$SnPh_2Br_2{\cdot}OPPh_3$
Sn(1)–O(1)	2.278(2)	2.287(4)
Sn(1)–X(1)	2.3543(8)	2.5000(9)
Sn(1)–X(2)	2.4703(9)	2.6325(9)
Sn(1)–C(7)	2.119(3)	2.101(6)
Sn(1)–C(1)	2.126(3)	2.131(6)
P(1)–O(1)	1.501(2)	1.504(4)
P(1)–O(1)–Sn(1)	148.04(13)	148.3(3)
C(7)–Sn(1)–C(1)	131.05(13)	132.0(3)
C(7)–Sn(1)–O(1)	86.35(10)	86.0(2)
C(1)–Sn(1)–O(1)	84.35(10)	84.1(2)
C(7)–Sn(1)–X(1)	113.51(9)	113.06(19)
C(1)–Sn(1)–X(1)	113.53(9)	113.16(19)
O(1)–Sn(1)–X(1)	85.72(6)	87.11(11)
C(7)–Sn(1)–X(2)	96.88(9)	96.05(18)
C(1)–Sn(1)–X(2)	94.89(9)	94.76(18)
O(1)–Sn(1)–X(2)	176.25(6)	177.89(12)
X(1)–Sn(1)–X(2)	91.23(3)	91.67(3)

During the second phase of the present work, when only the 1:1 adduct of diphenyltin dichloride could be isolated, reactions of several other diorganotin dihalides and diisothiocyanates with the phosphine oxide were investigated. Reactions with $SnPh_2Br_2$ failed to yield anything other than the 1:1 adduct; the crystal structure of this adduct was determined. On the other hand, it did prove possible to isolate both 1:1 and 1:2 adducts for both $SnMe_2Cl_2$ and $SnBu^n_2Cl_2$. Only the 1:2 adducts were previously reported [1–5]. Only 1:2 adducts were isolated for the thiocyanate containing Lewis acids.

The trigonal bipyramidal geometry about tin in $SnPh_2Cl_2{\cdot}OPPh_3$ (see Fig. 1) is similar to that previously reported for the pyrazine and benzthiazole adducts of diphenyltin dichloride [23,24]. Sn–Cl bond lengths for the latter adducts compare favourably with those for $SnPh_2Cl_2{\cdot}OPPh_3$ and the C–Sn–C bond angles of 133.1(2) and 132.5(7)° for the pyrazine and benzthiazole adducts, respectively compare with a corresponding angle of 131.05(13)° for $SnPh_2Cl_2{\cdot}OPPh_3$. $SnPh_2Cl_2{\cdot}OPPh_3$ and $SnPh_2Br_2{\cdot}OPPh_3$ are isostructural and replacement of chloride by bromide has remarkably little effect on angles about tin (see Table 3), the biggest change been registered in the O–Sn–X (X = Cl or Br) bond angle which increases by 1.64°. The C–Sn–C bond angles of 131.05(13)° for the chloride compares with 132.0(3)° for the bromide. The bonding of the phosphine oxide to $SnPh_2Cl_2$ and $SnPh_2Br_2$ (monitored by the Sn–O–P bond angles, the Sn–O bond lengths and, in particular, the P–O bond lengths) is remarkably constant despite the difference in Lewis acidity of the organotin species. Thus, the crystallographic data account for the very similar ν(P=O) stretching frequencies for the two adducts (see Table 6).

The addition of the second mole of triphenylphosphine oxide to $SnPh_2Cl_2{\cdot}OPPh_3$ gives the centrosymmetric six-coordinated tin adduct (see Fig. 2). This appears to be the only occasion where crystallographic data have been made available for both a five-coordinated (1:1) and six-coordinated (1:2) diorganotin dihalide adduct with the same donor ligand. Notable changes in bond lengths occur as a result of the addition of the second mole of ligand (compare data in Tables 3 and 4). A detectable increase in Sn–C bond lengths is observed along with a decisive increase in Sn–Cl bond lengths. By contrast, the Sn–O bond length decreases from the value of 2.278(2) Å in the 1:1 adduct to a value of 2.214 Å in the 1:2 adduct. The decrease in Sn–O donor bond length can be attributed to increased $Sn^{\delta+}$–$Cl^{\delta-}$ character on formation of the 1:2 adduct. Despite this decrease in Sn–O bond length, the P–O bond length remains unchanged and this accounts for the fact that the ν(P=O) stretching frequency remains

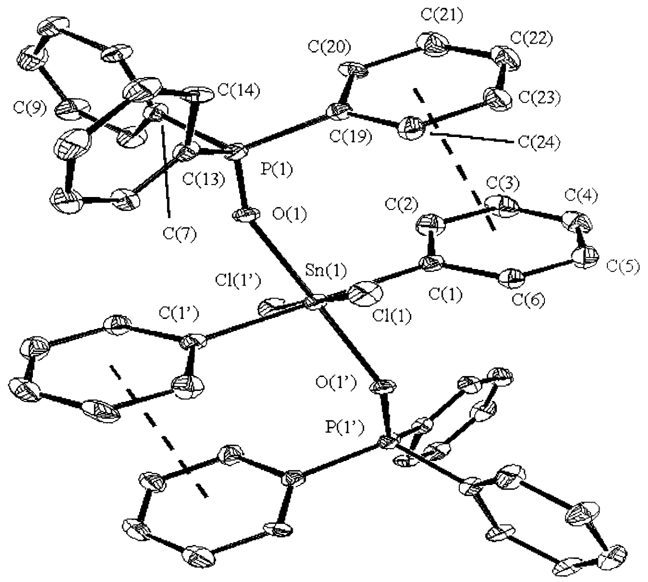

Fig. 2. The atomic labelling scheme for $SnPh_2Cl_2{\cdot}2OPPh_3$. Dashed lines connect aromatic rings involved in π-interactions. Close ring contacts (Å) are as follows: C(1)–C(19), 3.82; C(2)–C(20), 3.89; C(6)–C(24), 3.89.

Table 4
Selected bond lengths (Å) and angles (°) for $SnPh_2Cl_2{\cdot}2OPPh_3$

Sn(1)–C(1)	2.140(5)
Sn(1)–O(1)	2.214(4)
Sn(1)–Cl(1)	2.5537(10)
P(1)–O(1)	1.503(3)
C(1)–Sn(1)–O(1′)	91.61(17)
C(1′)–Sn(1)–O(1′)	88.39(17)
P(1)–O(1)–Sn(1)	145.66(18)
C(1)–Sn(1)–Cl(1)	90.20(11)
O(1′)–Sn(1)–Cl(1)	87.08(8)
O(1)–Sn(1)–Cl(1)	92.92(8)
C(1)–Sn(1)–Cl(1′)	89.80(11)
O(1′)–Sn(1)–Cl(1′)	92.92(8)
O(1)–Sn(1)–Cl(1′)	87.08(8)

essentially unchanged on addition of the second mole of triphenylphosphine oxide to diphenyltin dichloride (see Table 6).

Addition of triphenylphosphine oxide to $SbPh_2Cl_3$ produces the expected octahedral 1:1 adduct (see Fig. 3). The Sb–C bond lengths (see Table 5) are similar to the Sn-C bond lengths in $SnPh_2Cl_2{\cdot}2OPPh_3$ but the Sb–Cl bond lengths are, on average, shorter than the Sn–Cl bond lengths. In actual fact, there is a disparity in the Sb–Cl bond lengths that is difficult to rationalise, since the unique Sb–Cl bond (*trans* to the donor bond) has a length that falls between the lengths of the trans Sb–Cl bonds. Comparison of the M–O and P–O bond lengths and the ν(P–O) stretching frequency for $SbPh_2Cl_3{\cdot}OPPh_3$ [2.148(3), 1.514(3) Å and 1126 cm^{-1}, respectively) with those for the organotin halide phosphine oxide adducts whose structures are described in this paper [2.214(4)–2.287(4), 1.501(2)–1.504(4) Å, and 1138–1140 cm^{-1}, respectively) suggest greater Lewis acidity for $SbPh_2Cl_3$ than for $SnPh_2Cl_2$. This is contrary to the weak Lewis acidity of $SbPh_2Cl_3$ that is suggested by the long Sb–OH_2 donor bond in $SbPh_2Cl_3{\cdot}H_2O$ [14]. The anomalous nature of this latter donor bond will be discussed in a later paper. The longer P–O bond length for the antimony adduct compared to those for the tin adducts accounts for the ν(P=O) stretching frequency

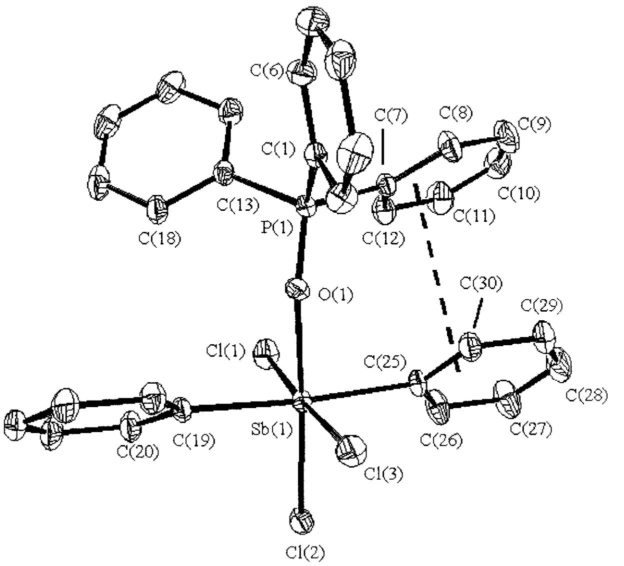

Fig. 3. The atomic labelling scheme for $SbPh_2Cl_3{\cdot}OPPh_3$. Dashed line connects aromatic rings involved in π-interactions. Close ring contacts (Å) are as follows: C(7)–C(25), 3.74; C(8)–C(30), 3.66; C(9)–C(29), 3.86; C(12)–C(26), 4.02.

Table 5
Selected bond lengths (Å) and angles (°) for $SbPh_2Cl_3{\cdot}OPPh_3$

Sb(1)–C(25)	2.133(4)
Sb(1)–C(19)	2.138(4)
Sb(1)–O(1)	2.148(3)
Sb(1)–Cl(1)	2.4071(12)
Sb(1)–Cl(2)	2.4224(12)
Sb(1)–Cl(3)	2.4787(12)
P(1)–O(1)	1.514(3)
C(25)–Sb(1)–C(19)	172.80(15)
C(25)–Sb(1)–O(1)	88.74(15)
C(19)–Sb(1)–O(1)	84.89(13)
O(1)–Sb(1)–Cl(2)	177.47(8)
Cl(1)–Sb(1)–Cl(3)	176.03(5)
P(1)–O(1)–Sb(1)	152.71(18)
C(25)–Sb(1)–Cl(1)	91.11(13)
C(19)–Sb(1)–Cl(1)	92.18(13)
O(1)–Sb(1)–Cl(1)	89.42(9)
C(25)–Sb(1)–Cl(2)	93.73(13)
C(19)–Sb(1)–Cl(2)	92.62(11)
Cl(1)–Sb(1)–Cl(2)	91.05(5)
C(25)–Sb(1)–Cl(3)	87.14(13)
C(19)–Sb(1)–Cl(3)	89.17(13)
O(1)–Sb(1)–Cl(3)	86.98(9)
Cl(2)–Sb(1)–Cl(3)	92.62(5)

Table 6
Selected IR and ^{119}Sn Mössbauer data for adducts of triphenylphosphine oxide

	δ [a] (mm s^{-1})	Δ [a] (mm s^{-1})	ν(P=O) (cm^{-1})
$SnPh_2Cl_2 \cdot OPPh_3$	1.25	3.04	1140
$SnPh_2Cl_2 \cdot 2OPPh_3$			1139
$SnPh_2Br_2 \cdot OPPh_3$	1.35	3.08	1138
$SnMe_2Cl_2 \cdot OPPh_3$	1.39	3.14	1153
$SnMe_2Cl_2 \cdot 2OPPh_3$	1.44	4.14	1139
$SnBu^n_2Cl_2 \cdot OPPh_3$	1.16	3.46	1156
$SnBu^n_2Cl_2 \cdot 2OPPh_3$	1.60	4.09	1150
$SnPh_2(NCS)_2 \cdot 2OPPh_3$	1.26	3.94	1140
$SnBu^n_2(NCS)_2 \cdot 2OPPh_3$	1.59	4.32	1138
$SbPh_2Cl_3 \cdot OPPh_3$			1126

[a] ± 0.03 mm s^{-1}.

data in Table 6, e.g. for the antimony adduct ν(P=O) is observed at 1126 cm^{-1} while for $SnPh_2Cl_2 \cdot 2OPPh_3$ it is observed at 1139 cm^{-1}.

There is an interesting structural feature common to all of the adducts described above in that, in each, a phenyl ring of the phosphine oxide is involved in π-aromatic interactions with a phenyl attached to the metal. In the case of the tin 1:1 adducts and the antimony adduct, only one of the phenyl groups attached to the metal is involved in such interactions (with a phenyl of the phosphine oxide) but in the case of the tin 1:2 adduct both phenyl groups attached to the metal are involved (as a result of their symmetry relationship). The presence of the interactions is strongly suggested both by the short carbon–carbon contacts between the rings and the relative positioning of the rings (see Figs. 1–3) [25].

The Mössbauer quadrupole splittings of 3.04 and 3.08 mm s^{-1} for $SnPh_2Cl_2 \cdot OPPh_3$ and $SnPh_2Br_2 \cdot OPPh_3$, respectively are totally consistent with the their trigonal bipyramidal structures and the lower chemical shift of the chloride is consistent with the electronegativity order $Cl > Br$. Unlike 1:1 adducts of $SnPh_2Cl_2$, 1:1 adducts of $Sn(alkyl)_2Cl_2$ tend to exhibit intermolecular Sn–Cl contacts thus giving tin octahedral (or pseudo octahedral) coordination geometry. However, the quadrupole splitting of 3.14 mm s^{-1} for $SnMe_2Cl_2 \cdot OPPh_3$ is consistent with a trigonal bipyramidal structure with no intermolecular Sn-Cl contacts. For example, the true trigonal bipyramidal 1:1 aqua adduct of dimethyltin dichloride in $SnMe_2Cl_2 \cdot H_2O$/ Ni(MeOsalen) [H_2MeOsalen = *N*,*N*′-bis(3-methoxysalicylidene)ethane-1,2-diamine] exhibits almost identical Mössbauer parameters ($\Delta = 3.12$ mm s^{-1} and $\delta = 1.35$ mm s^{-1} [26]) to those of $SnMe_2Cl_2 \cdot OPPh_3$. However, the considerably greater quadrupole splitting of 3.46 mm s^{-1} for $SnBu^n_2Cl_2 \cdot OPPh_3$ points to the presence of intermolecular Sn–Cl bonds, just as a similar quadrupole splitting of 3.48 mm s^{-1} for the mono aqua adduct of dimethyltin dichloride in $SnMe_2Cl_2 \cdot H_2O$/ Ni(MeOsal - 1,2pn) [H_2MeOsal - 1,2pn = *N*,*N*′ - bis(3-methoxysalicylidene)propane-1,2-diamine] reflected the presence of the intermolecular Sn–Cl interactions [26]. The large Mössbauer quadrupole splittings ranging from 3.94–4.32 mm s^{-1} for the 1:2 adducts clearly point to trans organo-octahedral tin complexes. The point should also be made that the large increases in quadrupole splitting associated with the addition of the second phosphine oxide ligand to both $SnMe_2Cl_2 \cdot OPPh_3$ and $SnBu^n_2Cl_2 \cdot OPPh_3$ clearly establish that the extra phosphine oxide is coordinated to tin rather than having merely a lattice role.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 143186 ($SbPh_2Cl_3 \cdot OPPh_3$), 143187 ($SnPh_2Cl_2 \cdot 2OPPh_3$), 143188 ($SnPh_2Cl_2 \cdot OPPh_3$), 143189 ($SnPh_2Br_2 \cdot OPPh_3$). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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