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Diorganotin(IV) derivatives of arenephosphinothiol ligands. The crystal structure of $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ and $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$

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Abstract

The diorganotin complexes, $[Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ (**1**), $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ (**2**), $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**3**) and $[Ph_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**4**), have been prepared by reacting the corresponding diorganotin(IV) chloride with $2\text{-}(Ph_2P)C_6H_4SH$ and $2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH$. Compound **2** crystallises in the monoclinic space group and the tin atom is tetrahedrally coordinated to two ligands acting as monodentate through the thiolate sulphur atoms. Compound **3** also crystallises in the monoclinic space group and, in this compound, the tin atom is octahedrically coordinated $[SnC_2O_2S_2]$. Spectral data for the complexes (IR, NMR, FAB and Mössbauer spectra) are discussed and related to the structural information. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organotin complexes; Tin complexes; Phosphinothiolate complexes; Crystal structure

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1. Introduction

Interest in the coordination chemistry of metal–sulphur complexes arises from their potential relevance to active sites in metalloenzymes and also from their ability to adopt various nuclearities and significant structural complexity [1–3]. In addition, interaction of toxic main group metals with biological systems frequently involves bonding to enzyme sulfhydryl groups and main group metal complexes are of some interest in the design of detoxification reagents [4]. This interest has led us to study organotin compounds that in a biological medium react with thiol groups in relevant molecules, yielding products characterised by Sn–S bonds. As a result of our continuing interest in the interaction of main group metals with thiolate ligands, we report on the synthesis and characterisation of complexes of dimethyl and diphenyltin(IV) with arenephosphinothiol ligands incorporating both thiolate sulphur and tertiary phosphorous atoms as donor groups. The crystal structures of $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ and $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ are also reported.

2. Experimental

All manipulations were carried under an inert atmosphere of dry nitrogen. Dimethyltin dichloride and diphenyltin dichloride (Aldrich) were used as supplied. Syntheses of ligands were carried out using standard literature procedures with some minor modifications [4]. Elemental analyses were performed in a Carlo–Erba EA 1108 microanalyser. IR spectra were recorded in KBr disks using a Bruker IFS 66V spectrophotome-

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ter. ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker AMX300 MHz instrument using $CDCl_3$ as solvent. ^{1}H chemical shifts were determined against TMS and ^{31}P chemical shifts against 85% H_3PO_4 as internal standard. ^{119}Sn-NMR spectra were recorded on a Bruker AMX500 instrument and referred to Me_4Sn as external reference. The mass spectra were recorded on a Kratos MS50TC spectrophotometer connected to a DS90 data system, using 3-nitrobenzyl alcohol (3-NBA) a matrix material. The Mössbauer spectra were recorded at 80 K on a constant acceleration apparatus with a $Ca^{119}SnO_3$ source.

2.1. Synthesis of [$Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2$] (**1**)

To a refluxing solution of 2-(Ph_2P)C_6H_4SH (0.200 g, 0.680 mmol) in 50 ml of methanol was added a solution of dimethyltin dichloride (0.075 g, 0.340 mmol) in 15 ml of methanol. To the mixture NEt_3 (0.071 g, 0.700 mmol) was added. The solution was stirred at room temperature (r.t.) for 4 h, filtered and evaporated to give a white crystalline solid (0.212 g, 85%). M.p.: 99°C. Anal. Calc. for $C_{38}H_{34}P_2S_2Sn$ (mol. wt. 735): C, 62.04; H, 4.62; S, 8.70. Found: C, 61.56; H, 4.62; S, 8.62%. IR (KBr, cm^{-1}): 3050(m), 2938(m), 2678(m), 1570(m), 1477(m), 1433(m), 1249(w), 1099(m), 748(s), 696(s), 506(s). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.9–6.6 (m, 28H), 0.9 (s, 6H). ^{13}C-NMR ($CDCl_3$, ppm): δ 143–125, 8.6(s). ^{31}P-NMR ($CDCl_3$, ppm): δ −14.0. ^{119}Sn-NMR ($CDCl_3$, ppm): δ 75.

2.2. Synthesis of [$Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2$] (**2**)

The same procedure was used for the synthesis of the diphenyltin derivative as that described for **1**. A solution of Ph_2SnCl_2 (0.117 g, 0.340 mmol), 2-(Ph_2P)C_6H_4SH (0.200 g, 0.680 mmol) and NEt_3 (0.071g, 0.700 mmol) in 40 ml of methanol was refluxed for 3 h. The solution was concentrated to give monocrystals suitable for X-ray studies. (0.236 g, 81%). M.p.: 180°C. Anal. Calc. for $C_{48}H_{38}P_2S_2Sn$ (mol. wt. 859): C, 67.05; H, 4.42; S, 7.45. Found: C, 67.06; H, 4.26; S, 7.38%. IR (KBr, cm^{-1}): 1573(m), 1479(m), 1433(s), 1250(w), 1098(m), 745(s), 695(s), 508(s). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.9–6.5 (m). ^{13}C-NMR ($CDCl_3$, ppm): δ 142–126. ^{31}P-NMR ($CDCl_3$, ppm): δ −15.3. ^{119}Sn-NMR ($CDCl_3$, ppm): δ −60.

2.3. Synthesis of [$Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)\text{-}C_6H_3S\}_2$] (3)

A solution of Me_2SnCl_2 (0.043 g, 0.196 mmol), 2-(Ph_2PO)-6-(Me_3Si)C_6H_3SH (0.150 g, 0.393 mmol) and NEt_3 (0.040g, 0.400 mmol) in 30 ml of methanol was stirred and refluxed for 4 h. The resulting solution was evaporated to give white crystals suitable for X-ray studies (0.14 g, 78%). M.p.: 190°C. Anal. Calc. for $C_{44}H_{50}P_2O_2S_2Si_2Sn$ (mol. wt. 911): C, 57.96; H, 5.49; S, 7.02. Found: C, 57.75; H, 5.49; S, 6.99%. IR (KBr, cm^{-1}): 2939(m), 2740(m), 2677(s), 2491(m), 1545(m), 1475(m), 1436(m), 1357(m), 1131(s), 1044(m), 852(s), 794(m), 695(s), 556(s). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.8–6.5 (m, 26H), 1.0 (s, 6H), 0.5 (s, 9H), 0.4 (s, 9H). ^{13}C-NMR ($CDCl_3$, ppm): δ 150–123, 8.5(s), 0.01(s), −0.01(s). ^{31}P-NMR ($CDCl_3$, ppm): δ 38.8, 35.1. ^{119}Sn-NMR ($CDCl_3$, ppm): δ −93.

2.4. Synthesis of [$Ph_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)\text{-}C_6H_3S\}_2$] (4)

A solution containing 0.067 g (0.196 mmol) of diphenyltin dichloride, 0.15 g (0.393 mmol) of 2-diphenylphosphinyl-6-trimethylsilylbenzenethiol and 0.040 g (0.400 mmol) of triethylamine in 30 ml of methanol was refluxed for 3 h. The resulting solution was evaporated to give white needles (0.17 g, 84%). M.p.: 245°C. Anal. Calc. for $C_{54}H_{54}P_2O_2S_2Si_2Sn$ (mol. wt. 1035): C, 62.61; H, 5.22; S, 6.17. Found: C, 62.19; H, 5.29; S, 6.13%. IR (KBr, cm^{-1}): 2941(m), 2678(m), 2492(m), 1545(m), 1437(m), 1357(m), 1133(s), 1048(m), 852(s), 729(m), 694 (s), 556(s). ^{1}H-NMR ($CDCl_3$, ppm): δ 8.1–6.5 (m, 36H), 0.4 (s, 9H), 0.3 (s, 9H). ^{13}C-NMR ($CDCl_3$, ppm): δ 150–123, 0.09(s), −0.01(s). ^{31}P-NMR ($CDCl_3$, ppm): δ 41.5, 35.2. ^{119}Sn-NMR ($CDCl_3$, ppm): δ −260.

Table 1
Crystallographic data for [$Ph_2Sn\{2\text{-}(Ph_2P)C_6H_3S\}_2$] (**2**) and [$Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2$] (**3**)

	2	**3**
Chemical formula	$C_{48}H_{38}P_2S_2Sn$	$C_{44}H_{50}P_2O_2S_2Si_2Sn$
Molecular weight	859.53	911.85
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystalline system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Cell constants		
a (Å)	18.8213(3)	10.0595(2)
b (Å)	9.7058(2)	19.1870(4)
c (Å)	23.84480(10)	23.9621(4)
β (°)	107.233(2)	95.390(1)
V (Å^3)	4160.32(11)	4604.5(2)
Z	4	4
Absorption coefficient (mm^{-1})	0.824	0.801
Size (mm)	0.15 × 0.10 × 0.08	0.30 × 0.20 × 0.15
Collected reflections	25117	29138
Independent reflections	9688	10890
R	0.0602	0.0436
R_w	0.1065	0.1086

2.5. *X-ray crystallography*

Compounds **2** and **3** were studied on a Siemens SMART system using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). All data collections were carried out at r.t. The crystal parameters and other experimental details of the data collection are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Section 4. The structures were solved by direct methods [5]. Neutral atomic scattering factors were taken from Cromer and Waber [6] and anomalous dispersion corrections were taken from those of Creagh and McAuley [7]. All calculations were performed using SHELXTL [8] for compound **3** and SHELXL-97 [9] for compound **2**. Non-hydrogen atoms were refined anisotropically. No anomalies were encountered in the refinements of any of the structures. Atomic positional parameters and isotropic temperature factors for the structures are presented in Tables 2 and 3.

3. Results and discussion

The reactions between Me_2SnCl_2, Ph_2SnCl_2 and the arenephosphinothiol ligands, [RP–SH], lead to white air stable crystalline compounds, whose analytical data are concordant with a general formulation $[R_2Sn(RP\text{–}S)_2]$.

3.1. *Crystal structure of* $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ (**2**)

The crystal structure of $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_3S\}_2]$ is shown in Fig. 1, together with the atomic numbering scheme. Selected bond distances and angles are in Table 4. The compound consists of discrete molecules with the tin atom bonded to two carbon atoms from the phenyl groups and two sulphur atoms from two monoanionic ligands. The phosphorus atoms do not interact with the metal. It is tempting to speculate that the steric hindrance produced by the phenyl groups precludes bidentate coordination by the ligand.

The environment around the tin atom is tetrahedrally distorted with bond angles around the metal of 126.7(2)°, C–Sn–C, and 83.74(4)°, S(2)–Sn–S(1), in both cases far from those expected for the idealized values. The Sn–S bond distances (2.5034(12) and 2.4941(13) Å) are close to the sum of covalent radii (2.42 Å) [10].

3.2. *Crystal structure of* $[Me_2Sn\{2\text{-}(Ph_2PO)6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**3**)

The molecular structure of $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ is shown in Fig. 2. A selection of bond distances and angles are shown in Table 5. In this compound the tin atom is in a distorted octahedral environment coordinated by two methyl groups and two monoanionic bidentate ligands, which coordinate to the metal through the thiolato sulphur and the oxygen atoms.

Table 2
Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ (**2**)

	x	*y*	*z*	U_{eq}
Sn(1)	9627(1)	8001(1)	2242(1)	25(1)
S(1)	9035(1)	9071(1)	1264(1)	37(1)
S(2)	9239(1)	10188(1)	2626(1)	29(1)
P(1)	9997(1)	6309(1)	1304(1)	29(1)
P(2)	9804(1)	8024(1)	3684(1)	26(1)
C(1)	8902(3)	6378(5)	2330(2)	28(1)
C(2)	9143(3)	5191(5)	2664(2)	36(1)
C(3)	8631(4)	4219(6)	2736(3)	49(2)
C(4)	7874(4)	4459(7)	2483(3)	54(2)
C(5)	7630(3)	5621(7)	2155(2)	48(2)
C(6)	8145(3)	6561(6)	2069(2)	34(1)
C(7)	10814(2)	8044(6)	2596(2)	33(1)
C(8)	11190(3)	9284(7)	2602(3)	50(2)
C(9)	11964(4)	9328(11)	2810(3)	82(3)
C(10)	12351(4)	8159(14)	3025(4)	98(3)
C(11)	12000(4)	6907(12)	3037(3)	88(3)
C(12)	11214(3)	6855(8)	2811(2)	55(2)
C(13)	8695(3)	7702(5)	757(2)	32(1)
C(14)	9100(3)	6498(5)	742(2)	31(1)
C(15)	8787(3)	5477(6)	315(2)	38(1)
C(16)	8105(3)	5695(7)	−95(2)	44(1)
C(17)	7712(3)	6907(7)	−91(2)	45(1)
C(18)	8004(3)	7901(6)	337(2)	40(1)
C(19)	10223(3)	4493(5)	1266(2)	32(1)
C(20)	10705(3)	3981(5)	970(2)	34(1)
C(21)	10845(3)	2584(5)	953(2)	38(1)
C(22)	10508(4)	1663(6)	1242(2)	48(2)
C(23)	10020(4)	2157(6)	1535(3)	58(2)
C(24)	9884(4)	3550(6)	1552(2)	47(2)
C(25)	10659(3)	7225(5)	1002(2)	29(1)
C(26)	11407(3)	7272(6)	1342(2)	41(1)
C(27)	11925(3)	7963(7)	1137(3)	56(2)
C(28)	11709(4)	8624(7)	598(3)	60(2)
C(29)	10976(3)	8596(7)	263(3)	54(2)
C(30)	10454(3)	7900(6)	464(2)	42(1)
C(31)	9988(2)	10619(5)	3256(2)	26(1)
C(32)	10228(2)	9742(5)	3750(2)	25(1)
C(33)	10815(3)	10180(5)	4229(2)	33(1)
C(34)	11160(3)	11445(6)	4236(2)	41(1)
C(35)	10918(3)	12309(5)	3747(2)	39(1)
C(36)	10338(3)	11903(5)	3266(2)	34(1)
C(37)	10310(2)	7167(5)	4374(2)	27(1)
C(38)	10196(3)	7436(6)	4916(2)	40(1)
C(39)	10576(3)	6719(7)	5415(2)	52(2)
C(40)	11075(3)	5717(6)	5388(3)	53(2)
C(41)	11197(3)	5408(6)	4855(3)	51(2)
C(42)	10818(3)	6131.(S)	4351(2)	41(1)
C(43)	8897(2)	8313(5)	3815(2)	28(1)
C(44)	8366(3)	7279(5)	3642(2)	32(1)
C(45)	7683(3)	7365(6)	3760(2)	40(1)
C(46)	7527(3)	8507(7)	4049(2)	48(2)
C(47)	8047(3)	9561(7)	4215(2)	47(2)
C(48)	8733(3)	9477(6)	4100(2)	37(1)

The four donor atoms of the two ligands are located in equatorial positions with the S_2O_2 grouping deviating from planarity, O(1) and S(2) 0.024 Å above and S(1) and O(2) 0.023 Å below the best plane defined by the donor atoms. The oxygen atoms are in a *cis* arrangement. The bond angles involving atoms *trans* to each other (173.90(5) and 172.89(6)°) are close to the theoretical value (180°). The two methyl groups are *trans* to each other, with a Me–Sn–Me bond angle of 152.8(2)°. The deviation from the regular geometry is probably due to steric hindrance produced by the trimethylsilyl groups.

Table 3
Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for [$Me_2Sn\{2\text{-}(Ph_2PO)6\text{-}(Me_3Si)C_6H_3S\}_2$] (**3**)

	x	y	z	U_{eq}
Sn(1)	2755(1)	4962(1)	2560(1)	24(1)
S(1)	3079(1)	4172(1)	3419(1)	27(1)
S(2)	3611(1)	4012(1)	1932(1)	25(1)
P(1)	1436(1)	5523(1)	3791(1)	27(1)
P(2)	3165(1)	5366(1)	1163(1)	22(1)
Si(1)	1816(1)	2577(1)	3475(1)	31(1)
Si(2)	6559(1)	3239(1)	2130(1)	41(1)
O(1)	1910(2)	5751(1)	3243(1)	33(1)
O(2)	2556(2)	5628(1)	1672(1)	28(1)
C(1)	693(3)	4831(2)	2314(1)	35(1)
C(2)	4496(4)	5576(2)	2728(2)	39(1)
C(3)	1443(3)	4072(2)	3627(1)	26(1)
C(4)	706(3)	4658(2)	3784(1)	27(1)
C(5)	−588(4)	4572(2)	3931(1)	35(1)
C(6)	−1146(4)	3914(2)	3937(2)	39(1)
C(7)	−414(4)	3339(2)	3800(2)	35(1)
C(8)	890(3)	3398(2)	3643(1)	28(1)
C(9)	3361(4)	2478(2)	3968(2)	46(1)
C(10)	691(4)	1820(2)	3575(2)	46(1)
C(11)	2207(4)	2541(2)	2732(2)	43(1)
C(12)	156(4)	6114(2)	3986(1)	32(1)
C(13)	−67(4)	6250(2)	4537(2)	47(1)
C(14)	−1083(5)	6695(2)	4666(2)	54(1)
C(15)	−1875(5)	7007(3)	4245(2)	55(1)
C(16)	−1663(6)	6878(4)	3696(2)	85(2)
C(17)	−646(5)	6438(3)	3568(2)	65(2)
C(18)	2706(4)	5555(2)	4370(1)	34(1)
C(19)	2621(4)	5166(3)	4853(2)	48(1)
C(20)	3544(5)	5281(3)	5318(2)	68(2)
C(21)	4518(6)	5770(3)	5298(2)	79(2)
C(22)	4619(6)	6143(3)	4820(3)	76(2)
C(23)	3721(5)	6042(2)	4351(2)	54(1)
C(24)	4987(3)	4406(2)	1649(1)	23(1)
C(25)	4814(3)	5008(2)	1310(1)	23(1)
C(26)	5919(3)	5336(2)	1113(1)	28(1)
C(27)	7186(3)	5062(2)	1240(2)	35(1)
C(28)	7350(3)	4450(2)	1549(2)	33(1)
C(29)	6271(3)	4105(2)	1760(1)	27(1)
C(30)	8364(5)	3003(3)	2115(3)	77(2)
C(31)	6186(5)	3269(3)	2877(2)	61(1)
C(32)	5548(5)	2555(2)	1724(2)	60(1)
C(33)	2142(3)	4730(2)	772(1)	24(1)
C(34)	764(3)	4761(2)	796(1)	32(1)
C(35)	−64(4)	4296(2)	494(2)	42(1)
C(36)	456(4)	3803(2)	159(2)	45(1)
C(37)	1824(4)	3774(2)	125(2)	43(1)
C(38)	2669(3)	4229(2)	431(1)	31(1)
C(39)	3282(3)	6075(2)	672(1)	25(1)
C(40)	3002(4)	6750(2)	840(2)	36(1)
C(41)	3023(5)	7294(2)	459(2)	48(1)
C(42)	3304(4)	7171(2)	−86(2)	45(1)
C(43)	3598(4)	6504(2)	−254(2)	40(1)
C(44)	3571(4)	5957(2)	123(1)	33(1)

The Sn–S bond distances in the compound (2.5627(8) and 2.5513(8) Å) are slightly higher than the sum of the covalent radii for the tin and sulphur atoms (2.42 Å) and similar to those found in other hexacoordinate organotin compounds containing thiolate ligands. Thus, the values do not differ much from those found in [$Me_2Sn(pyt)_2$] (2.487 Å) [11], where pyt stands for pyridine-2-thiolate. On the other hand, the bond distances Sn–C (2.118(3) and 2.117(3) Å) are characteristic of [$R_2Sn(bidentate)_2$] complexes [12].

3.3. IR spectra

The IR spectra of these complexes do not show the band associated with ν(S–H), which in the free ligands appears in the range 2550–2400 cm^{-1}. This is indicative of the anionic form of the ligand in the complexes. In the case of the complexes containing the ligand 2-(Ph_2PO)-6-(Me_3Si)C_6H_3SH, the spectra also show intense bands at 855–840 and 1130–1125 cm^{-1} due to ν(Si–C) and ν(P=O), respectively.

3.4. NMR spectra

In all cases, the ^1H-NMR spectra show that the signal due to the S–H group, which in the free ligands appears at about δ 4.1 ppm is absent. This confirms the IR conclusion that the ligands are in the anionic form in the complexes. The ^1H-NMR spectrum of [$Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2$] shows a signal at δ 0.9 ppm (6H) as a singlet, accompanied by satellites due to the ^1H–^{119}Sn coupling that corresponds to the hydrogen atoms of the methyl of the Me_2Sn moiety. The ^{13}C-NMR spectrum shows the signal of the methyl groups at δ 8.6 ppm. The ^{31}P spectrum displays a signal at − 14.0 ppm, the same position as that of the free ligand. This shows that, in solution, the phosphorous atoms are not coordinated to the metal. On the other hand, the ^{119}Sn-NMR spectrum shows a signal at δ 75 ppm, a value in the range found for tetrahedral complexes of tin, and confirms that the phosphorous atoms are not coordinated to the tin atom, and that the tin is in a tetrahedral [SnC_2S_2] environment.

The ^{31}P-NMR spectrum of [$Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2$] again shows a signal at − 15.3 ppm, which is practically the same value as the chemical shift in the free ligand (− 14.6 ppm) showing that the phosphorus atom is not coordinated to the metal. The X-ray structure of the compound in the solid state confirms this conclusion. The ^{119}Sn spectrum shows a signal at δ − 60 ppm, a value in the range for four-coordinate tin compounds.

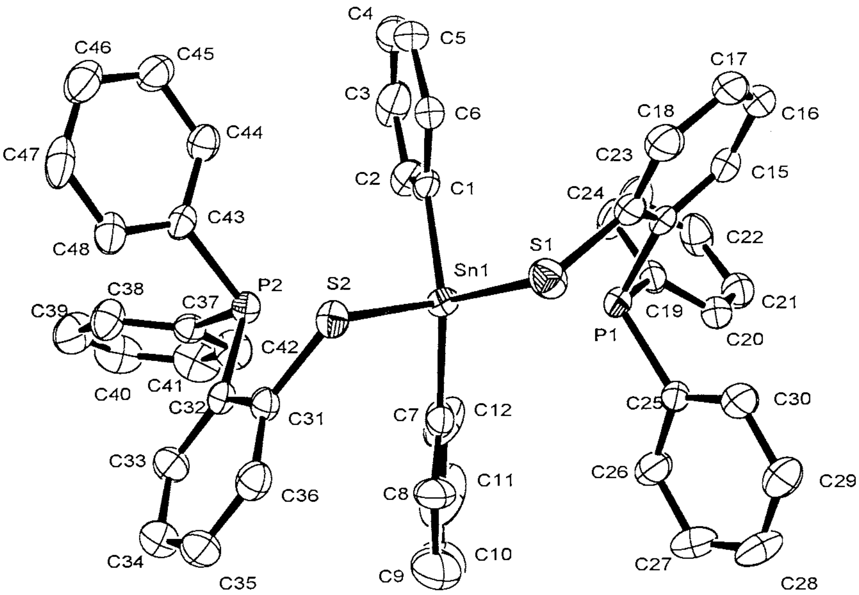

Fig. 1. Molecular structure of [$Ph_2Sn\{2-(Ph_2P)C_6H_4S\}_2$] (**2**).

It is worth nothing, that in the case of [$Me_2Sn\{2-(Ph_2P)C_6H_4S\}_2$] and [$Ph_2Sn\{2-(Ph_2P)C_6H_4S\}_2$] the phosphorus signal is accompanied by satellites due to $^{31}P-^{119}Sn$ long-distance coupling.

The ^1H-NMR spectrum of [$Me_2Sn\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_2$] shows two singlet signals integrating to nine protons at high field at δ 0.5 and 0.4 ppm due to two different trimethylsilyl groups. This inequivalence is confirmed by the presence of two signals at 0.01 and -0.01 ppm in the ^{13} C-NMR spectrum. These observations suggest the presence of two bidentate ligands in the complex. The ^{31}P-NMR spectrum shows two signals at δ 38.79 and 35.14 ppm, again demonstrating the presence of two inequivalent ligands. The ^{119}Sn-NMR spectrum shows a signal at δ -93.31 ppm, which is in the range for six-coordinate tin compounds. Taken as a whole, the above results show that in [$Me_2Sn\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_2$] the tin atom is in an octahedral [$SnC_2O_2S_2$] environment. This structure contrasts the tetrahedral environment around the metal in [$Me_2Sn\{2-(Ph_2P)C_6H_4S\}_2$], an observation which can be rationalized as the result of minimized steric congestion resulting from the insertion of the oxygen atom donor between the tin and the phosphorous so as to remove the organic substituents from the vicinity of the metal. These conclusions are supported by the X-ray diffraction structure in the solid state.

The ^1H-NMR spectrum of [$Ph_2Sn\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_2$] again shows two singlets at δ 0.4 and 0.3 ppm due to the hydrogen atoms of two non-equivalent silyl groups. The ^{13}C-NMR spectrum shows the signals of these groups at δ 0.09 and -0.01 ppm. As in the case of [$Me_2Sn\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_2$], the ^{31}P-NMR spectrum shows two signals at δ 41.52 and

Table 4
Selected bond distances (Å) and angles (°) for [$Ph_2Sn\{2-(Ph_2P)C_6H_4S\}_2$] (**2**)

Bond distances			
Sn(1)–C(1)	2.133(4)	Sn(1)–C(7)	2.142(5)
Sn(1)–S(1)	2.4941(13)	Sn(1)–S(2)	2.5034(12)
P(1)–C(14)	1.826(5)	P(1)–C(19)	1.821(5)
P(1)–C(25)	1.841(4)	P(2)–C(32)	1.835(5)
P(2)–C(37)	1.838(5)	P(2)–C(43)	1.845(4)
Bond angles			
C(1)–Sn(1)–C(7)	126.7(2)	C(1)–Sn(1)–S(1)	106.08(13)
C(7)–Sn(1)–S(1)	119.04(14)	C(1)–Sn(1)–S(2)	109.05(12)
C(7)–Sn(1)–S(2)	102.87(14)	S(1)–Sn(1)–S(2)	83.74(4)

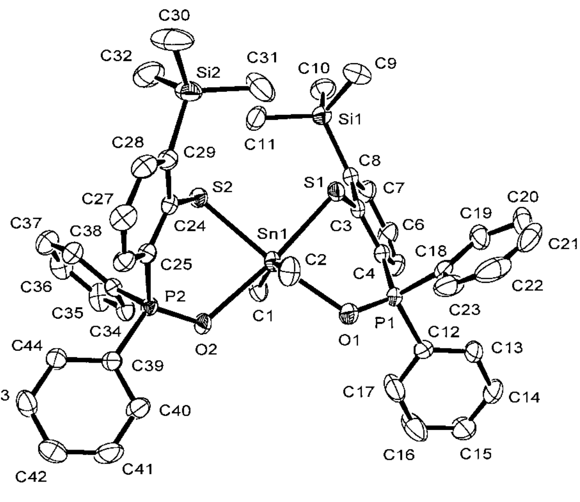

Fig. 2. Molecular structure of [$Me_2Sn\{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S\}_2$] (**3**).

Table 5
Selected bond distances (Å) and angles (°) for $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**3**)

Bond distances			
Sn(1)–C(1)	2.117(3)	Sn(1)–C(2)	2.118(3)
Sn(1)–O(1)	2.441(2)	Sn(1)–O(2)	2.475(2)
Sn(1)–S(1)	2.5513(8)	Sn(1)–S(1)	2.5627(8)
P(2)–O(2)	1.502(2)	P(1)–O(1)	1.504(2)
Bond angles			
C(1)–Sn(1)–C(2)	152.8(2)	C(1)–Sn(1)–O(1)	82.30(12)
C(2)–Sn(1)–O(1)	82.00(12)	C(1)–Sn(1)–O(2)	79.82(11)
C(2)–Sn(1)–O(2)	82.76(12)	O(1)–Sn(1)–O(2)	104.49(8)
C(1)–Sn(1)–S(1)	101.65(10)	C(2)–Sn(1)–S(1)	97.90(11)
O(1)–Sn(1)–S(1)	81.60(6)	O(2)–Sn(1)–S(1)	173.90(5)
C(1)–Sn(1)–S(2)	97.30(10)	C(2)–Sn(1)–S(2)	100.95(11)
O(1)–Sn(1)–S(2)	172.89(6)	O(2)–Sn(1)–S(2)	82.36(5)
S(1)–Sn(1)–S(2)	91.56(3)		

35.21 ppm. On the other hand, the ^{119}Sn-NMR spectrum shows a signal at δ -260 ppm. This value is compatible with the presence of a six-coordinate tin atom. Consequently, it is proposed that in $[Ph_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ the tin atom is in an octahedral $[SnC_2O_2S_2]$ environment.

3.5. Mössbauer spectra

The Mössbauer parameters for these compounds are collected in Table 6. The quadrupole splitting data for $[Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ and $[Ph_2Sn\{2\text{-}(Ph_2P)\text{-}C_6H_4S\}_2]$ are compatible with a tetrahedral arrangement around the metal, although the value for $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ seems to be somewhat high and at the limit of the normally accepted interval for a tetrahedral compound, this geometry having been confirmed by X-ray diffraction. The parameters for $[Me_2Sn\{2(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ are reasonable for the distorted octahedral structure found by X-ray diffraction.

The isomer shift of the compound $[Ph_2Sn\{2\text{-}(Ph_2PO)6\text{-}(Me_3Si)C_6H_3S\}_2]$ is compatible with a *trans* octahedral structure, but the value of the quadrupole splitting is too low for a six-coordinate *trans* tin compound.

3.6. Mass spectra

The tin complexes were also characterized by mass spectroscopy using the technical FAB (m/z) of the positive ion in 2-nitrobenzyl alcohol (NBA) as base. In all cases the molecular peak, $[M]^+$, for each compound is observed, as well as other peaks corresponding to fragments of the parent peak from the loss of different groups of the compound.

In the spectrum of the compound $[Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ the molecular ion peak is observed at m/z 735, as well as a peak at m/z 442, corresponding to the $[Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}]^+$ ion. In the spectrum of $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ the molecular ion m/z 859 is also observed, as well as a peak at m/z 567, corresponding peak to the $[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}]^+$ ion, and also a peak assigned to the ligand at m/z 293.

For $[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, the molecular ion peak is observed at m/z 911, as well as peaks at m/z 531 and m/z 383 corresponding to the $[Me_2Sn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}]^+$ ion and protonated ligand, respectively. For the $[Ph_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ complex, the molecular ion at m/z 1035 is observed, as well as the peak corresponding to the $[Me_2Sn\{2\text{-}(Ph_2PO)6\text{-}(Me_3Si)C_6H_3S\}]^+$ ion at m/z 655.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic data Centre, CCDC nos. 127416 for compound **2** and 127300 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 6
Mössbauer parameters for the complexes [a]

Compound	δ [b] (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	$\Gamma_{2/1}$
$[Me_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$	1.54	2.35	0.80	1.11
$[Ph_2Sn\{2\text{-}(Ph_2P)C_6H_4S\}_2]$	1.46	3.21	0.75	0.96
$[Me_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$	1.54	2.99	0.83	1.14
$[Ph_2Sn\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$	1.43	2.60	0.81	0.98

[a] Spectra were recorded at 80 K.

[b] Relative to SnO_2 at room temperature.

Acknowledgements

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