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Synthesis and spectroscopic characterization of dimethyl/di(*n*-butyl)tin(IV)bis(*O,O′*-ditolyl dithiophosphate) complexes. Crystal structures of $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ and $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$†

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Organotin(IV) complexes of the type, $R_2Sn[S_2P(OR')_2]_2$ (where R = Me, *n*-Bu and R′ = *o*-, *m*-, *p*-C_6H_4Me) have been obtained by the reaction of Me_2SnCl_2 or *n*-Bu_2SnCl_2 with ammonium salts of the corresponding *O,O′*-ditolyl dithiophosphates on stirring in benzene and have been characterized by elemental analysis and IR, ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectroscopy. Trends in data are discussed. The crystal structures of $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ and *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ are reported. The environment around the tin atom in both molecules may be described as having skew-trapezoid bipyramidal geometry. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) complexes; di(*o*-, *m*- or *p*-tolyl) dithiophosphates; X-ray crystal structures; NMR spectroscopy

INTRODUCTION

The synthesis of coordination compounds with sulfur-containing ligands has been an active area of research, reflecting the importance of these compounds in various fields. Studies over the last few decades have consistently shown interest in the versatility of bonding modes of metals with sulfur-containing ligands, including those on a variety of dithio ligating systems of tin with *O,O′*-dialkyl dithiophosphates[1–10] and *O,O′*-alkylene dithiophosphate,[11–14] for which monodentate,[1,9,10] anisobidentate as well as bidentate[4,9,10] forms have been reported. The biocidal importance[15] of organotin moieties as well as organophosphorus compounds is well known. The synthesis of organotin(IV) dithiophosphate compounds provides model systems of interest because the presence of both biologically active organotin and organophosphorus moieties in a single molecule could provide more powerful and lasting effects. High miticidal[16,17] and acaricidal[18] activities have been shown by various organotin(IV) dithiophosphates and several diorganotin complexes have shown antitumour activity.[19]

Di(*n*-butyl)tin(IV)bis(decyl dithiophosphate) is an effective additive in water-based drilling mud, reducing the tendency of drill pipes to become stuck during drilling.[20] Di(*n*-butyl)tin(IV)bis(dimethylcyclohexyl dithiophosphate) and di(*n*-butyl)tin(IV)bis-(dioctylphenyl dithioposphate) are used as lubricating additives,[21] where they act as anticorrosive agents reducing corrosion of copper–lead and cadmium–silver bearings employed in internal combustion engines. In addition to antioxidant properties, they also impart extreme pressure properties to gear oil.[21] A few

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triorganotin(IV) dithiophosphates are used as insecticides and miticides.[22,23]

The extensive applications of organotin(IV) dithiophosphate compounds in various fields make it worthwhile to explore the coordination and bonding properties of sulfur-containing ligands such as *O,O′*-di(*o*-, *m*- or *p*-tolyl) dithiophosphate moieties. Therefore, a systematic, consolidated and comparative discussion on the complexes $R_2Sn[S_2P(OR')_2]_2$ is presented along with the single crystal X-ray structures of two derivatives, $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ and $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$.

RESULTS AND DISCUSSION

Reactions of dimethyl/di(*n*-butyl)tin(IV) dichloride with ammonium salts of *O,O′*-di(*o*-, *m*- or *p*-tolyl) dithiophosphates in 1:2 molar ratio in benzene yield dimethyl/di (*n*-butyl)tin(IV)bis{di(*o*-, *m*- or *p*-tolyl) dithiophosphate} complexes of the type, $R_2Sn[S_2P(OR')_2]_2$.

$$R_2SnCl_2 + 2NH_4S_2P(OR')_2 \xrightarrow{24\ \text{h stirring}} R_2Sn[S_2P(OR')_2]_2 + 2NH_4Cl$$

(R = Me, *n*-Bu and R′ = *o*-, *m*-, *p*-C_6H_4Me).

All of these organotin(IV)bis{ di(*o*-, *m*- or *p*-tolyl) dithiophosphate} complexes, except $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}m)_2]_2$, are white crystalline solids which are soluble in common organic solvents such as benzene, *n*-hexane and chloroform. The products were characterized by elemental analysis as well as by IR, ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectroscopy.

The relevant assignments of the IR bands were made on the basis of comparisons with the spectra of the salts of *O,O′*-di(*o*-, *m*- or *p*-tolyl) dithiophosphates[24,25] and analogous organotin(IV) *O,O′*-dialkyl dithiophosphates.[2–4] Two strong intensity bands that were present in the 1185–1102 and 825–790 cm^{-1} regions were assigned to ν[(P)–O–C] and ν[P–O–(C)] stretching vibrations, respectively, in complexes**1–6.** Bands due to ν(P═S) or $\nu(P-S)_{asym}$ and ν(P–S) or $\nu(P-S)_{sym}$ observed at 715–670 and 565–543 cm^{-1}, respectively, in the ammonium salts of the corresponding di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids were shifted to lower frequency by 40–50 cm^{-1} in the corresponding organotin(IV) complexes consistent with coordination to the metal atom. Bands due to ν(Sn–C) lay[12] in the region 525–502 cm^{-1}.

The ^1H NMR spectra were recorded in $CDCl_3$ solution at room temperature. The data for organotin(IV)bis{di(*o*-, *m*- or *p*-tolyl) dithiophosphate} complexes were similar to those of the corresponding salts of dithiophosphates,[24,25] probably due to the large separation between tin and the hydrogen atoms. Negligible shifts for the methyl protons on tin were observed in complexes **1–3** when compared with the corresponding salts showing a singlet in the range 2.22–2.29 ppm with $^2J(^{119}Sn-^1H)$ values 84(**1**), 87.2(**2**) and 85(**3**) Hz, which are consistent with six coordination around tin.[26] Similar values of coupling constants were observed in the analogous dimethyltin(IV) dialkyl dithiophosphates.[2] The value of the bond angle, C–Sn–C for **1** was calculated (136.1°) by substituting the coupling constant [$^2J(^{119}Sn-^1H)$ = 84 Hz] in the equation given by Lockhart *et al.*,[27] viz. $\theta = 0.0161|^2J|^2 - 1.32|^2J| + 1.33.4$. Interestingly, this bond angle was found to be 132.80(9)° in the X-ray structure determination. Coupling constant values for compounds **4–6** could not be interpreted from the spectra due to the complexity of the methylene multiplets of the *n*-butyl group. The phenyl protons appear in the expected range for these complexes, 6.92–7.17 ppm, undergoing a negligible upfield shift of ca. 0.03–0.20 ppm as compared with their position in the free ligand, presumably as a consequence of coordination.

The ^{13}C NMR spectra were recorded in $CDCl_3$ solution at room temperature. The methyl carbon attached to tin in the dimethyltin(IV)bis{di(*o*-, *m*- or *p*-tolyl) dithiophosphate} complexes **1–3** was seen in the expected range of 16.8–21.3 ppm and peaks for the carbon atoms present on the *n*-butyl group were observed in the range 13.2–27.8 ppm in the di(*n*-butyl)tin(IV)bis{di(*o*-, *m*- or *p*-tolyl) dithiophosphate} complexes **4–6.** The carbon atoms of *o*-, *m*- or *p*-tolyl were also seen in the expected region 121.3–149.3 ppm. The values of the coupling constants $^1J(^{119}Sn-^{13}C)$ for **1–3** in the region 578–584 Hz were as observed for other analogous dimethyltin(IV) dialkyl dithiophosphates,[28] suggesting six coordination around tin, where dithiophosphate moieties were weakly associated in solution. The values of the coupling constants $^1J(^{119}Sn-^{13}C)$ for **4–6** could not be resolved. The bond angle for C–Sn–C bond was estimated to be 127.98° for **1** on substituting the coupling constant $^1J(^{119}Sn-^{13}C)$ value (584 Hz) in the equation [$^1J(^{119}Sn-^{13}C) = 11.4\theta - 875$][27] comparable to the value of 132.80(9)° in the solid state.

The ^{31}P NMR spectra of the complexes were recorded in $CDCl_3$. A relatively sharp singlet in the region 90–93 ppm indicated coordination of the dithiophosphate group to the metal centre in the molecules. It also revealed that all phosphorus nuclei were equivalent and only one type of phosphorus was present in each case in solution. The ^{31}P NMR chemical shifts for these complexes were shifted 15–20 ppm upfield from those of the corresponding salts of *o*-, *m*- or *p*-tolyl dithiophosphoric acids, indicating the anisobidentate nature[29] of the dithiophosphate moieties.

The ^{119}Sn NMR spectra of two representative compounds **1** and **4** scanned in chloroform showed singlets at −186.77 and −204.82 ppm, respectively, in agreement with the analogous diorganotin(IV) dialkyl dithiophosphates.[28] These ^{119}Sn resonances appear at significantly lower frequencies than those of their precursors,[28] Me_2SnCl_2 (+137 ppm) and $n\text{-}Bu_2SnCl_2$ (+123 ppm), indicative of the removal of the electronegative group from the precursors and an increase in the coordination number of tin. In general, the ^{119}Sn

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NMR chemical shifts[28] were observed in the region −125 to −365 ppm for six-coordinated organotin derivatives, depending on the nature of the substituents.

$Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**1**) and $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**4**), crystallized as monoclinic and triclinic in space groups $P2_1/n$ and $P-1$, respectively. The ORTEP diagrams in Figs 1 and 2 demonstrate the presence of two anisobidentate dithiophosphate ligands. The Sn–S(1) and Sn–S(3) bond distances were 2.5111(6) and 2.5044(6) Å, respectively, for **1** and 2.5467(6) and 2.5455(6) Å, respectively, for **4**, consistent with the sum of the covalent radii of tin (1.40 Å) and sulfur (1.04 Å).[30] The other two sulfur atoms, S2 and S4, were considerably further from the tin atom, 3.2603(6) and 3.0723(6) Å, respectively, in **1** and 3.0953(6) and 3.1409(6) Å, respectively, in **4**, but still well within the sum of the Van der Waals radii of 4.0 Å.[31] Similar anisobidentate behaviour with one weak interaction was seen in the analogous tin compounds, $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}p)_2]_2$,[32] $Ph_2Sn[S_2P(OEt)_2]_2$,[33] $Ph_2Sn[S_2P(O\text{-}iPr)_2]_2$[34] and $Me_2Sn[S_2POCMe_2CMe_2O]_2$,[35] as well as in alkyl derivatives such as $Me_2Sn[S_2PMe_2]_2$ and $SnI_2[S_2PEt_2]_2$.[36] It is also consistent with the anisobidentate chelating nature of these ligands, that the average S(1)–P(1) and S(3)–P(2) bond distance in **1** and **4** of 2.0274(8) Å is clearly longer than the value of 1.938(8) Å in P(1)–S(2) and P(2)–S(4), as noted elsewhere.[32–36]

It has been argued that these structures are better described as having skew-trapezoidal bipyramidal geometry[37] rather than distorted octahedral when the C–Sn–C bond angle is within the range 121.8(5)–150.2(4)°. Those involving C(1)–Sn(1)–C(2) and C(1)–Sn(1)–C(5) [132.80(9)° in **1** and 136.3(1)° in **4**] are well within the suggested range. The trapezoid plane is defined by the four sulfur atoms derived from the two asymmetrically coordinating dithiophosphate ligands. The sum of the four angles S(1)–Sn(1)–S(3), S(1)–Sn(1)–S(3), S(2)–Sn(1)–S(4) and S(1)–Sn(1)–S(2) of 360.1° in **1** and 360.0° in **4** emphasizes the plane formed by tin and the four sulfur atoms. Table 1 provides an interesting comparison of the relevant bonds and angles in related molecules. All of these have C–Sn–C angle within 121.8(5)–150.2(4)° with the exception of $Ph_2Sn[S_2P(O\text{-}iPr)_2]_2$[34], where it is 180°, and hence octahedral rather than skew-trapezoidal bipyramidal. It was suggested that tighter packing resulted in the octahedral environment around tin in $Ph_2Sn[S_2P(O\text{-}iPr)_2]_2$. It is difficult to assume any trends in steric effects, including those arising from the presence of methyl groups in the *ortho* or *para* positions of the phenyl groups, that could result in this difference and the similarity of the overall arrangement around tin in $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**1**), $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**4**), $n\text{-}Bu_2Sn[S_2P(OC_6H_4Me\text{-}p)_2]_2$, $Ph_2Sn[S_2P(OEt)_2]_2$, $Me_2Sn[S_2PMe_2]_2$ and $Me_2Sn[S_2PEt_2]_2$.

When only the shorter Sn–S bonds are considered, the bond angles involving the C–Sn–S bonds are fairly close to the ideal tetrahedral angle ranging from 104.21(7)° and 104.94(9)° for S(1)–Sn(1)–C(1) in **1** and **4** to 109.85(7)° and 108.19(7)° for C(1)–Sn(1)–S(3) in **1** and **4**. However, S(1)–Sn(1)–S(3) [81.68(2)° in **1** and 83.69(2)° in **4**] and, as noted above, those involving C(1)–Sn(1)–C(2) and C(1)–Sn(1)–C(5) [132.80(9)° in **1** and 136.3(1)° in **4**] reveal a marked deviation from ideal tetrahedral values, emphasizing the distortion.

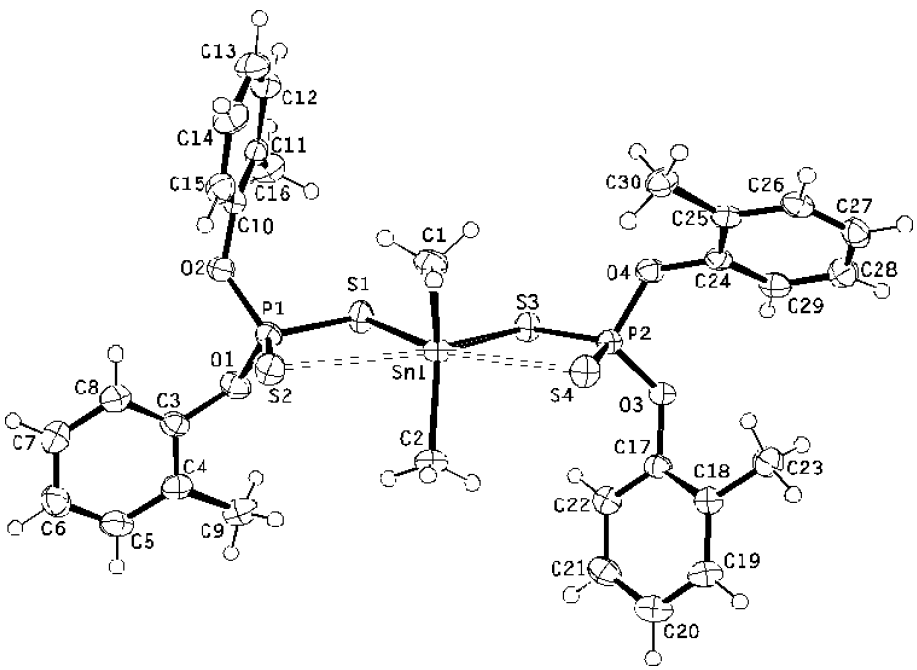

Figure 1. ORTEP plot of the molecule $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$. The non-hydrogen atoms are drawn with 50% probability ellipsoids.

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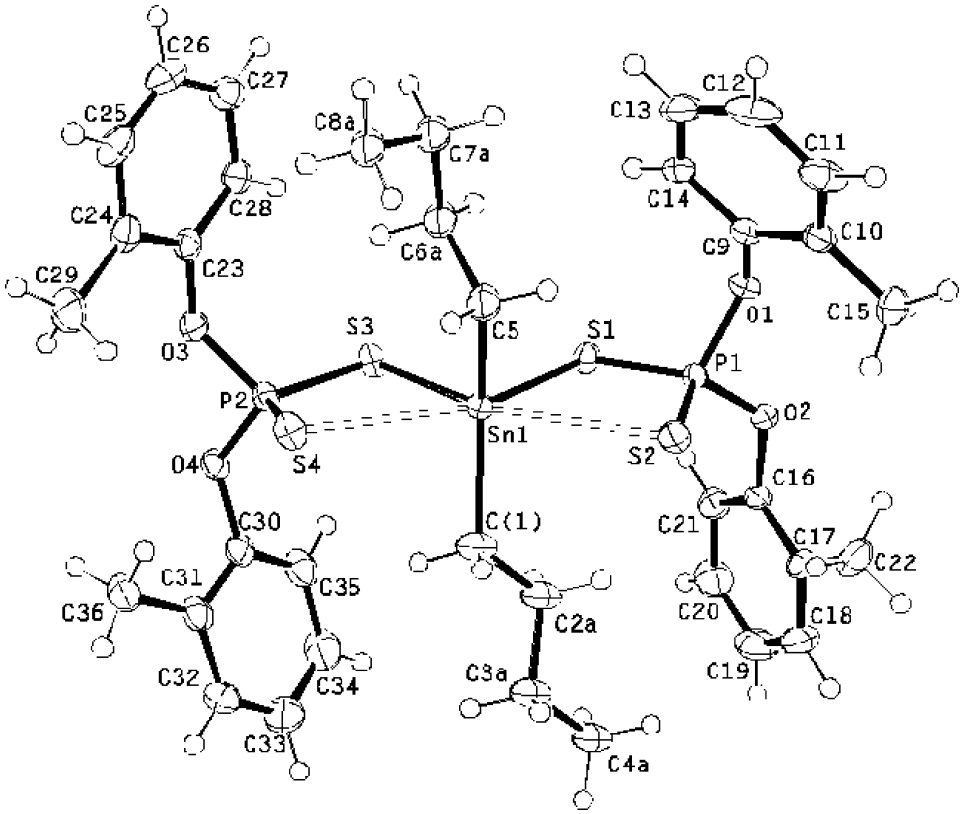

Figure 2. ORTEP plot of the molecule *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$. The non-hydrogen atoms are drawn with 50% probability ellipsoids. Only the major component of the disordered butyl groups is displayed for clarity.

Table 1. Comparison of selected bond lengths (Å) and angles (deg) for some diorganotin(IV) dithiophosphates and dthiophosphinates

Compound	Sn–S(av.)	Sn–C	P–S(av.)	C–Sn–C	S–Sn–S (bite angle)	S–P–S
$Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**1**)	2.5078(6)	2.118(2)	2.0263(8)	132.80(9)	69.53(2)	115.51(4)
	3.1663(6)	2.117(2)	1.9390(7)		72.66(2)	114.20(4)
n-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**4**)	2.5461(6)	2.151(3)	2.0317(8)	136.3(1)	70.87(2)	112.38(4)
	3.1181(6)	2.144(2)	1.9380(8)		70.37(2)	113.24(4)
n-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}p)_2]_2$	2.495(2)	2.146(4)	1.931(4)	128.5(1)	69.11(3)	113.69(5)
	3.236(9)	2.195(4)	2.027(2)		69.46(3)	113.75(5)
$Ph_2Sn[S_2P(OEt)_2]_2$	2.486(4)	2.10(2)	1.930(2)	135(1)	69.2(3)	112.4(7)
	3.215(1)	2.12(2)	2.032(2)		69.7(3)	113.2(6)
$Ph_2Sn[S_2P\{O(i\text{-}Pr)\}_2]_2$	2.678(1)	2.145(4)	1.998(2)	180.00	76.03(3)	111.26(7)
	2.689(1)	2.145(4)	2.006(2)		76.03(3)	111.26(7)
$Me_2Sn[S_2PMe_2]_2$	2.482(2)	2.132(8)	2.047 (2)	122.6(8)	68.9(1)	113.8(3)
	3.334(2)	2.132(8)	1.969 (2)		68.9(1)	113.8(3)
$Me_2Sn[S_2PEt_2]_2$	2.476(2)	2.121(8)	2.054 (2)	123.7(4)	68.1(1)	112.2(1)
	3.336(2)	2.121(8)	1.961 (2)		68.1(1)	112.2(1)

CONCLUSION

We successfully prepared and characterized the following dimethyl/di(*n*-butyl)tin(IV)bis(*O*,*O*′-ditolyldithiophosphate) complexes: $R_2Sn[S_2P(OR')_2]_2$ (where R = Me, *n*-Bu and R′ = *o*-, *m*-, *p*-OC_6H_4Me). The IR, ^1H, ^{13}C, ^{31}P and ^{119}Sn spectra of all of these organotin(IV) complexes and the molecular structures of $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**1**) and *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**4**) were determined. They are consistent with a six-coordinate environment around the tin atom in solution and skew-trapezoidal bipyramid in the solid state.

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EXPERIMENTAL

Me_2SnCl_2, *n*-Bu_2SnCl_2, *o*-, *m*- and *p*-cresols were purchased from E. Merck. Solvents (benzene and *n*-hexane) were dried by standard methods before use. Stringent precautions were taken to exclude moisture during experimental manipulation. Literature methods were used for preparation of *O*,*O*′-ditolyl dithiophosphoric acids.[24,25] Ammonium salts of the dithiophosphoric acids were prepared by reaction of parent acid with ammonia in benzene.

Sulfur was estimated gravimetrically as barium sulfate (Messenger's method) and tin as tin oxide. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in KBr pellets in the range (4000–400) cm^{-1}. ^1H, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker DRX-300 spectrometer in $CDCl_3$ using TMS as an internal standard and H_3PO_4 as an external standard, respectively. ^{119}Sn NMR spectra were scanned on a Bruker 400 Advance II spectrometer using Me_4Sn as an external standard.

Synthesis of $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$(1)

Typically, to a solution of dimethyltindichloride (0.26g, 1.18 mmol) in benzene (5–10 ml) was added a suspension of $NH_4S_2P(OC_6H_4Me\text{-}o)_2$ (0.78g, 2.38 mmol) in the same solvent (10 ml) in 1 : 2 molar ratio with constant stirring. After stirring for 24 h at room temperature the mixture was filtered and solvent was removed *in vacuo* resulting in a pale yellow viscous oily liquid. The oily liquid was dissolved in *n*-hexane and the solution kept for 2–3 days in the refrigerator to obtain a white crystalline solid. Yield: 0.84g, 93%; m.p. 60 °C. Calcd for $C_{30}H_{34}O_4P_2S_4Sn$: Sn, 15.47; S, 16.71. Found: Sn, 15.60; S, 16.82%. ^1H NMR ($CDCl_3$): δ 1.19 [s, CH_3Sn, $^2J(^{119}Sn-^1H) = 84$ Hz], 2.21 (s, Me), 7.05–7.40 (m, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 16.8 [s, CH_3Sn, $^1J(^{119}Sn-^{13}C) = 584$ Hz], 121.3, 125.7, 126.6, 130.7, 131.3, 149.3 ($J_{PC} = 40.2$ Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 90.83 ppm; ^{119}Sn NMR ($CHCl_3$): $\delta -186.77$; IR (KBr) (cm^{-1}): 1130s, ν\{(P)–O–C\}; 790m, ν\{P–O–(C)\}; 680s, 650m, ν(P═S); 540m, ν(P–S); 502w, ν(Sn– C).

Synthesis of $Me_2Sn[S_2P(OC_6H_4Me\text{-}m)_2]_2$(2)

Method as above gave white crystalline solid. Yield: 0.70g, 91%; m.p. 59 °C. Calcd for $C_{30}H_{34}O_4P_2S_4Sn$: Sn, 15.47; S, 16.71. Found: Sn, 15.38; S, 16.93%. ^1H NMR ($CDCl_3$): δ 1.06 [s, CH_3Sn, $^2J(^{119}Sn-^1H) = 87.2$ Hz], 2.29 (s, Me), 6.92–7.19 (dm, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 21.3 [s, CH_3Sn, $^1J(^{119}Sn-^{13}C) = 580$ Hz], 121.8, 126.0, 126.5, 129.2, 139.5, 150.2 ($J_{PC} = 31.5$ Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 91.72 ppm. IR (KBr) (cm^{-1}): 1102s, ν\{(P)–O–C\}; 800m, ν\{P–O–(C)\}; 700s, 650m, ν(P═S); 550m, ν(P–S); 520w, ν(Sn– C).

Synthesis of $Me_2Sn[S_2P(OC_6H_4Me\text{-}p)_2]_2$(3)

Method as above gave white crystalline solid. Yield: 0.64g, 88%; m.p. 79 °C. Calcd for $C_{30}H_{34}O_4P_2S_4Sn$: Sn, 15.47; S, 16.71. Found: Sn, 15.52; S, 16.87%. ^1H NMR ($CDCl_3$): δ 1.06 [s, CH_3Sn, $^2J(^{119}Sn-^1H) = 85$ Hz], 2.27 (s, Me), 7.02–7.17(m, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 20.7 [s, CH_3Sn, $^1J(^{119}Sn-^{13}C) = 578$ Hz], 121.6, 121.7, 130.0, 134.8, 148.3 ($J_{PC} = 38.4$ Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 92.93 ppm. IR (KBr) (cm^{-1}): 1180m, ν\{(P)–O–C\}; 822m, ν\{P–O–(C)\}; 655s, 640m, ν(P═S); 545m, ν(P–S); 509w, ν(Sn– C).

Synthesis of *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$(4)

The method above gave white crystalline solid. Yield: 0.61g, 84%; m.p. 61 °C. Calcd for $C_{36}H_{46}O_4P_2S_4Sn$: Sn, 13.94; S, 15.06. Found: Sn, 13.84; S, 15.27%. ^1H NMR ($CDCl_3$): δ 0.64–0.69(t, Me) 1.46–1.75 {m, $Sn(CH_2)_3$}, 2.21 (s, Me), 6.97–7.04 (m, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 13.3, 17.1, 25.9, 27.8 ($CH_3CH_2CH_2CH_2Sn$), 121.3, 125.5, 126.5, 130.3, 130.7, 149.3 ($J_{PC} = 39.4$ Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 92.97 ppm. ^{119}Sn NMR ($CHCl_3$): $\delta -204.82$; IR (KBr) (cm^{-1}): 1160s, ν\{(P)–O–C\}; 705m, ν\{P–O–(C)\}; 680s, 652m, ν(P═S); 540s, ν(P–S); 500w, ν(Sn– C).

Synthesis of *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}m)_2]_2$(5)

Method as above gave viscous liquid. Yield: 0.76g, 90%; calcd for $C_{36}H_{46}O_4P_2S_4Sn$: Sn, 13.94; S, 15.06. Found: Sn, 14.20;

Table 2. Selected bond lengths (Å) and angles (deg) for $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**1**) and *n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ (**4**)

1		**4**	
Sn–C1	2.118(2)	Sn–C1	2.151(3)
Sn–C2	2.117(2)	Sn–C5	2.144(2)
Sn–S1	2.5111(6)	Sn–S1	2.5467(6)
Sn–S2	3.2603(6)	Sn–S2	3.0953(6)
Sn–S3	2.5044(6)	Sn–S3	2.5455(6)
Sn–S4	3.0723(6)	Sn–S4	3.1409(6)
S1–P1	2.0242(8)	S1–P1	2.0306(8)
S2–P1	1.9339(8)	S2–P1	1.9422(8)
S3–P2	2.0283(7)	S3–P2	2.0328(8)
S4–P2	1.9440(8)	S4–P2	1.9337(8)
C1–Sn–C2	132.80(9)	C1–Sn–C5	136.3(1)
S1–Sn–S3	81.68(2)	S1–Sn–S3	83.69(2)
C1–Sn–S1	104.21(7)	C1–Sn–S1	104.94(9)
C1–Sn–S3	109.85(7)	C1–Sn–S3	108.19(7)
C2–Sn–S1	108.53(7)	C5–Sn–S1	106.93(7)
C2–Sn–S3	107.75(7)	C5–Sn–S3	104.30(8)
S1–Sn–S2	69.53(2)	S1–Sn–S2	70.87(2)
S3–Sn–S4	72.66(2)	S3–Sn–S4	70.37(2)
S1–Sn–S4	154.14(2)	S1–Sn–S4	154.05(2)
S3–Sn–S2	150.95(2)	S3–Sn–S2	154.39(2)
S2–Sn–S4	136.27(2)	S2–Sn–S4	135.08(2)
C1–Sn–S2	81.82(7)	C1–Sn–S2	81.97(7)
C1–Sn–S4	82.09(7)	C1–Sn–S4	83.03(9)
C2–Sn–S2	78.93(7)	C5–Sn–S2	81.12(7)
P1–S1–Sn	97.24(3)	P1–S1–Sn	94.92(3)
P2–S3–Sn	93.62(3)	P2–S3–Sn	95.29(3)
P1–S2–Sn	77.70(2)	P1–S2–Sn	81.11(3)
P2–S4–Sn	79.43(2)	P2–S4–Sn	80.34(3)
S1–P1–S2	115.51(4)	S1–P1–S2	112.38(4)
S3–P2–S4	114.20(4)	S3–P2–S4	113.24(4)

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S, 14.94%. ^{1}H NMR ($CDCl_3$): δ 0.77–0.82 (t, Me), 1.51–1.82 {m, $Sn(CH_2)_3$}, 2.32 (s, Me), 7.05–7.33 (dm, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 13.6, 17.3, 25.8, 27.6 ($CH_3CH_2CH_2CH_2Sn$), 121.6, 125.8, 126.5, 129.3, 139.8, 150.3 (J_{PC} = 33.5 Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 93.95 ppm. IR (KBr) (cm^{-1}): 1108s, ν\{(P)–O–C\}; 716m, ν\{P–O–(C)\}; 620m, 600m, ν(P═S); 563m, ν(P–S); 512m, ν(Sn– C).

Synthesis of *n*-$Bu_2Sn[S_2P(OC_6H_4Me$-*p*$)_2]_2$(6)

Method as above gave white crystalline solid. Yield: 0.69g, 91%; m.p. 80 °C. Calcd for $C_{36}H_{46}O_4P_2S_4Sn$: Sn, 13.94; S, 15.06. Found: Sn, 13.80; S, 15.26%. ^{1}H NMR ($CDCl_3$): δ 0.72–0.77 (t, Me), 1.41–1.73 {m, $Sn(CH_2)_3$}, 2.28 (s, Me), 7.02–7.23(m, OC_6H_4); ^{13}C NMR ($CDCl_3$): δ 13.1, 17.0, 25.6, 27.6 ($CH_3CH_2CH_2CH_2Sn$), 121.7, 122.0, 129.7, 135.0, 147.9 (J_{PC} = 37.8 Hz) ($OC_6H_4CH_3$); ^{31}P NMR ($CDCl_3$): δ 95.02 ppm. IR (KBr) (cm^{-1}): 1185m, ν\{(P)–O–C\}; 825s, ν\{P–O–(C)\}; 670s, 650m, ν(P═S); 540m, ν(P–S); 520w, ν(Sn– C).

Crystal structure determination

Colourless block-like crystals of $Me_2Sn[S_2P(OC_6H_4Me$-*o*$)_2]_2$ (**1**) and *n*-$Bu_2Sn[S_2P(OC_6H_4Me$-*o*$)]_2$ (**4**) were mounted on glass fibres. Crystallographic data were collected at 120(2) K on a Bruker-Nonius Kappa CCD area detector using Mo–$K\alpha$ radiation (λ = 0.71073 Å). $C_{30}H_{34}O_4P_2S_4Sn$ (**1**), M = 767.44, monoclinic, $P2_1/n$, a = 11.2853(2), b = 20.7881(6), c = 15.3190(5) Å, β = 110.937(2)°, V = 3356.6(2) Å^3, Z = 4, R [6395 data with $I \geq 2\sigma(I)$; θ_{max} 27.5°] = 0.029, R_w (all 7603 data) = 0.062.

$C_{36}H_{46}O_4P_2S_4Sn$ (**4**), M = 851.60, triclinic, $P-1$, a = 12.1519(2), b = 13.0311(2), c = 13.4239(2) Å, α = 70.931(1), β = 75.255(1), γ = 82.402(1)°, V = 1940.10(5) Å^3, Z = 2, R [7959 data with $I \geq 2\sigma(I)$; θ_{max} 27.5°] = 0.032, R_w (all 8844 data) = 0.073. CCDC deposition nos 619258 and 619259 for (**1**) and (**4**), respectively.

The structures were solved by direct-methods[38] and were refined using the WinGX version[39] of SHELX-97.[40] An absorption correction was applied.[41] The disordered (*n*-butyl) groups (55 : 45) in **4** were successfully modelled in two conformations with restraints placed on the C–C distances. Selected bond distances and angles are given in Table 2 and the molecules are displayed as ORTEP diagrams in Figs 1 and 2.

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