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Hypervalent organotin(IV) derivatives containing [2-(Me_2NCH_2)C_6H_4]Sn moieties. Competition between nitrogen and chalcogen atoms for coordination to the metal centre

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Abstract

[2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**) was prepared by reacting Ph_2SnCl_2 with [2-(Me_2NCH_2)C_6H_4]Li in toluene. The reactions of (**1**) with the ammonium salt of the appropriate thiophosphinato ligand in 1:1 molar ratio afford the isolation of [2-(Me_2NCH_2)C_6H_4]$SnPh_2L$ [L = S(S)PPh_2 (**2**), O(S)PPh_2 (**3**)] as white crystalline solids. The molecular structure of **1**–**3** was determined by single-crystal X-ray diffraction. Their crystals contain monomeric units with the metal atom exhibiting a distorted trigonal bipyramidal coordination environment. The SnC_3 moiety is almost planar. The N atom of the pending CH_2NMe_2 arm is strongly coordinated to the metal centre (Sn(1)–N(1) 2.519(2), 2.548(3), 2.481(2) Å for **1**, **2** and **3**, respectively), *trans* to the Cl, O or S atoms (N(1)–Sn(1)–Cl(1) 170.49(6)°, N(1)–Sn(1)–S(1) 169.06(8)°, N(1)–Sn(1)–O(1) 168.58(8)°, respectively). The S atom double bonded to phosphorus is not involved in intra- or intermolecular coordination to tin. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hypervalent organotin(IV) derivatives; Nitrogen; Chalcogen; Metal centre

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1. Introduction

Several organotin(IV) compounds containing the [2-(Me_2NCH_2)C_6H_4] group have been investigated so far by single crystal X-ray diffraction and in all cases hypervalent structures were obtained as a result of the strong intramolecular N → Sn [1–7]. However, no derivatives with anionic ligands containing a second potential coordinating atom, to compete the nitrogen atom of the CH_2NMe_2 pending arm for coordination to the metal centre have been prepared so far. On the other hand, thiophosphorus ligands of the type $[R_2P(S)X]^-$ (R = alkyl, aryl, alkoxy; X = O, S) are well known to involve usually both chalcogen atoms in coordination to the metal atom in organotin(IV) derivatives [8–12].

Here we report on the synthesis and spectroscopic characterisation of some new organotin(IV) derivatives, i.e. [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**), [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[S(S)PPh_2] (**2**) and [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[O(S)PPh_2] (**3**), as well as their crystal and molecular structure.

2. Results and discussion

2.1. Preparation

The *C,N*-[2-(dimethylaminomethyl)phenyl]diphenyltin(IV) chloride, [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**), was prepared according to Eq. (1), by reacting [2-(Me_2NCH_2)C_6H_4]Li with Ph_2SnCl_2, in toluene, at −78°C:

$$[2\text{-}(Me_2NCH_2)C_6H_4]Li + Ph_2SnCl_2 \rightarrow \underset{\mathbf{1}}{[2\text{-}(Me_2NCH_2)C_6H_4]SnPh_2Cl} + LiCl \quad (1)$$

The methatesis reaction between stoichiometric amounts of **1** and the ammonium salt of the appropriate organophosphorus ligand (Eq. (2)), affords the isolation of compounds [2-(Me_2NCH_2)C_6H_4]$SnPh_2$-

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$[S(S)PPh_2]$ (**2**) and $[2\text{-}(Me_2NCH_2)C_6H_4]SnPh_2[O(S)\text{-}PPh_2]$ (**3**) as colorless, crystalline solids:

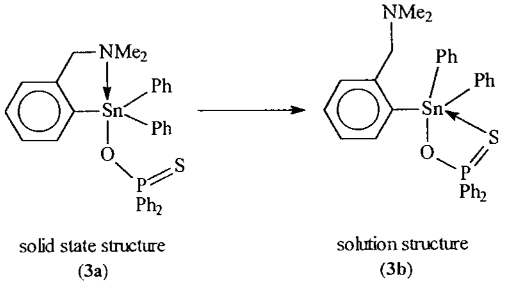
$$[2\text{-}(Me_2NCH_2)C_6H_4]SnPh_2Cl + NH_4[XSPPh_2] \rightarrow [2\text{-}(Me_2NCH_2)C_6H_4]SnPh_2[X(S)PPh_2] + NH_4Cl \quad (2)$$

X = S (**2**), O (**3**)

All compounds are air-stable products and were characterised by IR and multinuclear NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn) spectroscopy and their crystal and molecular structures have been determined by single crystal X-ray diffraction.

2.2. IR spectra

The infrared spectra of **2** and **3** exhibit, in addition to the expected strong absorptions due to the organic groups bonded to tin, strong bands in the 660–530 cm^{-1} region and around 1020 cm^{-1} (for **3**), which were assigned to phosphorus–sulfur and phosphorus–oxygen stretching vibrations. The presence of absorption bands corresponding to P=S double bond (645 cm^{-1}) and P–O(Sn) single bond (1017 cm^{-1}) in the infrared spectrum of **3** indicates a primary coordination of the phosphorus ligand through the oxygen atom (c.f. the methyl esters: 1027 (P–O), 635 (P=S) cm^{-1} for $Ph_2P(S)OMe$ [13]; 1200 (P=O), 568 (P–S) cm^{-1} for $Ph_2P(O)SMe$ [13]; for a detailed discussion see Ref. [11]). For both compounds the infrared data are consistent with a monodentate behavior of the phosphorus ligand in solid state. This behavior of a monothiophosphinato moiety contrasts with its ability to exhibit a bridging pattern and thus to increase the coordination number of the metal centre in a triorganotin(IV) group from 4 to 5, leading to chain polymeric structures, e.g. $[Ph_3SnOSPPh_2]_n$ [12]; $[Me_3SnOSPMe_2]_n$ [14]. However, the coordination number of tin in **2** and **3**, at least in solid state, is increased to five through the intramolecular N → Sn, as proved by single-crystal X-ray diffraction (see below). The solution IR spectrum of **3** (in $CHCl_3$) exhibits a shift of the absorption bands corresponding to phosphorus–sulfur and phosphorus–oxygen stretching vibrations to lower (613 cm^{-1}) and higher (1200 cm^{-1}), which supports the bidentate coordination of the ligand moiety as suggested by ^{31}P chemical shift (see subsequent discussion).



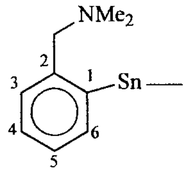
solid state structure
(3a)

solution structure
(3b)

Scheme 1.

2.3. NMR spectra

The assignment of the ^1H and ^{13}C chemical shifts according to the numbering scheme (a) was made using literature data for related organotin compounds [4,8]. The NMR data indicate that in solution the compounds **1** and **2** have structures comparable to that found in solid state, i.e. a trigonal bipyramidal coordination geometry around the tin atom due to the intramolecular N → Sn coordination. Although the observed single resonances for the benzylic as well as for the aminomethyl protons are compatible either with a tetrahedral or with a pentacoordinate structure, the presence of tin satellites for these signals is consistent with an intramolecular N → Sn coordination. The magnitude of these $^{117/119}Sn$–H coupling constants (1.87s (N–CH_3, $^3J_{SnH}$ 38.7 Hz), 3.55s (–CH_2–, $^3J_{SnH}$ 38.9 Hz) for **1**, and 1.68s (N–CH_3, $^3J_{SnH}$ 34.1 Hz), 3.45s (–CH_2–, $^3J_{SnH}$ 28.7 Hz) for **2**, respectively) is comparable with those observed for $Ph_3Sn\text{–}NMe_2$ ($^3J_{SnH}$ 41.5/43.5 Hz), a compound containing a covalent tin–nitrogen bond [15].



(a)

By contrast, no tin satellites were observed in the ^1H-NMR spectrum of compound **3**. On the other hand, the magnitude of the ^{31}P chemical shift (δ 64.7 ppm) is indicative for a monothiophosphinato moiety, $[OSPPh_2]^-$, involving both chalcogen in coordination to tin (c.f. δ(^{31}P) 83.5 ppm for $Ph_2P(S)OMe$ [16]; 42.8 ppm for $Ph_2P(O)SMe$ [16]; 64.9 ppm for $Ph_3SnOSPPh_2$ [11]; for a detailed discussion see Ref. [11]). This behavior suggests that a competition for the metal centre between the nitrogen atom of the pendant arm and the sulfur double bonded to phosphorus can occur in solution, and for **3**, at least at room temperature, the intramolecular N → Sn bond is broken (Scheme 1).

The magnitude of the chemical shifts in the ^{119}Sn-NMR spectra of **1** and **3** is in the range for 5-coordinated triaryltin(IV) derivatives, thus supporting the proposed structures in solution [3,17]. For compound **3** the ^{119}Sn resonance shows a doublet pattern due to tin–phosphorus coupling ($^2J_{SnP}$ 122.9 Hz).In addition to the resonances due to organic groups attached to tin, proton and carbon resonances corresponding to the

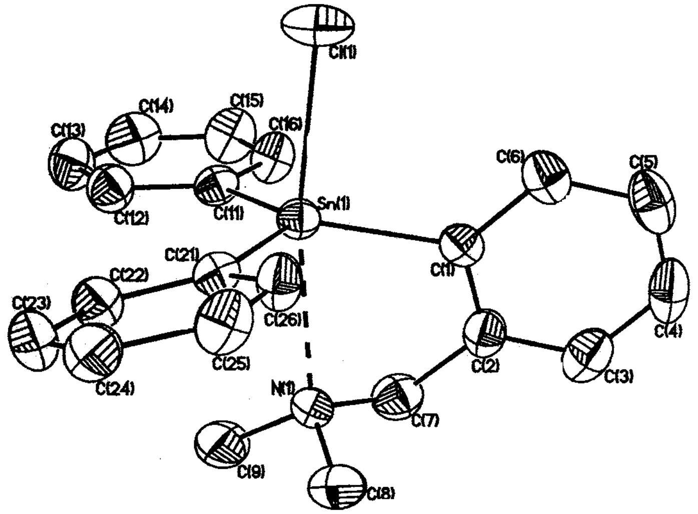


Fig. 1. General view (SHELXTL-PLUS) of the molecular structure of **1** showing 30% probability displacement ellipsoids and the atom numbering scheme.

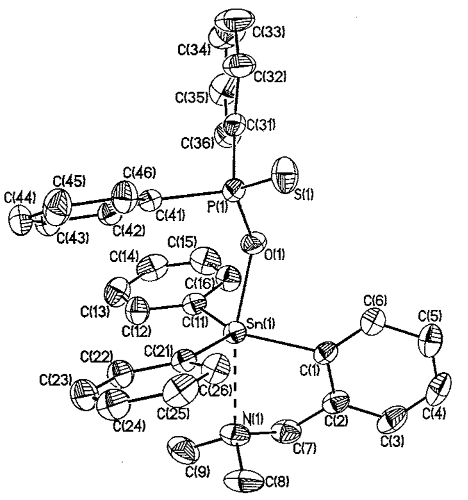


Fig. 3. General view (SHELXTL-PLUS) of the molecular structure of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme.

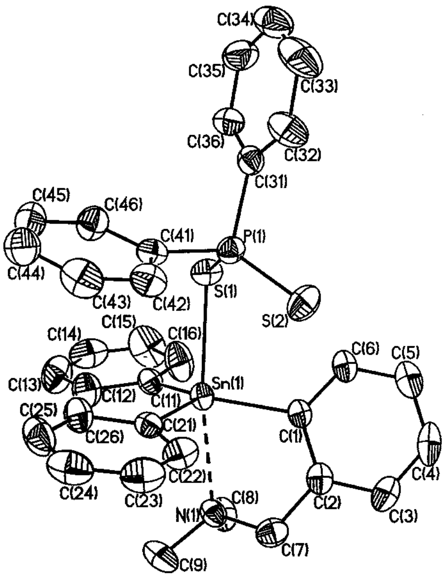


Fig. 2. General view (SHELXTL-PLUS) of the molecular structure of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme.

phenyl groups bonded to phosphorus are observed for compounds **2** and **3**; as expected, they are split into two components of equal intensity, due to phosphorus–proton and phosphorus–carbon coupling, respectively.

*2.4. Crystal and molecular structure of [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**), [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[S(S)PPh_2] (**2**) and [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[O(S)PPh_2] (**3**)*

The molecular structure of compounds **1**–**3** with the atom numbering scheme is shown in Figs. 1–3, respectively, and selected interatomic distances and angles are

Table 1
Relevant interatomic distance (Å) and angles (°) in [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**), [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[S(S)PPh_2] (**2**) and [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[O(S)PPh_2] (**3**)

	1, X = Cl	**2**, X = S	**3**, X = O
Bond distances			
Sn(1)–C(21)	2.125(3)	2.123(4)	2.124(3)
Sn(1)–C(11)	2.125(3)	2.130(4)	2.129(3)
Sn(1)–C(1)	2.126(3)	2.130(4)	2.124(3)
Sn(1)–N(1)	2.519(2)	2.548(3)	2.481(2)
Sn(1)–X(1)	2.4691(9)	2.5837(11)	2.1302(17)
Sn(1)···S(y) [a]		4.0487(14)	4.7337(9)
P(1)–O(1)			1.5325(18)
P(1)–S(1)		2.0599(16)	1.9501(10)
P(1)–S(2)		1.9489(14)	
Bond angles			
C(21)–Sn(1)–C(11)	122.05(10)	117.52(17)	123.73(10)
C(21)–Sn(1)–C(1)	121.34(9)	118.87(16)	120.59(10)
C(11)–Sn(1)–C(1)	114.15(10)	120.79(16)	114.16(10)
C(21)–Sn(1)–X(1)	93.35(7)	101.26(10)	96.03(8)
C(11)–Sn(1)–X(1)	96.46(8)	87.66(10)	93.39(9)
C(1)–Sn(1)–X(1)	95.96(8)	97.85(11)	92.69(9)
C(21)–Sn(1)–N(1)	89.22(9)	89.31(13)	90.36(8)
C(11)–Sn(1)–N(1)	89.90(9)	89.93(13)	90.89(9)
C(1)–Sn(1)–N(1)	74.92(9)	74.28(13)	75.91(9)
X(1)–Sn(1)–N(1)	170.49(6)	169.06(8)	168.58(8)
P(1)–X(1)–Sn(1)		105.28(5)	143.62(11)
X(1)–P(1)–C(41)		107.08(14)	108.26(11)
X(1)–P(1)–C(31)		104.17(15)	104.03(12)
C(41)–P(1)–C(31)		103.01(18)	103.60(12)
X(1)–P(1)–S(y)[a]		117.59(7)	117.11(8)
C(41)–P(1)–S(y)[a]		112.59(14)	110.75(9)
C(31)–P(1)–S(y)[a]		111.11(15)	112.06(10)

[a] For S(y) atom, $y = 2$ for **2**, and $y = 1$ for **3**, respectively.

listed in Table 1. The crystal structure of all three compounds consists of discrete monomeric molecular units separated by normal van der Waals distances.

The structure of compounds **1**–**3** reveals some common trends. Thus, the coordination geometry around the tin atom is distorted trigonal bipyramidal as result of a strong intramolecular N → Sn interaction. The axial positions are occupied by nitrogen and X(1) atoms (N(1)–Sn(1)–X(1) 170.49(6)° in **1** (X = Cl), 169.06(8)° in **2** (X = S), and 168.58(8)° in **3** (X = O)), while the carbon atoms of the phenyl groups are in the equatorial plane. The Sn(1) atom is displaced from the equatorial C_3 plane on the side of the axial X(1) atom with 0.193 Å (**1**), 0.208 Å (**2**) and 0.152 Å (**3**), thus resulting in significant deviation of the X–Sn–C (93.35(7)–96.46(8)°) and N–Sn–C (74.92(9)–89.90(9)°) from the ideal value of 90°.

The tin–nitrogen interatomic distances (Sn(1)–N(1) 2.519(2), 2.548(3) and 2.481(2) Å for **1**, **2** and **3**, respectively) are similar to that observed in the related bromo derivative, [2-(Me_2NCH_2)C_6H_4]$SnPh_2Br$ (2.511 Å) [1], and the longer Sn(1)–N(1) distance in **2** reflects the lower electronegativity of the sulfur atom placed in the *trans* position relative to N in the N → Sn–S fragment. The resulting five-membered SnC_3N rings are folded along the Sn(1)···$C_{methylene}$ axis (SnC_3/SnCN dihedral angle: 40.5° in **1**, 41.2° in **2** and 41.5° in **3**, respectively), with the nitrogen atom 0.736 Å (**1**), 0.766 Å (**2**) and 0.755 Å (**3**) out from the best plane of the rest of the atoms. The small bite of the *C*,*N*-bidentate ligand is reflected in the magnitude of the N(1)–Sn(1)–C(1) angle (74.92(9)° in **1**, 74.28(13)° in **2** and 75.91(9)° in **3**, respectively).

In **1** the Sn(1)–Cl(1) bond distance is significantly larger (2.4691(9) Å) than in the tetrahedral Ph_3SnCl (average 2.355 Å, for the two independent molecules present in the unit cell) [18], consistent with the *trans* influence of the strong intramolecular N → Sn interaction.

In both **2** and **3** the organophosphorus ligands act as monodentate moieties, being connected to the tin atom only through one of the chalcogen atoms, i.e. Sn(1)–S(1) 2.5837(11) Å in **2**, and Sn(1)–O(1) 2.1302(17) Å in **3**. The second chalcogen atom of the 1,1-dichalcogenophosphinato ligands (Sn(1)···S(2) 4.0487(14) Å in **2**, and Sn(1)···S(1) 4.7337(9) Å in **3**) is not involved in any intra- or intermolecular interaction to metal centres.

The monodentate coordination pattern of the 1,1-dithiophosphinato group in **2** might be considered normal since for related triorganotin(IV) derivatives, $R_3SnS(S)PR'_2$, a tetrahedral structure was suggested on the basis of IR and Mössbauer data [19–21]. This is also consistent with the structure of the related tetrahedral $Ph_3SnS(S)P(OEt)_2$ (Sn–S 2.458, Sn···S (non-bonding) 5.326 Å) [22]. The *trans* influence of the N → Sn interaction is again reflected in a Sn–S bond distance ca. 0.13 Å larger than in the above dithiophosphato derivative. The tin–sulfur bond distance in **2** is also ca. 0.067 Å larger than in $Me_3Sn[SPPh_2NPPh_2S]$ (2.517 Å) [23], for which a distorted trigonal bipyramidal *trans*-S_2SnC_3 environment was described as a result of the bridging nature of the phosphorus ligand (weak *inter*-molecular Sn···S interaction, 3.627 Å). The monodentate behavior of the dithio ligand in **2** (P(1)–S(1) 2.0599(16) Å, P(1)–S(2) 1.9489(14) Å) is also reflected in the phosphorus–sulfur bond distances within the ligand moiety, which are consistent with P–S single and P=S double bonds (cf. $Ph_2P(S)SH$ [24]: P–S 2.077(1) Å and P=S 1.954(1) Å).

The monomeric nature of **3** is in contrast with the polymeric structure established for the related $[Ph_3SnOSPPh_2]_n$ [12], which can be considered as the parent compound of **3**. Both compounds contain 5-coordinated metal centres as result of the different behavior of the monothiophosphinato moiety. In the triphenyltin(IV) derivative the phosphorus ligand exhibit an *O*,*S*-bridging pattern (Sn(1)–O(1) 2.172 Å, Sn(1)–S(1′) 2.785 Å), thus leading to a SnC_3OS core. By contrast, in the title compound **3** the monothiophosphinato ligand is attached to tin through its oxygen atom and the *trans* axial position is occupied by the nitrogen atom of the CH_2NMe_2 pending arm, resulting in a SnC_3ON core. Thus, the competition for the coordination to the metal centre between the ‘hard’ nitrogen and the ‘soft’ sulfur atoms is the driving force which results in a monomeric structure of **3**. Consequently, a *O*-monodentate coordination pattern of the monothiophosphinato ligand is achieved in **3** and this behavior is best reflected in the magnitude of the phosphorus–oxygen and phosphorus–sulfur bond distances within the ligand moiety: P(1)–O(1) 1.5325(18) Å, P(1)–S(1) 1.9501(10) Å in **3** versus P(1)–O(1) 1.517(6) Å, P(1)–S(1) 2.002(4) Å in $[Ph_3SnOSPPh_2]_n$ [12].

3. Experimental

3.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and freshly distilled prior to use. Diphenyltin(IV) dichloride, *N*,*N*-dimethylbenzylamine and butyllithium were commercially available. The other starting materials were prepared according to literature methods: [2-(Me_2NCH_2)C_6H_4]Li [25], $NH_4[S_2PPh_2]$ [26], and $NH_4[OSPPh_2]$ [27,28]. Infrared spectra were recorded in the range 4000–250 cm^{-1} as KBr pellets on a Jasco FTIR-615 instrument. The ^1H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively, using solutions in dried $CDCl_3$. The chemical shifts are reported in ppm relative to TMS and H_3PO_4 85%, respectively. The ^{119}Sn-NMR were recorded on a RMN Bruker DPX-400 instrument and the chemical shifts are reported in ppm relative to $SnMe_4$.

*3.2. Preparation of C,N-[2-(dimethylaminomethyl)phenyl]diphenyltin(IV) chloride, [2-(Me_2NCH_2)C_6H_4]$SnPh_2Cl$ (**1**)*

A solution of BuLi in hexane (23 ml, 1.63 M, 10% excess) was added dropwise to a stirred solution of *N*,*N*-dimethylbenzylamine (4.58 g, 0.034 mol) in 100 ml anhydrous diethyl ether, at room temperature, under argon, using Schlenk techniques. After 24 h a white precipitate deposited which was washed with 3 × 30 ml of hexane. The solid product was suspended in toluene and added dropwise under stirring to a cooled (−78°C) solution of Ph_2SnCl_2 (11.64 g, 0.034 mol) in 200 ml toluene. After the organotin dichloride solution was added, the reaction mixture was stirred for 1 h at −78°C, then stirred over night to reach the room temperature. The reaction mixture was filtered in open atmosphere and the solvent removed under vacuum. The white solid residue was recrystallized from toluene to give 8.76 g (58,4%) of the title compound as colorless crystals. M.p. 204–206°C. Anal. Found: C, 56.72; H, 5.00; N, 3.25. Calc. for $C_{21}H_{22}ClNSn$: C, 56.99; H, 5.01; N, 3.16%. ^{1}H-NMR: δ 1.87s (6H, N–C*H*$_3$, $^3J_{SnH}$ 38.7 Hz), 3.55s (2H, –C*H*$_2$–, $^3J_{SnH}$ 38.9 Hz), 7.19d (1H, –C_6*H*$_4$–, H_3, $^3J_{HH}$ 7.3 Hz), 7.44m (8H, –C_6*H*$_4$–, $H_{4,5}$, Sn–C_6*H*$_5$-*meta* + *para*), 7.72d (4H, Sn–C_6*H*$_5$-*ortho*, $^3J_{HH}$ 5.7, $^3J_{SnH}$ 65.5 Hz), 8.50d (1H, –C_6*H*$_4$–, H_6, $^3J_{HH}$ = 7.1, $^3J_{SnH}$ 71.4 Hz); ^{13}C-NMR: δ 45.84s (N–*C*H_3), 64.87s (–*C*H_2–, $^2J_{SnC}$ 28.2 Hz), 127.26s ($^3J_{SnC}$ 63.8 Hz), 128.34s ($^3J_{SnC}$ 71.5 Hz) ($C_{3,5}$), 128.96s (Sn–*C*$_6H_5$-*meta*, $^3J_{SnC}$ 68.6 Hz), 129.52s (Sn–*C*$_6H_5$-*para*), 130.17s (C_4), 135.64s (Sn–*C*$_6H_5$-*ortho*, $^2J_{SnC}$ 45.5 Hz), 138.83s (*C*$_6$, $^2J_{SnC}$ 44.9 Hz), 141.51s ($^1J_{SnC}$ 50.4 Hz), 142.79s ($^1J_{SnC}$ 42.1 Hz) (C_1, Sn–*C*$_6H_5$-*ipso*); ^{119}Sn-NMR: δ −176.9s.

*3.3. Preparation of C,N-[2-(dimethylaminomethyl)-phenyl]diphenyltin(IV)diphenyldithiophosphinate, [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[S(S)PPh_2] (**2**)*

A mixture of **1** (0.271 g, 0.6 mmol) and $NH_4[S_2PPh_2]$ (0.164 g, 0.6 mmol) in 50 ml anhydrous CH_2Cl_2 was stirred at room temperature for 3 h. The reaction mixture was filtered to remove NH_4Cl and the clear filtrate was evaporated in vacuo to give the title compound as a white solid. Recrystallization from CH_2H_2/*n*-hexane affords colorless crystals. Yield: 0.37 g (92%), M.p. 196–198°C. Anal. Found: C, 60.11; H, 4.78; N, 2.01. Calc. for $C_{33}H_{32}NPS_2Sn$: C, 60.38; H, 4.91; N, 2.13%. IR (cm^{-1}): 655vs [$\nu_{as}(PS_2)$], 538vs [$\nu_s(PS_2)$]. ^{1}H-NMR: δ 1.68s (6H, N–C*H*$_3$, $^3J_{SnH}$ 34.1 Hz), 3.45s (2H, –C*H*$_2$–, $^3J_{SnH}$ 28.7 Hz), 7.16–7.50m (15H, –C_6*H*$_4$–, H_{3-5}, Sn–C_6*H*$_5$-*meta* + *para*, P–C_6*H*$_5$-*meta* + *para*), 7.65d (4H, Sn–C_6*H*$_5$-*ortho*, $^3J_{HH}$ 6.5, $^3J_{SnH}$ 65.4 Hz), 7.70dd (4H, P–C_6*H*$_5$-*ortho*, $^3J_{HH}$ 7.3, $^3J_{PH}$ 13.7 Hz), 8.59d (1H, –C_6*H*$_4$–, H_6, $^3J_{HH}$ 6.9, $^3J_{SnH}$ 70.3 Hz); ^{13}C-NMR: δ 45.65s (N–*C*H_3), 64.63s (–*C*H_2–), 127.27s ($^3J_{SnC}$ 62.6 Hz), 128.02s ($C_{3,5}$), 127.61d (P–*C*$_6H_5$-*meta*, $^3J_{PC}$ 13.1 Hz), 128.38s (Sn–*C*$_6H_5$-*meta*), 128.99s (Sn–*C*$_6H_5$-*para*), 129.72s (P–*C*$_6H_5$-*para*, C_4), 130.72d (P–*C*$_6H_5$-*ortho*, $^2J_{PC}$ 11.3 Hz), 136.29s (Sn–*C*$_6H_5$-*ortho*, $^2J_{SnC}$ 43.5 Hz), 138.82d (P–*C*$_6H_5$-*ipso*, $^1J_{PC}$ 90.2 Hz), 140.16s (*C*$_6$, $^2J_{SnC}$ 41.8 Hz), 141.12s, 143.21s (C_1, Sn–*C*$_6H_5$-*ipso*); ^{31}P-NMR: δ 57.9s ($^2J_{SnP}$ 21.2 Hz).

*3.4. Preparation of C,N-[2-(dimethylaminomethyl)-phenyl]diphenyltin(IV)diphenylmonothiophosphinate, [2-(Me_2NCH_2)C_6H_4]$SnPh_2$[O(S)PPh_2].0.5CH_2Cl_2 (**3**)*

A mixture of **1** (0.276 g, 0.62 mmol) and $NH_4[OSPPh_2]$ (0.16 g, 0.62 mmol) in 50 ml anhydrous toluene was stirred at room temperature for 3 h. The reaction mixture was filtered to remove NH_4Cl and the clear filtrate was evaporated in vacuo to give the title compound as a white solid. Recrystallization from CH_2Cl_2/*n*-hexane affords colorless crystals. Yield: 0.36 g (84%), M.p. 149–151°C. Anal. Found: C, 59.02; H, 5.17; N, 1.93. Calc. for $C_{33}H_{32}NOPSSn.0.5CH_2Cl_2$: C, 58.93; H, 4.84; N, 2.05%. IR (cm^{-1}): 1017vs [ν(P–O)], 645s [ν(P=S)]. ^{1}H-NMR: δ 1.53s (6H, N–C*H*$_3$), 3.15s (2H, –C*H*$_2$–), 6.95–7.50m (15H, –C_6*H*$_4$–, H_{3-5}, Sn–C_6*H*$_5$-*meta* + *para*, P–C_6*H*$_5$-*meta* + *para*), 7.60d (4H, Sn–C_6*H*$_5$-*ortho*, $^3J_{HH}$ 6.8, $^3J_{SnH}$ 60.0 Hz), 7.70dd (4H, P–C_6*H*$_5$-*ortho*, $^3J_{HH}$ 8.2, $^3J_{PH}$ 13.0 Hz), 8.79d (1H, –C_6*H*$_4$–, H_6, $^3J_{HH}$ 7.5, $^3J_{SnH}$ 66.6 Hz); ^{31}P-NMR: δ 64.7s ($^2J_{SnP}$ 122.3, 117.6 Hz); ^{119}Sn-NMR: δ −209.1d ($^2J_{SnP}$ 122.9 Hz).

3.5. X-ray structure determination

Intensity data for the colorless crystals of **1**–**3** were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoKα radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 5s (**2**) 10s (**1**), and 30s (**3**) per frame. The crystal-to-detector distance was 2.8 for **1** and **2**, and 3.0 cm with a detector-θ-offset of 5° for **2** and **3**, respectively. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay. The structure was solved by direct methods SHELXS-97 [29] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL-97 [30].

Table 2
X-ray crystal data and structure refinement for **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{21}H_{22}ClNSn$	$C_{33}H_{32}NPS_2Sn$	$C_{33}H_{32}NOPSSn \cdot 0.5CH_2Cl_2$
Formula weight	442.54	656.38	682.78
Temperature (K)	291(1)	291(1)	291(1)
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a (Å)	8.490(1)	9.133(1)	10.120(1)
b (Å)	15.330(1)	8.855(1)	20.614(1)
c (Å)	15.296(1)	37.885(1)	15.770(1)
β (°)	92.622(1)	93.134(1)	107.381(1)
V (Å^3)	1988.7(3)	3059.3(5)	3139.6(4)
Z	4	4	4
D_{calc} (g cm^{-3})	1.478	1.425	1.444
Absorption coefficient (mm^{-1})	1.421	1.046	1.043
$F(000)$	888	1336	1388
Crystal size (mm)	$0.18 \times 0.15 \times 0.15$	$0.30 \times 0.20 \times 0.20$	$0.35 \times 0.22 \times 0.20$
θ range for data collections (°)	4.20–27.48	4.11–25.41	2.91–27.48
Reflections collected	26230	30958	40441
Complete collected θ_{max}	98.2	92.3	99.8
Independent reflections	4473 [$R_{int} = 0.040$]	5199 [$R_{int} = 0.063$]	7177 [$R_{int} = 0.028$]
Data/restraints/parameters	4473/0/220	5199/0/346	7177/0/365
Goodness-of-fit on F^2	0.950	0.897	0.944
Final R indicies [$I > 2\sigma(I)$]	$R_1 = 0.0282$, $wR_2 = 0.0637$	$R_1 = 0.0341$, $wR_2 = 0.0767$	$R_1 = 0.0316$, $wR_2 = 0.0773$
R indicies (all data)	$R_1 = 0.0541$, $wR_2 = 0.0684$	$R_1 = 0.0716$, $wR_2 = 0.0839$	$R_1 = 0.0584$, $wR_2 = 0.0812$
Largest difference peak and hole (e Å^{-3})	0.477 and −0.298	0.541 and −0.469	0.826 and −0.713

The H atoms were placed in geometrically calculated positions using a riding model and refined with common isotropic temperature factors (C–H_{aryl} 0.93, C–H_{prim} 0.96, C–H_{sec} 0.97 Å, U_{iso} 0.086(2) (**1**), 0.095(3) (**2**), 0.081(2) (**3**)) and for the methylene dichloride molecule in **3** with isotropic temperature factors constrained to be 1.5 times to those of the carrier atom. The C atom of the disordered solvent molecule methylene dichloride was refined with an occupancy of 0.5.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography [31]. The figures were created by SHELXTL [32]. Crystallographic data are given in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis of compounds **1**–**3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148292 (**1**), 148291 (**2**), 148293 (**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).

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