ELSEVIER

Journal of Organometallic Chemistry 642 (2002) 71–79

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Solution and solid state structural investigations of organotin(IV) compounds containing asymmetric imidodiphosphinato ligands. X-ray structures of $R''_2Sn[(OPMe_2)(OPPh_2)N]_2$ (R = Me, Bu^n, Ph)

Cristian Silvestru [a,*], Roland Rösler [a], Anca Silvestru [a], John E. Drake [b,*]

[a] *Facultatea de Chimie, Universitatea Babes-Bolyai, R-3400 Cluj-Napoca, Romania*
[b] *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4*

Received 1 June 2001; accepted 30 August 2001

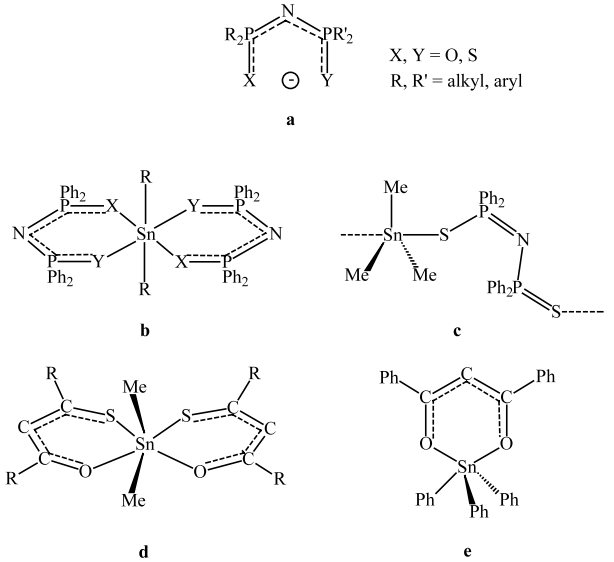
Abstract

Organotin(IV) derivatives of the type $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ (R = Me, Bu^n, Bz, Ph) were prepared by metathesis reactions between R_2SnCl_2 and the potassium salt of the imidodiphosphinic acid, in toluene. Me_3SnCl and $K[(OPMe_2)(OPPh_2)N]$ (1:1 molar ratio) in chloroform at room temperature gives $Me_3Sn[(OPMe_2)(OPPh_2)N]$, while the NMR studies indicate that the corresponding triphenyltin(IV) derivative disproportionates gradually in solution to give $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$. Attempts to grow crystals of the trimethyltin(IV) derivative also gives $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ as a redistribution product. The compounds were characterized by IR and multinuclear NMR spectroscopy. The crystal and molecular structures of $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (**1**), Bu^n (**2**), Ph (**4**)] were established by X-ray diffractometry. The compounds exhibit similar spiro-bicyclic structures, with the tin atom as spiro atom and chelating ligands with the oxygen atoms of the similar OPR_2 groups in *trans* positions. The coordination geometry around the central metal atom is octahedral, with C–Sn–C and O–Sn–O (*trans*) angles of 180°. No significant differences were noted in the length of the tin–oxygen, phosphorus–oxygen and phosphorus–nitrogen bonds, respectively, in relation to the different organic groups attached to tin or phosphorus atoms in a ligand moiety. The solution and solid state structures of the title compounds are discussed comparatively.

Keywords: Organotin(IV) compounds; Asymmetric imidodiphosphinato ligands

1. Introduction

Organotin(IV) derivatives of 1,1-dithiophosphorus ligands (dithiophosphates, $[(RO)_2PS_2]^-$, dithiophosphinates, $[R_2PS_2]^-$) have been the subject of numerous structural studies [1–4] and it has often been suggested that the restricted S···S bite distance plays an important role in the distortion from ideal geometry around the central tin atom. Structural studies on analogous organotin(IV) complexes containing $[R_2PSO]^-$ and $[R_2PO_2]^-$ groups revealed a general tendency for association through bridging phosphorus ligands, i.e. $[Me_3SnO_2PPh_2]_4$ [5], $[Ph_3SnO_2P(OPh)_2]_6$ [6], $[R'_3Sn\text{-}OSPR_2]_n$ (R′ = R = Me, Ph) [7,8], $[Me_2Sn\{O(S)\text{-}PPh_2\}_2]_n$ [9], $[R'_2Sn(O_2PR_2)_2]_n$ (R′ = Et, Ph; R = Me, Ph) [10,11].



* Corresponding authors. Fax: +40-64-190-818.
E-mail address: cristi@chem.ubbcluj.ro (C. Silvestru).

0022-328X/02/$ - see front matter
PII: S0022-328X(01)01200-1

In order to explore structural changes produced in the absence of a restrictive ligand 'bite' we have studied organotin(IV) complexes containing ligands of general formula $[(XPR_2)(YPR'_2)N]^-$ (**a**), which exhibit a flexible XPNPY skeleton.

We have previously reported that $R_2Sn[(XPPh_2)(YPPh_2)N]_2$ (X, Y = O, S) derivatives are monomeric, with an almost perfect *trans*-$C_2SnX_2Y_2$ octahedral core (**b**) [12–16], while $Me_3Sn[(SPPh_2)_2N]$ exhibits a chain polymeric structure (**c**) with the ligand acting as an asymmetric bridge (Sn–S 2.517 Å, Sn···S 3.627 Å) [15]. By comparison, interesting structural differences have been reported for the related organotin(IV) derivatives of β-diketones and thio analogs. Thus, $Me_2Sn[(OCMe)_2CH]_2$ exhibits a similar perfect *trans*-C_2SnO_4 octahedral core (C–Sn–C 180°) [17], in $Me_2Sn[(OCR)(SCR)CH]_2$ (R = Me, Ph) the C_2Sn moiety is angular (C–Sn–C 139.4° for R = Me, and 134.2° for R = Ph) (**d**) [18], while $Ph_3Sn[(OCPh)_2CH]$ is monomeric with an asymmetric monometallic biconnective ligand (**e**) [19].

To establish possible changes which might be produced by the presence of different organic groups at the phosphorus atoms of the ligand unit, we have synthesized and characterized $R_nSn[(OPMe_2)(OPPh_2)N]_{4-n}$ derivatives both in solution and the solid state. The molecular structures of $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (**1**), Bu^n (**2**), Ph (**4**)] were established by X-ray diffractometry.

2. Results and discussion

2.1. Preparation

The title compounds were obtained as white crystalline solids by reacting the potassium salt of the imidodiphosphinic acid with the appropriate organotin chloride, in toluene or chloroform, according to Eq. (1):

$$R_nSnCl_{4-n} + (4-n)K[(OPMe_2)(OPPh_2)N] \rightarrow R_nSn[(OPMe_2)(OPPh_2)N]_{4-n} + (4-n)KCl \quad (1)$$

$n = 2$ R = Me(**1**), Bu^n(**2**), Bz(**3**), Ph(**4**)

$n = 3$ R = Me (**5**)

The corresponding triphenyltin(IV) derivative could not be isolated as a pure compound from the reaction mixture, due to a quite fast redistribution process of the expected product according to Eq. (2):

$$2R_3Sn[(OPMe_2)(OPPh_2)N] \rightarrow R_2Sn[(OPMe_2)(OPPh_2)N]_2 + R_4Sn \quad (2)$$

A similar process has been previously noted for the related $R_3Sn[(OPPh_2)(SPPh_2)N]$ (R = Me, Ph) [16] and the (β-diketonato)triorganotin(IV) analogues [19]. No attempts have been made so far to obtain any chemical or spectroscopic proof on the formation of R_4Sn, but ^{31}P-NMR spectra are consistent with the conversion of the Ph_3Sn(IV) derivative into the Ph_2Sn(IV) compound **4** (see below). Although the NMR data of a freshly prepared sample of the trimethyltin(IV) complex **5** were consistent with the presence of a SnC_3 fragment, attempts to grow single crystals suitable for X-ray diffraction studies led only to isolation of $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**1**).

2.2. IR studies

The strong infrared absorptions observed for all organotin complexes in the regions 1250–1200 and 1120–1055 cm^{-1} were assigned to $\nu_{as}(P_2N)$ and ν(PO) stretching vibrations, respectively, by comparison with the spectra of the free acid and its potassium salt, thus suggesting bidentate coordination of the ligand unit through both oxygen atoms. The SnC_n stretching vibrations could not be assigned in the case of alkyltin derivatives, being obscured by strong absorption bands of the phenyl rings and Sn–O bonds.

2.3. NMR studies

All the diorganotin(IV) and $Me_3Sn[(OPMe_2)(OPPh_2)N]$ derivatives, as well as the free imidodiphosphinic acid and its potassium salt, were investigated by solution NMR spectroscopy. Either the free acid and its K salt or the organotin compounds displayed good solubility in $CDCl_3$ and their ^{1}H and ^{13}C spectra showed the expected doublet pattern (due to phosphorus–proton and phosphorus–carbon couplings, respectively) for the organic groups attached to phosphorus atoms. For the $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (**1**), Bu^n (**2**), Bz (**3**)] and $Me_3Sn[(OPMe_2)(OPPh_2)N]$ (**5**) complexes the spectra also contain characteristic resonance signals for equivalent organic groups bonded to tin. The coordination geometry of organotin(IV) derivatives is reflected in the NMR parameters [20]. Thus, the values of the $^2J(^{119}SnC^1H)$ and $^1J(^{119}Sn^{13}C)$ coupling constants fall in the region for six-coordinate tin in the case of diorganotin derivatives [21]. Table 1 contains the calculated C–Sn–C angles based on the reported relationships between $^2J(^{119}SnC^1H)$ and $^1J(^{119}Sn^{13}C)$ coupling constants and the C–Sn–C angle [21–23]. In contrast with the monothio derivatives $R_2Sn[(OPPh_2)(SPPh_2)N]_2$, the $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (**1**), Bu^n (**2**)] compounds in solution display a C–Sn–C angle close to 180° as was found in the solid state (see below). The ^{119}Sn resonances for the diorganotin(IV) complexes appear as sharp signals and their chemical shifts fall in the expected range for six-coordinated tin [20].

The ^{31}P-NMR spectrum of $(OPMe_2)(OPPh_2)NH$ exhibits two singlet resonances at 44.7 (Me_2PO) and 22.4

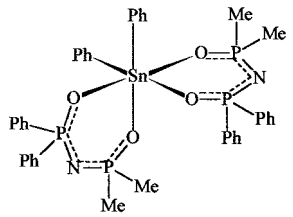
Table 1
Correlations between $^{119}SnC^{1}H$ and $^{119}Sn^{13}C$ coupling constants (Hz) and C–Sn–C angles (θ, °) in $R_nSn[(OPMe_2)(SPPh_2)N]_{4-n}$

Compound	^{1}H		^{13}C	
	$^{2}J(^{119}SnC^{1}H)$	C–Sn–C	$^{1}J(^{119}Sn^{13}C)$	C–Sn–C
$Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**1**)	120.0	178 [a]	1188.0	181 [b]
$Bu^n_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**2**)			1105.9	185 [c]
$Me_3Sn[(OPMe_2)(OPPh_2)N]$ (**5**)	72.5	120 [a]	566.9	126 [b]

[a] $\theta = 0.0105|^{2}J|^{2} - 0.799|^{2}J| + 122.4$ [21].
[b] $|^{1}J| = 11.4\theta - 875$ [22].
[c] $|^{1}J| = 9.99\theta - 746$ [23].

ppm (Ph_2PO), the splitting due to phosphorus–phosphorus coupling not being observed. The loss of the acidic proton in the K salt is reflected in a significant higher field (ca. 10–15 ppm) shift of the ^{31}P resonance signals [28.9 (Me_2PO), 13.7 ppm (Ph_2PO); the assignment being based on the $^{1}J(PC)$ coupling constants] and the splitting due to phosphorus–phosphorus coupling is observed [$^{2}J(PP)$ 7.8 Hz]. However, for the dialkyltin(IV) derivatives **1**–**3** and $Me_3Sn[(OPMe_2)(OPPh_2)N]$ (**5**) the $^{2}J(PP)$ is not resolved. The ^{31}P resonance assigned to Ph_2PO ($\delta = 10.3$ ppm) in the spectrum of **5** is even more shifted to higher field compared to the alkali metal starting material, suggesting a primary coordination of the imidodiphosphinato ligand through oxygen atom. The estimated C–Sn–C angle in this case is about 120° and consistent with a planar SnC_3 moiety with bridging imidodiphosphinato groups, a pattern observed in the solid state for the dithio analogue, $Me_3Sn[(SPPh_2)_2N]$ [structure (**c**)] [15].

The NMR spectra of the diphenyltin(IV) derivative, $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**4**), deserve some special comments. The ^{1}H-NMR spectrum in the aromatic region exhibits two doublet resonances for the *ortho* protons of the phenyl groups attached to tin. On the other hand, four singlets are observed in the ^{31}P-NMR spectrum of compound **4**: 20.90, 21.74 (Ph_2PO), 39.51, 39.63 ppm (Me_2PO) (Fig. 1). This behavior suggests nonequivalence of the phenyl groups attached to tin as well as nonequivalence of the phosphorus atoms bearing the same organic groups of the two ligand moieties, respectively, in $CDCl_3$ solution. Therefore a *cis*-C_2SnO_4 octahedral core with an angular C–Sn–C fragment might be proposed (structure **f**) for **4**, which contrasts with the *trans*-C_2SnO_4 cores suggested in solution for the dialkyltin(IV) analogues **1**–**3**. However, a *trans*-C_2SnO_4 core with a linear C–Sn–C fragment was established in the solid state for **4** by single-crystal X-ray diffraction (see below).



f

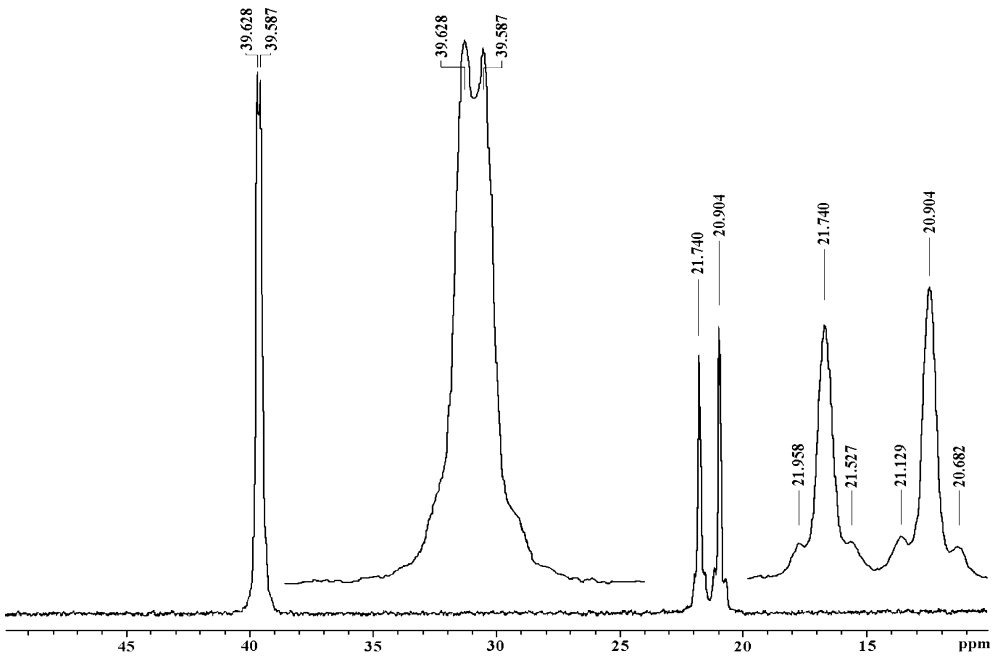


Fig. 1. ^{31}P-NMR spectrum of $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**4**).

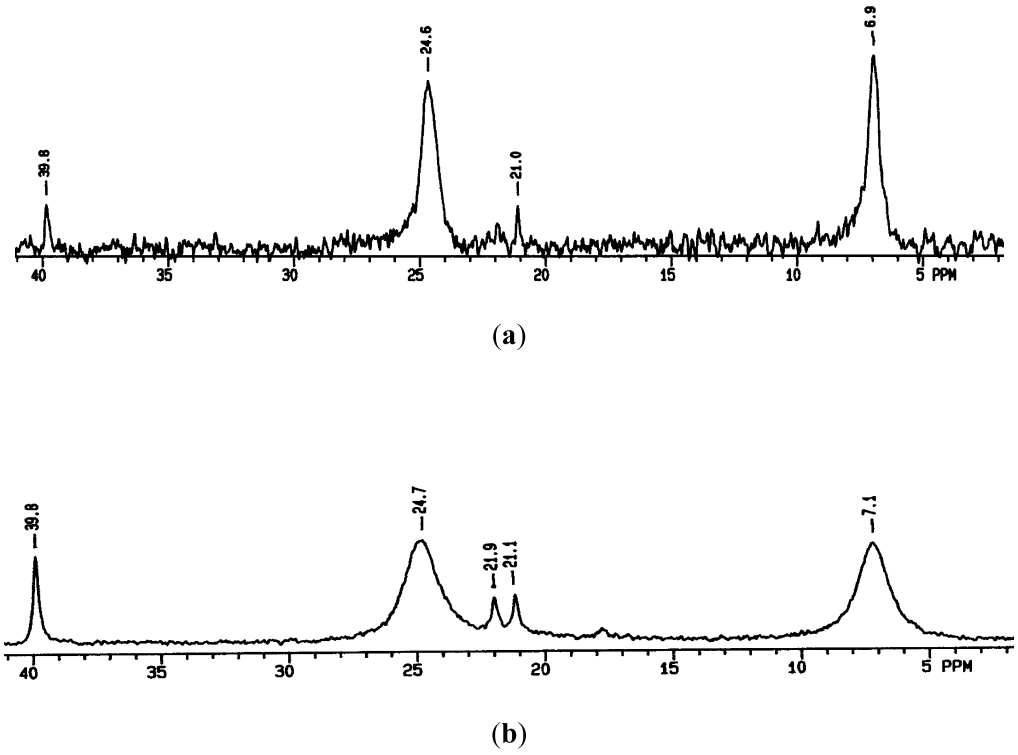
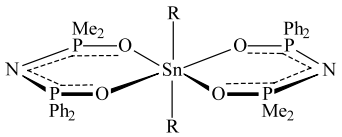
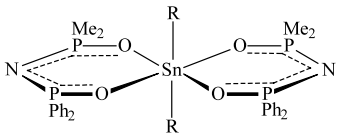


Fig. 2. ^{31}P-NMR spectrum of: (a) freshly prepared '$Ph_3Sn[(OPMe_2)(OPPh_2)N]$'; and (b) 6-h old '$Ph_3Sn[(OPMe_2)(OPPh_2)N]$'.

Alternatively, the presence of the two possible isomers (**g**) ($OPMe_2$ *trans* $OPMe_2$) and (**h**) ($OPMe_2$ *trans* $OPPh_2$) for a diorganotin(IV) derivative containing a linear C_2Sn moiety, in a 1:1 molar ratio, might also account for the observed NMR behavior of compound **4** in solution, if the interconversion between these forms is frozen at room temperature:



(**g**)



(**h**)

In contrast to the trimethyltin(IV) derivative **5**, the triphenyltin(IV) analogue, $Ph_3Sn[(OPMe_2)(OPPh_2)N]$, could not be obtained as a pure compound and attempts to purify the solid product by recrystallization from toluene, CH_2Cl_2 or MeCN, always resulted in isolation of the Ph_2Sn(IV) compound **4**. To obtain evidence for the redistribution process, a mixture of stoichiometric amounts of pure Ph_3SnCl and $K[(OPMe_2)(OPPh_2)N]$ was placed in an NMR tube and the reaction followed by ^{31}P-NMR spectroscopy. The spectrum of the fresh sample (Fig. 2a) exhibited two main broad resonances at 6.9 and 24.7 ppm for the triphenylltin(IV) derivative **5**, which were assigned to Ph_2PO and Me_2PO phosphorus atoms, respectively. In addition, the spectrum also contains resonances of low intensity (δ ca. 21 and 40 ppm) indicating that a small amount of the diphenyltin(IV) derivative **4** has already formed. Indeed, the ^{31}P spectrum of the same sample recorded after 6 h (Fig. 2b) exhibits resonances of increased intensity at 39.9, 22.0 and 21.2 ppm, consistent with the conversion of the $Ph_3Sn[(OPMe_2)(OPPh_2)N]$ into the diphenyltin(IV) derivative **4** (cf. δ 20.90, 21.74 (Ph_2PO), 39.51, 39.63 ppm (Me_2PO) for pure $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$).

2.4. Crystal and molecular structure of $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (1), Bu^n (2), Ph (4)]

The solid state structures of $R_2Sn[(OPMe_2)(OPPh_2)N]_2$, R = Me (**1**), Bu^n (**2**), Ph (**4**), were determined by single-crystal X-ray diffraction. Selected bond distances and angles are listed in Table 2. Figs. 3–5 show the ORTEP-like view of the molecular structures of **1**, **2** and **4**, with the atom numbering scheme. For all three compounds the crystal contains discrete molecular units, separated by normal van der Waals distances. The molecular structures are very similar regardless

of the nature of the organic groups attached to tin and therefore a general description for these compounds is given.

The central tin atom occupies a center of inversion. The SnC_2 unit is linear [C(1)–Sn(1)–C(1′) 180°]. The phenyl groups on tin in **4** are coplanar and their orientation is almost orthogonal to the N(1)···N(1)′ axis (173.6°). The two asymmetric ligand moieties are monometallic biconnective, thus resulting in a distorted octahedral coordination around tin, with the carbon atoms of the organic groups attached to tin in axial positions. The equatorial SnO_4 system is planar, with the *trans* positions occupied by oxygen atoms attached to phosphorus atoms bearing the same organic groups [O(1)–Sn(1)–O(1)′ and O(2)–Sn(1)–O(2)′ angles of 180°]. Thus, of two possible isomers (**g**) ($OPMe_2$ *trans* $OPMe_2$) and (**h**) ($OPMe_2$ *trans* $OPPh_2$), only isomer (**g**) is observed.

The distortion of the coordination octahedron is due to the very small differences between the endocyclic and exocyclic O–Sn–O angles (Table 2), and the slight deviation of the C–Sn–C axis from orthogonality to the equatorial plane [C–Sn–O range: 88.8–91.4°]. The Sn–O bond lengths within a molecule of a **1**, **2** and **4** are equivalent regardless of the nature of the organic groups attached to phosphorus atoms; they are of the same magnitude as observed in related analogues containing symmetric or asymmetric ligand units: $Bu^n_2Sn[(OPPh_2)_2N]_2$, average Sn–O 2.203(1) Å [14]; $R_2Sn[(OPPh_2)(SPPh_2)N]_2$ (R = Me, Ph), average 2.194(6) Å [16].

Table 2
Relevant interatomic distances (Å) and angles (°) in $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**1**), $Bu^n_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**2**) and $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**4**)

	1	2	4
Interatomic distances			
Sn(1)–C(1)	2.090(4)	2.127(8)	2.128(18)
Sn(1)–O(1)	2.210(3)	2.217(5)	2.156(12)
Sn(1)–O(2)	2.219(3)	2.214(5)	2.184(11)
P(1)–O(1)	1.515(3)	1.507(5)	1.531(13)
P(1)–N(1)	1.590(3)	1.583(6)	1.554(15)
P(2)–O(2)	1.517(3)	1.518(4)	1.513(11)
P(2)–N(1)	1.592(3)	1.578(6)	1.555(14)
O(1)···O(2)	3.146(3)	3.109(6)	3.11(2)
O(1)···O(2′)	3.118(4)	3.158(6)	3.04(1)
Bond angles			
O(1)–Sn(1)–O(2)	90.51(10)	89.11(16)	91.2(4)
O(1)–Sn(1)–O(2)′	89.49(10)	90.89(16)	88.8(4)
O(1)–Sn(1)–O(1)′	180.00	180.00	180.00
O(2)–Sn(1)–O(2)′	180.00	180.00	180.00
O(2)–Sn(1)–O(1)′	89.49(10)	90.89(16)	88.8(4)
O(2′)–Sn(1)–O(1′)	90.51(10)	89.11(16)	91.2(4)
C(1)–Sn(1)–C(1′)	180.00	180.00	180.00
C(1)–Sn(1)–O(1)	89.71(16)	88.8(3)	89.6(6)
C(1)–Sn(1)–O(2)	91.11(14)	91.4(2)	89.6(6)
C(1)–Sn(1)–O(1′)	90.29(16)	91.2(3)	90.4(6)
C(1)–Sn(1)–O(2′)	88.89(14)	88.6(2)	90.4(6)
C(1′)–Sn(1)–O(1)	90.29(16)	91.2(3)	90.4(6)
C(1′)–Sn(1)–O(2)	88.89(14)	88.6(2)	90.4(6)
C(1′)–Sn(1)–O(1′)	89.71(16)	88.8(3)	89.6(6)
C(1′)–Sn(1)–O(2′)	91.11(14)	91.4(2)	89.6(6)
Sn(1)–O(1)–P(1)	128.63(15)	130.9(3)	129.5(6)
O(1)–P(1)–N(1)	115.64(16)	116.0(3)	114.4(7)
P(1)–N(1)–P(2)	124.8(2)	130.0(4)	135.7(9)
O(2)–P(2)–N(1)	116.78(15)	117.6(3)	115.0(7)
Sn(1)–O(2)–P(2)	127.93(14)	129.2(3)	126.8(7)

Symmetry equivalent position ($-x$, $-y$, $-z$) given by a prime.

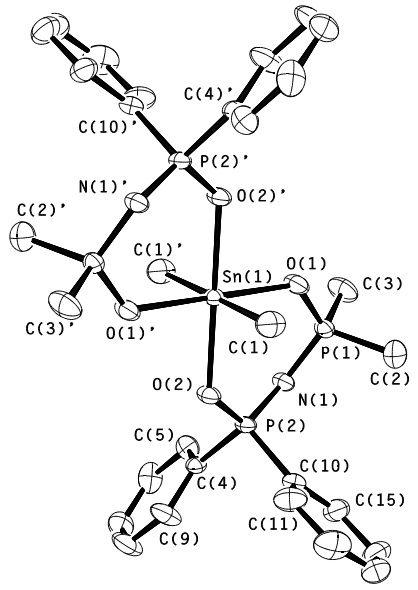


Fig. 3. ORTEP plot of the molecule $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**1**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are excluded for clarity.

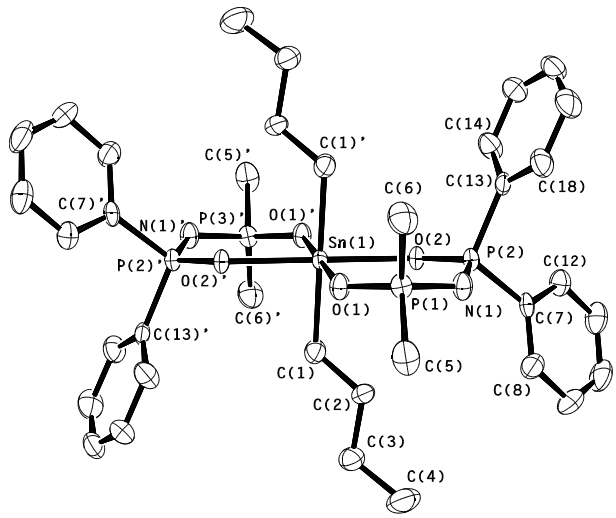


Fig. 4. ORTEP plot of the molecule $Bu_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**2**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are excluded for clarity.

In the coordinated ligand, the P–O [range: 1.507(5)–1.531(13) Å] bonds are of the same magnitude as the single phosphorus–oxygen bond in $Ph_2P(=O)OH$ [P–O 1.526(6), P=O 1.486(6) Å] [24]. Within a ligand unit the phosphorus–nitrogen bonds, regardless the nature of the organic groups attached to phosphorus atoms, are again equivalent within experimental errors and their magnitude [range 1.554(15)–1.592(3) Å] suggests considerable double bond character [cf. $[(Me_3Si)_2N–P(=NBu^t)S]_2$: P–N 1.662(2), P=N 1.529(2) Å)] [25].

The bidentate nature of the imidodiphosphinato ligand units within a $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ molecule leads to an inorganic bicyclic system, $NP_2O_2SnO_2P_2N$, with the metal as spiro atom. Although some delocalization of the π-electrons over the OPNPO systems is suggested by the magnitude of the bonds, the six-membered SnO_2P_2N rings are not planar but exhibit variable conformations close to planarity. Thus a chair conformation was found in **2** [the metal and N(1) atoms in the apices; deviations from the O_2SnO_2 plane: P(1) −0.116, P(2) −0.188, N(1) 0.000 Å], while in **1** and **4** the SnO_2P_2N rings exhibit boat conformation of variable distortion and with different atom types in the apices; the metal and N(1) atoms in **1** [almost planar SnO_2P_2 system; deviations from the O_2SnO_2 plane: P(1) 0.254, P(2) 0.251, N(1) 0.063 Å], and P(2) and O(1) atoms in **4** [deviations from the O_2SnO_2 plane: P(1) 0.163, P(2) −0.394, N(1) −0.121 Å]. For all three compounds the O–Sn–O, Sn–O–P and O–P–N angles are quite similar (Table 2), but the P(1)–N(1)–P(2) angles exhibit significant differences: 124.8(2)° for **1**, 130.0(4)° for **2**, and 135.7(9)° for **4**. The O(1)···O(2) bite in the ligand unit are also different, i.e. 3.146 Å for **1**, 3.109 Å for **2**, and 3.11 Å for **4**, thus supporting the high flexibility of the OPNPO skeleton which might account for the differences observed in the SnO_2P_2N ring conformation.

3. Experimental

3.1. Materials and procedures

Bz_2SnCl_2 was prepared from benzyl chloride and Sn powder [26], while the other organotin chlorides were commercial products. Solvents were dried and freshly distilled prior to use. Infrared spectra were run in the range 4000–200 cm^{-1} as KBr pellets on a Perkin–Elmer 283B instrument. The ^{1}H-, ^{13}C-, ^{31}P- and ^{119}Sn-NMR spectra were recorded as $CDCl_3$ or CD_3OD (for the K salt) solutions using VARIAN VXR 300S or GEMINI 300 instruments, operating at 299.5, 75.4, 121.4 and 111.9 MHz, respectively. The chemical shifts are reported in ppm relative to TMS, H_3PO_4 85%, and Me_4Sn, respectively. Abbreviations used in multiplicities are: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; tq, triplet of quartets; m, multiplet.

3.2. Preparation of *P,P*-dimethyl-*P'*,*P'*-diphenylimidodiphosphinic acid, $(OPMe_2)(OPPh_2)NH$

The compound was prepared as described previously [27]. m.p. 225 °C (lit. [27]: 217 °C). Anal. Found: C, 57.26; H, 5.89; N, 4.68. Calc. for $C_{14}H_{17}NP_2O_2$: C, 57.33; H, 5.85; N, 4.77%. IR (cm^{-1}): 1170s, 1155vs, 1130m [ν(PO)], 925s [$\nu_{as}(P_2NH)$]. ^{1}H-NMR: δ 1.52d [6H, P–CH_3, ^2J(PH) 14.2 Hz], 7.44m (6H, P–C$_6H_5$-*meta* + *para*), 7.83dd [4H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.8, ^3J(HH) 7.0 Hz]. ^{13}C-NMR: δ 19.54d [P–CH$_3$, ^1J(PC)

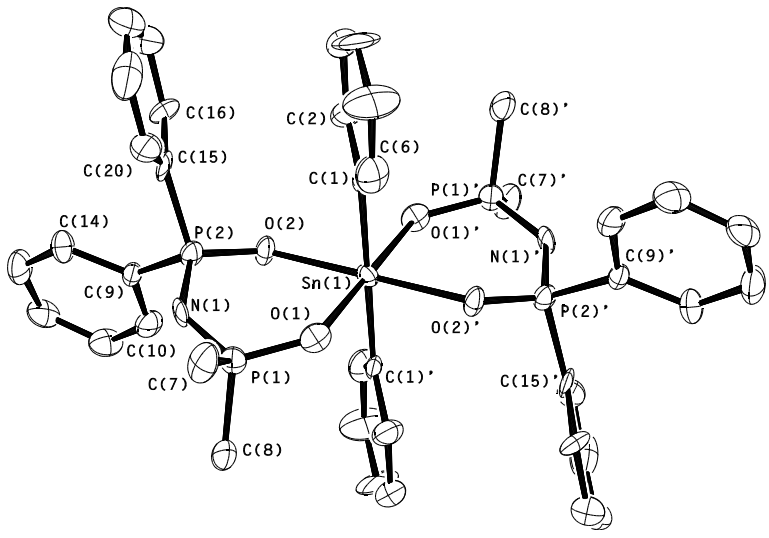


Fig. 5. ORTEP plot of the molecule $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**4**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are excluded for clarity.

85.8 Hz], 128.41d [C_m, ^3J(PC) 13.9 Hz], 131.24d [C_o, ^2J(PC) 10.4 Hz], 131.94s (C_p), 133.67d [C_i, ^1J(PC) 126.4 Hz]. ^{31}P-NMR: δ 22.4s [Ph_2PO, ^1J(PC) 126.3 Hz]; 44.7s (Me_2PO).

3.3. Preparation of potassium P,P-dimethyl-P′,P′-diphenylimidodiphosphinate, K[(OPMe$_2$)(OPPh$_2$)N]

A mixture of (OPMe$_2$)(OPPh$_2$)NH (9.82 g, 33.5 mmol) and KOBu^t (3.76 g, 33.5 mmol) in 250 ml anhydrous diethyl ether was stirred for 3 days. The solid product was filtered off, washed with anhydrous benzene, dried at 120 °C, and then extracted several times with acetonitrile in a Soxhlet apparatus. After removal of the organic solvent in a rotary evaporator, the title compound was isolated as fine, white crystals, which are very hygroscopic and deliquescent. Yield: 9.64 g (87%), m.p. 264–269 °C. IR (cm^{-1}): 1230vs, br [ν_{as}(P$_2$N)], 1170s, 1155vs, 1130 m [ν(PO)]. ^{1}H-NMR: δ 1.30d [6H, P–CH_3, ^2J(PH) 11.1 Hz], 7.36m (6H, P–C$_6H_5$-*meta* + *para*), 7.83ddd [4H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.0, ^3J(HH) 6.5, ^4J(HH) 2.1 Hz]. ^{13}C-NMR: δ 20.64dd [P–CH$_3$, ^1J(PC) 90.5, ^3J(PC) 3.5 Hz], 128.74d [C_m, ^3J(PC) 11.6 Hz], 131.02s (C_p), 132.44d [C_o, ^2J(PC) 10.4 Hz], 140.71dd [C_i, ^1J(PC) 131.7, ^3J(PC) 5.2 Hz]. ^{31}P-NMR: δ 13.7d [Ph_2PO, ^2J(PP) 7.8, ^1J(PC) 132.1 Hz], 28.9d [Me_2PO, ^2J(PP) 7.8, ^1J(PC) 89.7 Hz].

3.4. Preparation of bis(P,P-dimethyl-P′,P′-diphenylimidodiphosphinato)dimethyltin(IV), Me$_2$Sn[(OPMe$_2$)(OPPh$_2$)N]$_2$ (1)

A mixture of Me_2SnCl_2 (0.292 g, 1.33 mmol) and K[(OPMe$_2$)(OPPh$_2$)N] (0.883 g, 2.66 mmol) in 20 ml anhydrous toluene was stirred under reflux for 2 h, then filtered hot to remove the resulting KCl. On cooling and partial evaporation of the solvent colorless crystals started to deposit. The solid product was separated by filtration and recrystallized from methanol. Yield: 0.73 g (75%, after recrystallization), m.p. 232–234 °C. Anal. Found: C, 48.8; H, 4.8; N, 3.6; Calc. for $C_{30}H_{38}N_2O_4P_4Sn$: C, 49.1; H, 5.2; N, 3.8%. IR (cm^{-1}): 1200vs,br [ν_{as}(P$_2$N)], 1120s, 1080vs, 1060vs [ν(PO)]. ^{1}H-NMR: δ 0.86s [6H, Sn–CH_3, ^2J(^{119}SnH) 120.0, ^2J(^{117}SnH) 115.5 Hz], 1.42dd [12H, P–CH_3, ^2J(PH) 14.1, ^4J(PH) 1.2 Hz], 7.35 m (12H, P–C$_6H_5$-*meta* + *para*), 7.78ddd [8H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.8, ^3J(HH) 7.5, ^4J(HH) 1.8 Hz]. ^{13}C-NMR: δ 20.19s [Sn-CH$_3$, ^1J(^{119}SnC) 1188.0, ^1J(^{117}SnC) 1136.2 Hz], 20.63dd [P-CH$_3$, ^1J(PC) 95.9, ^3J(PC) 2.3 Hz], 128.00d [C_m, ^3J(PC) 12.9 Hz], 130.63s (C_p); 131.18d [C_o, ^2J(PC) 10.3 Hz], 137.49d [C_i, ^1J(PC) 135.0 Hz]. ^{31}P-NMR: δ 18.8s (Ph_2PO), 37.2s (Me_2PO). ^{119}Sn-NMR: δ −411.7s.

3.5. Preparation of bis(P,P-dimethyl-P′,P′-diphenylimidodiphosphinato)dibutyltin(IV), Bu$^n_2$Sn[(OPMe$_2$)(OPPh$_2$)N]$_2$ (2)

Prepared as above from $Bu^n_2SnCl_2$ (0.304 g, 1 mmol) and K[(OPMe$_2$)(OPPh$_2$)N] (0.662 g, 2 mmol) and recrystallized from methanol. Yield: 0.67 g (82%, after recrystallization), m.p. 197–9 °C. Anal. Found: C, 52.7; H, 6.3; N, 3.2; Calc. For $C_{36}H_{50}N_2O_4P_4Sn$: C, 52.9; H, 6.2; N, 3.4%. IR (cm^{-1}): 1225vs, br [ν_{as}(P$_2$N)], 1120ms, 1080s, 1060vs [ν(PO)]. ^{1}H-NMR: δ 0.57t [6H, Sn–(CH$_2$)$_3$CH_3, ^3J(HH) 7.3 Hz], 1.00tq [4H, Sn–(CH$_2$)$_2$CH_2CH$_3$, ^3J(HH) 7.1 Hz], 1.43m [8H, Sn–(CH_2)$_2$CH$_2$CH$_3$], 1.49d [12H, P–CH_3, ^2J(PH) 14.0 Hz], 7.37m (12H, P–C$_6H_5$-*meta* + *para*), 7.81ddd [8H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.4, ^3J(HH) 7.7, ^4J(HH) 1.9 Hz]. ^{13}C-NMR: δ 13.62s (C_δ), 20.52d [P–CH$_3$, ^1J(PC) 95.0 Hz], 26.44s [C_γ, ^3J($^{119/117}$SnC) 174.8 Hz], 28.38s [C_γ, ^2J($^{119/117}$SnC) 43.5 Hz], 38.09s [C_α, ^1J(^{119}SnC) 1105.9, ^1J(^{117}SnC) 1057.3 Hz], 127.88d [C_m, ^3J(PC) 13.7 Hz], 130.46s (C_p), 131.17d [C_o, ^2J(PC) 10.3 Hz], 137.70d [C_i, ^1J(PC) 136.2 Hz]. ^{31}P-NMR: δ 18.1s (Ph_2PO), 36.6s (Me_2PO). ^{119}Sn-NMR: δ −434.0s.

3.6. Preparation of bis(P,P-dimethyl-P′,P′-diphenylimidodiphosphinato)dibenzyltin(IV), Bz$_2$Sn[(OPMe$_2$)(OPPh$_2$)N]$_2$ (3)

Prepared as above from Bz_2SnCl_2 (0.372 g, 1 mmol) and K[(OPMe$_2$)(OPPh$_2$)N] (0.662 g, 2 mmol). The insoluble product was filtered, and then extracted with toluene in a Soxhlet apparatus for 24 h (very low solubility in toluene). Yield: 0.49 g (55%, after extraction), m.p. 269–271 °C. Anal. Found: C, 56.7; H, 4.8; N, 3.2; Calc. for $C_{42}H_{46}N_2O_4P_4Sn$: C, 57.0; H, 5.2; N, 3.2%. IR (cm^{-1}): 1250vs, br [ν_{as}(P$_2$N)], 1115m, 1075vs, 1060vs [ν(PO)]. ^{1}H-NMR: δ 1.03d [12H, P–CH_3, ^2J(PH) 14.1 Hz], 2.79s [4H, Sn–CH_2C$_6$H$_5$, ^2J(^{119}SnH) 155.3, ^2J(^{117}SnH) 149.9 Hz], 6.72s, br (4H, Sn–CH$_2$C$_6H_5$-*ortho*), 6.79s, br (6H, Sn–CH$_2$C$_6H_5$-*meta* + *para*), 7.36m (12H, P–C$_6H_5$-*meta* + *para*), 7.82ddd [8H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.6, ^3J(HH) 7.5, ^4J(HH) 2.1 Hz]. ^{13}C-NMR: δ 19.89d [P–CH$_3$, ^1J(PC) 96.1 Hz], 46.03s (Sn–CH$_2$C$_6$H$_5$, ^1J($^{119/117}$SnC) 1077.4 Hz) 123.84s (C_p, Sn–CH$_2$$C_6H_5$), 127.60s ($C_m$, Sn–CH$_2$$C_6H_5$), 128.07d [$C_m$, P–$C_6H_5$, ^3J(PC) 12.6 Hz], 129.49s [C_o, Sn–CH$_2$$C_6H_5$, ^3J(^{119}SnC) 59.6, ^3J(^{117}SnC) 47.1 Hz], 130.65s (C_p, P–C_6H$_5$), 131.25d [C_o, P–C_6H$_5$, ^2J(PC) 10.2 Hz], 137.69d [C_i, P–C_6H$_5$, ^1J(PC) 137.6 Hz], 141.10s (C_i, Sn–CH$_2$$C_6H_5$). ^{31}P-NMR: δ 17.8s (Ph_2PO), 38.5s (Me_2PO). ^{119}Sn-NMR: δ −512.0s.

3.7. Preparation of bis(P,P-dimethyl-P′,P′-diphenylimidodiphosphinato)diphenyltin(IV), Ph$_2$Sn[(OPMe$_2$)(OPPh$_2$)N]$_2$ (4)

Prepared as above from Ph_2SnCl_2 (0.344 g, 1 mmol)

and K[(OPMe$_2$)(OPPh$_2$)N] (0.662 g, 2 mmol) and recrystallized from toluene. Yield: 0.72 g (84%, after recrystallization), m.p. 235–237 °C. Anal. Found: C, 55.7; H, 4.8; N, 3.2; Calc. for $C_{40}H_{42}N_2O_4P_4Sn$: C, 56.0; H, 4.90; N, 3.3%. IR (cm^{-1}): 1230vs,br [ν_{as}(P$_2$N)], 1115m, 1075vs, 1055vs [ν(PO)]. ^{1}H-NMR: δ 1.23d [12H, P–CH_3, ^2J(PH) 14.3 Hz], 7.12m (complex signal) (14H, Sn–C$_6H_5$-*para*, P–C$_6H_5$-*meta* + *para*), 7.39m (complex signal) (12H, Sn–C$_6H_5$-*meta*, P–C$_6H_5$-*ortho*), 7.91d [2H, Sn–C$_6H_5$-*ortho*, ^3J(HH) 7.5, ^2J($^{119/117}$SnH) 115.7 Hz], 7.94d [2H, Sn–C$_6H_5$-*ortho*, ^3J(HH) 7.7, ^2J($^{119/117}$SnH) 113.9 Hz]. ^{13}C-NMR: δ 20.10d [P–CH$_3$, ^1J(PC) 95.9 Hz], 126.90s, 126.97s (C_m, SnC_6H$_5$), 127.30s (C_p, Sn–C_6H$_5$), 127.57d [C_m, P–C_6H$_5$, ^3J(PC) 13.7 Hz], 130.36s (C_p, P–C_6H$_5$), 131.33m [C_o, P–C_6H$_5$], 135.30s [C_o, Sn–C_6H$_5$, ^3J($^{119/117}$SnC) 68.5 Hz], 136.19d [C_i, P–C_6H$_5$, ^1J(PC) 134.1 Hz], 136.52d [C_i, P–C_6H$_5$, ^1J(PC) 137.1 Hz], 156.03s (C_i, Sn–C_6H$_5$). ^{31}P-NMR: δ 20.90s [Ph$_2$$P$O, ^2J($^{119/117}$SnP) 55.9 Hz], 21.74s [Ph$_2$$P$O, ^2J($^{119/117}$SnP) 52.3 Hz], 39.51s (Me$_2$$P$O), 39.63s (Me$_2$$P$O).

3.8. Preparation of (*P*,*P*-dimethyl-*P*′,*P*′-diphenylimidodiphosphinato)trimethyltin(IV), $Me_3Sn[(OPMe_2)(OPPh_2)N]$ (**5**)

A mixture of Me$_3$SnCl (0.2 g, 1 mmol) and K[(OPMe$_2$)(OPPh$_2$)N] (0.331 g, 1 mmol) in 25 ml chloroform were stirred for 2 h at room temperature. The resulting KCl was filtered off and the solvent removed in vacuum to dryness. The white, solid product thus obtained was solved in CH_2Cl_2 and re-precipitated by slow addition of hexane to result in colorless microcrystalline Me$_3$Sn[(OPMe$_2$)(OPPh$_2$)N]. Yield: 0.35 g (77%), m.p. 139–142 °C. Anal. Found: C, 44.5; H, 5.8; N, 3.2; Calc. for $C_{17}H_{25}NO_2P_2Sn$: C, 44.8; H, 5.5; N, 3.1%. IR (cm^{-1}): 1230vs, br [ν_{as}(P$_2$N)], 1200s, 1125vs, 1110vs [ν(PO)]. ^{1}H-NMR: δ 0.45s [9H, Sn-CH_3, ^2J(^{119}SnH) 72.5, ^2J(^{117}SnH) 70.9 Hz], 1.24d [6H, P–CH_3, ^2J(PH) 13.5 Hz], 7.34m (6H, P–C$_6H_5$-*meta* + *para*), 7.71ddd [4H, P–C$_6H_5$-*ortho*, ^3J(PH) 12.5, ^3J(HH) 7.8, ^4J(HH) 2.1 Hz]. ^{13}C-NMR: δ 2.76s [Sn–CH$_3$, ^1J(^{119}SnC) 566.9, ^2J(^{117}SnH) 542.3 Hz]; 20.66dd [P–CH$_3$, ^1J(PC) 93.6,

Table 3
X-ray crystal data and structure refinement for (**1**), (**2**) and (**4**)

Parameter	**1**	**2**	**4**
Empirical formula	$C_{30}H_{38}N_2O_4P_4Sn$	$C_{36}H_{50}N_2O_4P_4Sn$	$C_{40}H_{42}N_2O_4P_4Sn$
Formula weight	733.19	817.35	857.33
Temperature (K)	299(2)	299(2)	299(2)
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.473(5)	12.365(9)	10.912(6)
b (Å)	10.794(5)	7.969(6)	11.045(5)
c (Å)	8.875(4)	20.306(9)	9.659(5)
α (°)	107.15(4)	90.00	104.36(5)
β (°)	90.56(4)	102.16(6)	91.93(5)
γ (°)	116.85(3)	90.00	116.54(5)
V (Å^{-3})	843.3(7)	1956(2)	994.8(9)
Z	1	2	1
D_{calc} (g cm^{-3})	1.444	1.388	1.431
Absorption coefficient (mm^{-1})	0.983	0.855	0.845
F(000)	374	844	438
Crystal size (mm)	0.30 × 0.25 × 0.22	0.32 × 0.28 × 0.26	0.25 × 0.20 × 0.20
θ range for data collection (°)	2.21–25.00	1.68–24.99	2.12–25.00
Reflections collected	3159	3605	3694
Independent reflections	2980 [R_{int} = 0.0495]	3433 [R_{int} = 0.1184]	3493 [R_{int} = 0.1289]
Max and min transmissions	0.8128 and 0.7570	0.8082 and 0.7715	0.8492 and 0.8165
Data/restraints/parameters	2980/0/188	3433/0/215	3493/6/220
Goodness-of-fit on F^2	1.032	1.033	1.051
Final R indices [$F^2 > 4\sigma(F^2)$]	R_1 = 0.0306, wR_2 = 0.0720	R_1 = 0.0401, wR_2 = 0.0931	R_1 = 0.0902, wR_2 = 0.2459
R indices (all data)	R_1 = 0.0510, wR_2 = 0.0796	R_1 = 0.1284, wR_2 = 0.1213	R_1 = 0.2362, wR_2 = 0.3242
Extinction coefficient	0.0013(9)	0.0019(3)	0.007(3)
Largest difference peak and hole (e Å^{-3})	0.423 and −0.743	0.570 and −0.575	2.072 and −0.940

^3J(PC) 3.0 Hz], 127.76d [C_m, ^3J(PC) 12.8 Hz]; 130.08s (C_p), 131.42d [C_o, ^2J(PC) 10.2 Hz], 138.38dd [C_i, ^1J(PC) 135.3, ^3J(PC) 4.5 Hz]. ^{31}P-NMR: δ 8.2s (Ph_2PO, ^1J(PC) 134.7 Hz); 24.3s (Me_2PO).

3.9. X-ray structure determination

Colourless block crystals of $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**1**), $Bu^n_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**2**), and $Ph_2Sn[(OPMe_2)(OPPh_2)N]_2$ (**4**), were mounted on glass fibers and sealed with epoxy glue. Data were collected on a Rigaku AFC6 diffractometer with graphite-monochromated Mo–K_α radiation, operating at 50 kV and 35 mA. Data collection and cell refinement [28] gave cell constants corresponded to triclinic (for **1** and **4**) and monoclinic (for **2**) cells whose dimensions are given in Table 3 along with other experimental parameters. An absorption correction was applied [29] which resulted in transmission factors ranging from 0.8128 to 0.7570 for **1**, 0.8082 to 0.7715 for **2**, and 0.8492 to 0.8165 for **4**.

The structures were solved by direct methods [30], and the structures were refined using the WINGX version [31] of SHELX-97 [32]. All of the non-hydrogen atoms were treated anisotropically and the hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [32] was based on 2980 for **1**, 3433 for **2**, and 3493 for **4** observed reflections [2390 for **1**, 1866 for **2**, and 1546 for **4** for $F^2 > 4s(F^2)$] and 188 for **1**, 215 for **2**, and 220 for **4** variable parameters and converged (largest parameter shift was 0.001 times its esd).

4. Supplementary material

Crystallographic data for the structural analysis of compounds **1**, **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 162460 (**1**), 162461 (**2**), 162462 (**4**)]. 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).

Acknowledgements

This work was supported by the Romanian National Council for High Education Scientific Research through research project No. 46174/1997 (CNCSIS Code 177). One of us (J.E.D.) wishes to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

[1] E.R.T. Tiekink, Main Group Met. Chem. 15 (1992) 161.
[2] V.K. Jain, Coord. Chem. Rev. 135/136 (1994) 809.
[3] I. Haiduc, D.B. Sowerby, S.-F. Lu, Polyhedron 14 (1995) 3389.
[4] I. Haiduc, D.B. Sowerby, Polyhedron 15 (1996) 2469.
[5] M.G. Newton, I. Haiduc, R.B. King, C. Silvestru, J. Chem. Soc. Chem. Commun. (1993) 1229.
[6] K.C. Molloy, F.A.K. Naser, C.L. Barnes, D. van der Helm, J.J. Zuckerman, Inorg. Chem. 21 (1982) 960.
[7] A.-F. Shihada, I.A.-A. Jassim, F. Weller, J. Organomet. Chem. 268 (1984) 125.
[8] A. Silvestru, J.E. Drake, J. Yang, Polyhedron 16 (1997) 4113.
[9] C. Silvestru, I. Haiduc, F. Caruso, M. Rossi, B. Mahieu, M. Gielen, J. Organomet. Chem. 448 (1993) 75.
[10] A.-F. Shihada, F. Weller, Z. Naturforsch. 51b (1996) 1111.
[11] A.-F. Shihada, F. Weller, Z. Naturforsch. 52b (1997) 587.
[12] R. Rösler, C. Silvestru, I. Haiduc, F. Kayser, M. Gielen, B. Mahieu, Main Group Met. Chem. 16 (1993) 436.
[13] I. Haiduc, C. Silvestru, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Polyhedron 12 (1993) 69.
[14] C. Silvestru, I. Haiduc, R. Cea-Olivares, A. Zimbron, Polyhedron 13 (1994) 3159.
[15] K.C. Molloy, M.F. Mahon, I. Haiduc, C. Silvestru, Polyhedron 14 (1995) 1169.
[16] R. Rösler, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, J. Chem. Soc. Dalton Trans. (1996) 391.
[17] G.A. Miller, E.O. Schlemper, Inorg. Chem. 12 (1973) 677.
[18] C. Sreelatha, D.K. Srivastava, V.D. Gupta, H. Nöth, J. Chem. Soc. Dalton Trans. (1988) 407.
[19] G.M. Bancroft, B.W. Davies, N.C. Payne, T.K. Sham, J. Chem. Soc. Dalton Trans. (1975) 973.
[20] A.G. Davies, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, Oxford, 1982, pp. 529–530.
[21] T.P. Lockhart, W.F. Manders, Inorg. Chem. 25 (1986) 892.
[22] T.P. Lockhart, W.F. Manders, J.J. Zuckerman, J. Am. Chem. Soc. 107 (1985) 4546.
[23] J. Holecek, A. Lycka, Inorg. Chim. Acta 118 (1986) L15.
[24] D. Fenske, R. Mattes, J. Löns, K.-F. Tebbe, Chem. Ber. 106 (1973) 1139.
[25] S. Pohl, Chem. Ber. 109 (1976) 3122.
[26] K. Shishido, Y. Takeda, J. Kinigawa, J. Am. Chem. Soc. 83 (1961) 538.
[27] A. Schmidpeter, J. Ebeling, Chem. Ber. 101 (1968) 815.
[28] Denzo: Z. Otwinowski, W. Minor, Methods in enzymology, in: C.W. Carter Jr., R.M. Sweet (Eds.), Macromolecular Crystallography, Part A, vol. 276, Academic Press, New York, 1997, p. 307.
[29] SORTAV: (a) R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33;
(b) R.H. Blessing, J. Appl. Cryst. 30 (1997) 421.
[30] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[31] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
[32] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.