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Two conformers in the solid state for a novel organotin(IV) complex of a phosphoramidate: Syntheses, spectroscopic study and crystal structures of several new organotin(IV) complexes of *N*-benzoylphosphoric triamides

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Abstract

Several novel organotin(IV) complexes with formula $SnCl_2(CH_3)_2(X)_2$, $X = C_6H_5C(O)NHP(O)(NC_4H_8)_2$ (**1**), $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$ (**2**), $C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$ (**3**), $C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$ (**4**) were synthesized and characterized by ^1H, ^{13}C, ^{31}P NMR, IR spectroscopy and elemental analysis. The structures have been determined for each of the four compounds. Compound **1** exists in the form of two symmetrically independent molecules in the crystalline state due to differences in their similar torsion angles. In all of the four structures there are intramolecular –Sn–Cl···H–N– hydrogen bonds, in addition to weak C–H···O and C–H···Cl hydrogen bonds. Both ^1H and ^{13}C NMR spectra show the coupling of $^{119/117}Sn$ nuclei with methyl proton and carbon atoms. The $\delta(^{31}P)$ of these complexes are in upfields with respect to their corresponding reported ligands. The spectroscopic and structural properties of these complexes were compared with those corresponding ligands.

Keywords: Organotin(IV) complexes; NMR spectroscopy; X-ray crystallography

1. Introduction

Organotin(IV) complexes are an important part of organometallic chemistry because of their applications as biocides like fungicides or antifouling agents [1], antitumor [2] and antimicrobial [3] compounds. Nowadays, the research on the preparation of different organotin(IV) complexes with O- [4], N- [5], and C-donor [6] ligands becomes a matter of great interest. Also, the preparation of stannylplatinum(IV) complexes in which the Sn(IV) atom adopts a tetrahedral coordination is a noticeable branch of organometallic chemistry [7]. Depending on the nature of different substituents, these compounds indicate diverse coordination environment for the central tin atom [8]. The Sn(IV) atoms in organotin(IV) complexes of O-donor ligands, such as phosphoramidates [9], imidodiphosphonic acids [10] and bis(diphenylphosphino)pyridine [11], exhibit a hypervalent octahedral geometry, while in thiophosphinates complexes [12] and some substituted dithiophosphate stannocanes [13] indicate a trigonal-bipyramidal coordination. It has been reported the synthesis and crystal structure of a chiral bicyclic stannylated phosphoric triamide in which the phosphoramide ligand act as a C-donor chelate [14]. The NMR spectroscopic properties of some diorganotin(IV) complexes with phosphates has been already considered [15]. Herein, we focused on the synthetic, spectroscopic and crystal structure characteristics of four novel diorganotin(IV) complexes with formula $SnCl_2(CH_3)_2(X)_2$, $X = C_6H_5C(O)NHP(O)(NC_4H_8)_2$ (**1**), $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$ (**2**), $C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$ (**3**),

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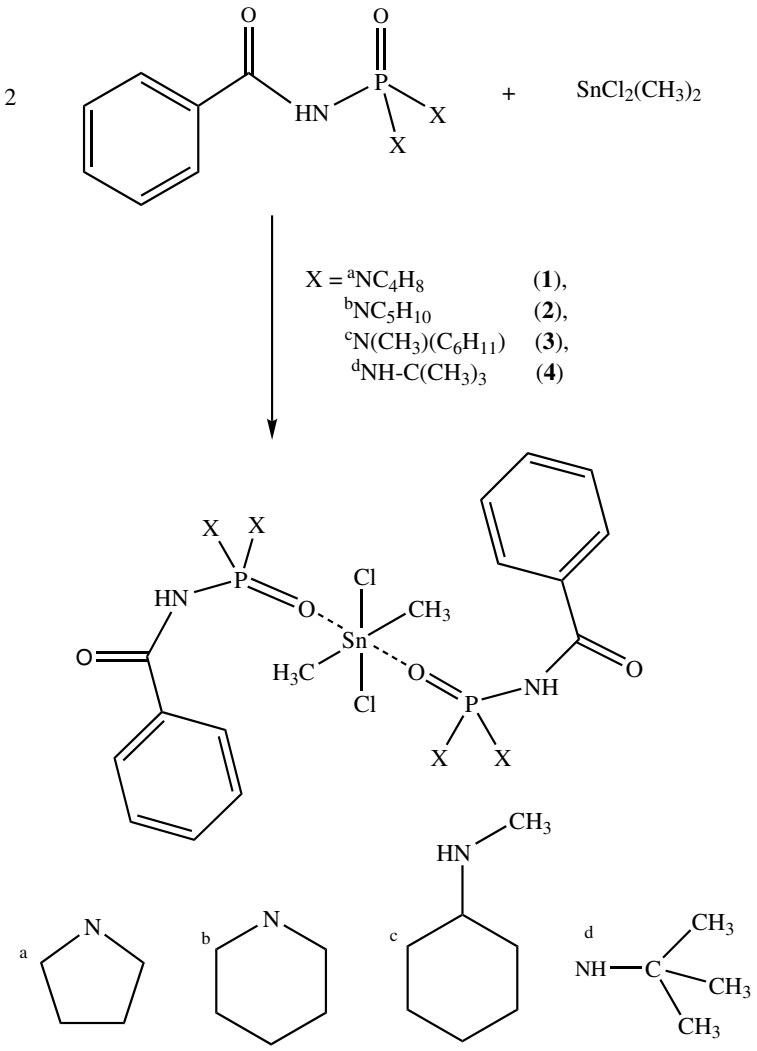
$C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$ (**4**) and their corresponding reported ligands to discuss on their different properties in solution and solid states. Compound **1** exists as two symmetrically independent molecules in the crystalline lattice and we believe that, to our knowledge, this is the first example for an organotin(IV) complex of a phosphoramidate with two conformers in the crystalline solid state.

2. Results and discussion

2.1. NMR and IR study

Synthesis of complexes **1**–**4** were performed by the reaction of dimethyltin(IV) dichloride with corresponding phosphoric triamide ligands, Scheme 1. Some spectroscopic data of compounds **1**–**4** and their corresponding ligands are listed in Table 1. ^{1}H NMR spectra of molecules **1**–**4** show the Sn(IV) satellites with $^2J(^{119}Sn,H)$ and $^2J(^{117}Sn,H)$ coupling constants about 110.0 and 40.0 Hz in d_6-DMSO and about 90.0 and 40.0 Hz in $CDCl_3$, respectively. ^{13}C NMR spectra reveal $^1J(^{119/117}Sn,C)$ coupling constants with a value of about 3000.0 Hz in compounds **1** and **2** (containing cyclic aliphatic amine groups) and a value of about 600.0 Hz in compounds **3** and **4** (containing acyclic aliphatic amine moieties). The carbon atoms of C=O groups in compounds **2**–**4** couple with their related phosphorus atoms with $^2J(P,C(O))$ coupling constant values from 1.9 Hz (**4**) to 2.5 Hz (**2** and **3**). The *ipso* carbon atoms of phenyl rings in compounds **1**–**9** show $^3J(P,C_{aromatic})$ coupling constants in the range from 7.7 Hz (**9**) to 8.8 Hz (**2**). ^{13}C NMR spectra of compound **3** (containing *N*-methylcyclohexyl groups) in both d_6-DMSO and $CDCl_3$ solvents show seven signals for aliphatic carbon atoms that five of them are doublet peaks. Therefore, the two CH and CH_2 groups of the two cyclohexyl rings (with two and three bond distances from phosphorus atom) are not equivalent and we observe two $^2J(P,C)$ coupling constants (as well as two $^3J(P,C)$ coupling constants). The *N*-CH_3 group indicates a $^2J(P,C)$ coupling constants equal to 4.2 Hz in d_6-DMSO and 4.7 Hz in $CDCl_3$. In our earlier study, we reported two conformers in solution and solid states for compound $C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$



Scheme 1. Preparation pathway of organotin(IV) complexes **1**–**4**.

Table 1
Spectroscopic NMR and IR data of compounds **1–9**

No.	$\delta(^{31}P)$ (ppm)	^2J(PNH(amide)) (Hz)	^2J(P,$C_{aliphatic}$) (Hz)	^3J(P,$C_{aliphatic}$) (Hz)	^3J(P,$C_{aromatic}$) (Hz)	$^2J(^{119}Sn,H)$ (Hz)	$^2J(^{117}Sn,H)$ (Hz)	$^1J(^{119/117}Sn,C)$ (Hz)	Solvent	ν(C=O) (cm^{-1})	ν(P=O) (cm^{-1})
1	6.85	6.6	4.9 (CH_2)	8.3	8.2	111.8	43.7	2832.3	d_6-DMSO	1672	1115
2	10.17	6.1	–	4.8	8.3	112.4	40.7	2705.9	d_6-DMSO	1678	1125
	10.46	–	3.2 (CH_2), 2.5 (C=O)	4.8	8.8	88.7	41.1	2767.9	$CDCl_3$		
3	13.60	–	4.2 (*N*-CH_3), 4.1, 3.9 (CH), 2.0 (C=O)	4.4, 2.2 (CH_2)	8.2	109.8	41.9	565.2 ($^1J(^{119}Sn,C)$), 566.4 ($^1J(^{117}Sn,C)$)	d_6-DMSO	1679	1153
	14.02	–	4.7 (*N*-CH_3), 3.6, 5.6 (CH), 2.5 (C=O)	2.1, 2.1 (CH_2)	8.6	91.2	31.5	574.8 ($^1J(^{119}Sn,C)$), 615.9 ($^1J(^{117}Sn,C)$)	$CDCl_3$		
4	2.95	6.8	1.9 (C=O)	5.0	7.8	110.9	42.6	586.5	d_6-DMSO	1648	1150
5[a]	10.33	–	(C=O) 1.9	4.9	8.2	111.4	42.1	2877.5	d_6-DMSO	1680	1126
6[b]	8.84	4.5	5.5	8.6	8.7	–	–	–	d_6-DMSO	1665	1202
7[c]	12.02	–	2.7	4.7	8.5	–	–	–	d_6-DMSO	1667	1203
8[d]	13.56	5.9	4.4, 4.2	3.8, 4.9	7.8	–	–	–	d_6-DMSO	1670	1183
9[e]	4.10, 4.70	6.9, 8.0	–	4.8, 4.9, 7.5	7.7, 8.6	–	–	–	d_6-DMSO	1634	1211, 1234

[a] The data of compound $SnCl_2(CH_3)_2[4\text{-}F\text{-}C_6H_4C(O)NHP(O)(NC_5H_{10})_2]_2$ (**5**) is reported in Ref. [9].
[b] The data of compound $C_6H_5C(O)NHP(O)(NC_4H_8)_2$ (**6**) is reported in Ref. [19].
[c] The data of compound $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$ (**7**) is reported in Ref. [20].
[d] The data of compound $C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$ (**8**) is reported in Ref. [30].
[e] The data of compound $C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$ (**9**) is reported in Ref. [16].

(**9**) [16] which showed two series of signals in ^1H, ^{13}C and ^{31}P NMR spectra due to the existence of two non-equivalent *tert*-butyl groups. In compound **4**, which is organotin(IV) complex of ligand **9**, we observe only one sets of peaks and the two *tert*-butyl groups are equivalent. Thus, it can be said that one of conformers with the two equal *tert*-butyl groups is isolated from the solution to react with $SnCl_2(CH_3)_2$ and produced complex **4**. ^{31}P NMR spectra of compounds **1** (with five-membered ring amine groups) and **2** (containing six-membered ring amine groups) indicate that with increasing the ring size of amine groups, $\delta(^{31}P)$ shifts to down fields (Table 1). The phosphorus-31 chemical shift of compound **5** with 4-fluorobenzoyl moiety (10.33 ppm) is in upfield relative to its analogous compound **2** (10.76 ppm). The $\delta(^{31}P)$ of compounds **1–4** are in upfields with respect to their corresponding ligands, Table 1. Therefore, complexation causes more shielding of phosphorus atoms than those of the ligands.

IR spectra of compounds **1–4** show that the ν(P=O) and ν(C=O) frequencies are in the range from 1153 cm^{-1} (**3**) to 1115 cm^{-1} (**1**) and 1679 cm^{-1} (**3**) to 1648 cm^{-1} (**4**), respectively. The P=O stretching frequencies in complexes **1–4** are weaker than in those related ligands, but for C=O frequencies opposite results were obtained (Table 1). The P=O and C=O frequencies of analogous compounds **2** and **5** are close to each other. In complexes **1–4**, the two bands at about 550 and 510 cm^{-1} are related to the asymmetric and symmetric stretching frequencies of Sn–C bonds [17], respectively, and the band at about 470 cm^{-1} corresponds to the vibration of Sn–O bond [18].

2.2. X-ray crystallography investigation

Single crystals of compounds **1–4** were obtained from a solution of methanol and acetonitrile after slow evaporation at room temperature. The crystal data and the details of the X-ray analysis are given in Table 2, selected bond lengths and bond angles in Tables 3 and 4 and hydrogen bonding data in Table 5. Molecular structures of these compounds are shown in Figs. 1–5. Complex **1** exists as two crystallographically independent molecules (**1** and **1′**) in the crystalline lattice due to the differences in similar torsion angles of these two independent molecules (Figs. 1 and 2) and we found that this is the first organotin(IV) complex of a phosphoramidate with two conformers in the crystalline state. The torsion angles Sn(1)–O(1)–P(1)–N(1) and Sn(1′)–O(1′)–P(1′)–N(1′) (**1** and **1′**) are −54.5(3)° and −55.1(3)°, respectively (also compare the torsion angles O(1)–P(1)–N(2)–C(8), O(1)–P(1)–N(2)–C(11) (**1**) with O(1′)–P(1′)–N(2′)–C(8′), O(1′)–P(1′)–N(2′)–C(11′) (**1′**) that are −121.3(3)°, 53.5(3)° and 51.6(3)°, −122.8(3)°). In each conformer of this compound, the two aliphatic rings of pyrrolidine groups have puckered shape and they are not planar. The C(13D), C(14D) and C(14A) carbon atoms and some hydrogen atoms of one pyrrolidinyl ring in each of the conformers **1** and **1′** show disorder in the crystal. Similarly, the crystal structure of the corresponding ligand

Table 2
Crystallographic data for complexes **1**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{32}H_{50}Cl_2N_6O_4P_2Sn$	$C_{36}H_{58}Cl_2N_6O_4P_2Sn$	$C_{44}H_{74}Cl_2N_6O_4P_2Sn$	$C_{32}H_{58}Cl_2N_6O_4P_2Sn$
Formula weight	834.31	890.41	1002.62	842.37
Temperature (K)	120(2)	120(2)	120(2)	200(2)
Wavelength (Å)	0.7173	0.7173	0.7173	0.7173
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions				
a (Å)	9.3670(6)	15.716(2)	8.8856(19)	9.283(8)
b (Å)	15.0510(9)	8.6542(12)	10.888(2)	10.298(7)
c (Å)	15.3223(9)	16.517(3)	14.064(3)	12.319(10)
α (°)	61.7326(11)		72.902(5)	66.47(5)
β (°)	90.1137(12)	111.688(3)	88.69(17)	71.69(6)
γ (°)	88.5574(13)		68.160(6)	89.38(6)
V (Å^3)	1901.7(2)	2087.4(5)	1201.4(4)	1016.1(14)
Z	2	2	1	1
D_{calc} (Mg m^{-3})	1.457	1.417	1.386	1.377
Absorption coefficient (mm^{-1})	0.939	0.861	0.756	0.880
$F(000)$	860	924	526	438
Crystal size (mm^3)	$0.2 \times 0.3 \times 0.2$	$0.4 \times 0.2 \times 0.2$	$0.3 \times 0.3 \times 0.2$	$0.15 \times 0.15 \times 0.15$
θ Range for data collection (°)	1.51–27.50	2.65–29.00	2.12–27.99	1.92–28.00
Limiting indices	$-12 \leqslant h \leqslant 10$, $-19 \leqslant k \leqslant 17$, $-19 \leqslant l \leqslant 19$	$-21 \leqslant h \leqslant 15$, $-10 \leqslant k \leqslant 11$, $-22 \leqslant l \leqslant 20$	$-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 16$
Reflections collected/unique (R_{int})	14756/8578 (0.0356)	12293/5492 (0.0656)	12425/5796 (0.0375)	5169/4875 (0.0155)
Completeness to θ (%)	98.1	98.7	99.6	99.2
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	None
Maximum and minimum transmission	0.8344 and 0.762	0.8467 and 0.7246	0.861 and 0.793	0.861 and 0.793
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8578/3/456	5492/66/234	5796/0/270	4875/0/220
Goodness-of-fit on F^2	0.964	1.072	1.032	1.021
Final R indices	$R_1 = 0.0451$, $wR_2 = 0.0869$	$R_1 = 0.0536$, $wR_2 = 0.1049$	$R_1 = 0.0424$, $wR_2 = 0.1001$	$R_1 = 0.0351$, $wR_2 = 0.0909$
R indices (all data)	$R_1 = 0.0649$, $wR_2 = 0.0908$	$R_1 = 0.0837$, $wR_2 = 0.1165$	$R_1 = 0.0558$, $wR_2 = 0.1076$	$R_1 = 0.0355$, $wR_2 = 0.0912$
Largest difference in peak and hole (e Å^{-3})	2.348 and −1.029	2.461 and −1.091	0.958 and −0.757	1.140 and −1.423

of **1** ($C_6H_5C(O)NHP(O)(NC_4H_8)_2$) showed two conformers in the solid state [19] and both of them had disorder in their structures.

The corresponding ligand of complex **2** ($C_6H_5C(O)NHP(O)(NC_5H_{10})_2$) consists of four independent molecules in the crystalline network (due to the differences in similar torsion angles of these four independent molecules) [20], but in the case of **2** we observe only one molecule in the lattice, Fig. 3. Compound **3** as well as its corresponding ligand indicate a symmetric molecule in the crystalline state (Fig. 4). In the structure of compound **4**, the C(9′), C(10′) and C(11′) atoms and their related hydrogen atoms of *tert*-butyl group indicate disorder (Fig. 5). The structure of corresponding ligand of **4** ($C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$) showed two conformers in solution and solid state that was confirmed by NMR and X-ray crystallography [16]. In structures **1**, **1′** and **4** due to the existence of disorder in the molecules the structures are asymmetric but in compounds **2** and **3** the structures are symmetric.

The data of hydrogen bonding in these structures are presented in Table 5. In each independent molecule of compound **1**, intramolecular –Sn–Cl···H–N– hydrogen bonds were formed. Considering weak intermolecular C–H···Cl and C–H···O hydrogen bonds leads to a three-dimensional polymeric cluster in the lattice. This is observed in the structures **2** and **3**, but in **3** a two-dimensional polymeric chain was obtained (Fig. 6). In the crystalline network of **4**, there are intramolecular –Sn–Cl···H–N– hydrogen bonds plus intermolecular N(3)–H(3B)···O(1) hydrogen bond that produced continuous dimmers leading to a polymeric chain. Also, the intramolecular N(2)–H(2A)···O(1) hydrogen bond was observed in this structure. These hydrogen bonds besides weak C–H···Cl and C–H···O hydrogen bonds produced a two-dimensional cluster. In previously reported organotin(IV) complex, $[4\text{-}F\text{-}C_6H_4C(O)NHP(O)(NC_5H_{10})_2]_2\text{-}SnCl_2(CH_3)_2$ [9], only weak intermolecular C–H···Cl hydrogen bonds (intramolecular –Sn–Cl···H–N– hydrogen bonds were present) formed a two-dimensional polymer.

Table 3
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound **1**		Compound **2**	
Sn(1)–C(1M)	2.100(4)	Sn(1)–C(1M)	2.111(4)
Sn(1)–O(1)	2.212(2)	Sn(1)–O(1)	2.223(2)
Sn(1)–Cl(1)	2.5846(10)	Sn(1)–Cl(1)	2.5658(8)
P(1)–O(1)	1.519(3)	O(1)–P(1)	1.505(3)
P(1)–N(2)	1.610(3)	O(2)–C(1)	1.218(4)
P(1)–N(3)	1.615(3)	N(1)–C(1)	1.390(4)
P(1)–N(1)	1.680(3)	N(1)–P(1)	1.689(3)
O(2)–C(1)	1.220(4)	N(1)–H(1N)	0.8585
Sn(1′)–C(1M′)	2.113(4)	N(2)–C(8)	1.469(5)
Sn(1′)–O(1′)	2.203(2)	N(2)–C(12)	1.482(5)
Sn(1′)–Cl(1′)	2.5768(10)	N(2)–P(1)	1.626(3)
O(1′)–P(1′)	1.516(3)	N(3)–C(13)	1.474(4)
N(1′)–P(1′)	1.687(3)	N(3)–C(17)	1.480(4)
N(2′)–P(1′)	1.617(3)	N(3)–P(1)	1.627(3)
N(3′)–P(1′)	1.608(3)	C(1)–C(2)	1.502(5)
O(2′)–C(7′)	1.218(4)	C(2)–C(3)	1.388(5)
C(1M)–Sn(1)–C(1M)#1	180.000(1)	C(1M)–Sn(1)–C(1M)#1	180.0
C(1M)–Sn(1)–O(1)	88.31(13)	C(1M)–Sn(1)–O(1)	87.21(13)
C(1M)#1–Sn(1)–O(1)	91.69(13)	C(1M)#1–Sn(1)–O(1)	92.79(13)
O(1)–Sn(1)–O(1)#1	180.000(1)	O(1)–Sn(1)–O(1)#1	180.00(11)
O(1)–Sn(1)–Cl(1)#1	88.76(7)	O(1)#1–Sn(1)–Cl(1)#1	88.16(7)
C(1M)–Sn(1)–Cl(1)	89.60(12)	C(1M)–Sn(1)–Cl(1)	89.49(10)
C(1M)#1–Sn(1)–Cl(1)	90.40(12)	C(1M)#1–Sn(1)–Cl(1)	90.51(10)
O(1)–Sn(1)–Cl(1)	91.24(7)	O(1)–Sn(1)–Cl(1)	88.16(7)
Cl(1)–Sn(1)–Cl(1)#1	180.0	O(1)#1–Sn(1)–Cl(1)	91.84(7)
O(1)–P(1)–N(2)	116.35(16)	Cl(1)#1–Sn(1)–Cl(1)	180.0
O(1)–P(1)–N(3)	107.35(16)	P(1)–O(1)–Sn(1)	144.41(15)
N(2)–P(1)–N(3)	107.57(17)	O(1)–P(1)–N(3)	109.47(15)
O(1)–P(1)–N(1)	105.61(15)	O(1)–P(1)–N(2)	117.54(16)
N(2)–P(1)–N(1)	105.86(16)	N(3)–P(1)–N(2)	106.40(16)
N(3)–P(1)–N(1)	114.36(16)	O(1)–P(1)–N(1)	104.11(15)
C(1M′)–Sn(1′)–C(1M′)#2	180.000(2)	N(3)–P(1)–N(1)	115.07(17)
C(1M′)–Sn(1′)–O(1′)#2	91.86(13)	N(2)–P(1)–N(1)	104.52(16)
C(1M′)–Sn(1′)–O(1′)	88.14(13)	C(1)–N(1)–P(1)	126.7(3)
O(1′)#2–Sn(1′)–O(1′)	180.000(1)	C(1)–N(1)–H(1N)	129.5
C(1M′)–Sn(1′)–Cl(1′)	89.84(13)	P(1)–N(1)–H(1N)	100.9
C(1M′)#2–Sn(1′)–Cl(1′)	90.16(13)	C(8)–N(2)–C(12)	111.4(3)
O(1′)#2–Sn(1′)–Cl(1′)	89.12(7)	C(8)–N(2)–P(1)	124.3(3)
O(1′)#1–Sn(1′)–Cl(1′)	90.88(7)	C(12)–N(2)–P(1)	120.8(2)
O(1′)#1–Sn(1′)–Cl(1′)#2	89.12(7)	C(13)–N(3)–C(17)	113.2(3)
Cl(1′)–Sn(1′)–Cl(1′)#2	180.000(1)	C(13)–N(3)–P(1)	123.7(2)
P(1′)–O(1′)–Sn(1′)	140.18(15)	C(17)–N(3)–P(1)	123.0(3)
O(1′)–P(1′)–N(3′)	107.42(16)	Sn(1)–C(1M)–H(1MA)	109.5
O(1′)–P(1′)–N(2′)	116.00(17)	Sn(1)–C(1M)–H(1MB)	109.5
N(3′)–P(1′)–N(2′)	107.74(16)	H(1MA)–C(1M)–H(1MB)	109.5
O(1′)–P(1′)–N(1′)	105.47(14)	Sn(1)–C(1M)–H(1MC)	109.5
N(3′)–P(1′)–N(1′)	114.62(17)	H(1MA)–C(1M)–H(1MC)	109.5
N(2′)–P(1′)–N(1′)	105.87(16)	H(1MB)–C(1M)–H(1MC)	109.5

In molecules **1**–**4**, like their related phosphoric triamide ligands, the phosphoryl and the carbonyl groups are anti. The phosphorus atoms in these structures have slightly distorted tetrahedral configuration. The bond angles around P(1) atoms in these compounds are in the range from 117.77(14)° (**3**) to 103.62(11)° (**4**), for the angles O(1)–P(1)–N(2) and N(2)–P(1)–N(1), respectively. In these compounds, the angles OPN_{amide} (N_{amide} is the nitrogen atom of P(O)N(H)C(O) moiety) are lower than the angles OPN_{amine} (N_{amine} is the nitrogen atom of P(O)NR moiety). The P=O bond lengths in molecules **1**–**4**, are [1.519(3), 1.516(3)], 1.505(3), 1.496(2) and 1.493(2) Å that are larger than the normal P=O bond length (1.45 Å) [21]. The P=O bond lengths in complexes **1**–**4** are larger than those of the corresponding ligands, Table 6. The C=O bond length in compound **4** has the longest, 1.225(3) Å, and in compounds **1**′ and **2**, 1.218(4) Å, has the lowest value. A comparison between the two similar compounds **2** and **5** revealed that the P=O and $P–N_{amine}$ bond lengths in **2** is slightly longer than in **5**, but the C=O and $P–N_{amide}$ bond lengths show an opposite result, Table 6.

Table 4
Selected bond lengths (Å) and angles (°) for compounds **3** and **4**

Compound **3**		Compound **4**	
Sn(1)–C(1)	2.111(3)	Sn(1)–C	2.105(3)
Sn(1)–O(1)	2.222(2)	Sn(1)–O(2)	2.242(3)
Sn(1)–Cl(1)	2.5750(9)	Sn(1)–Cl(1)	2.570(2)
P(1)–O(1)	1.496(2)	P(1)–O(2)	1.493(2)
P(1)–N(2)	1.625(3)	P(1)–N(3)	1.617(2)
P(1)–N(3)	1.633(3)	P(1)–N(2)	1.619(2)
P(1)–N(1)	1.692(3)	P(1)–N(1)	1.689(2)
O(2)–C(2)	1.221(4)	N(1)–C(1)	1.370(3)
N(1)–C(2)	1.378(4)	N(1)–H(1A)	0.8800
N(1)–H(1)	0.9521	N(2)–C(8)	1.488(3)
N(2)–C(9)	1.476(4)	N(2)–H(2A)	0.8800
N(2)–C(10)	1.494(4)	N(3)–C(12)	1.488(3)
N(3)–C(16)	1.462(4)	N(3)–H(3B)	0.8800
N(3)–C(17)	1.496(4)	O(1)–C(1)	1.225(3)
C(1)#1–Sn(1)–C(1)	180.000(1)	C–Sn(1)–C#1	180.0
C(1)#1–Sn(1)–O(1)	90.58(11)	C–Sn(1)–O(2)	92.03(11)
C(1)–Sn(1)–O(1)	89.42(11)	C#1–Sn(1)–O(2)	87.97(11)
O(1)–Sn(1)–O(1)#1	180.000(1)	O(2)#1–Sn(1)–O(2)	180.00(9)
C(1)#1–Sn(1)–Cl(1)	90.67(10)	O(2)#1–Sn(1)–Cl(1)#1	88.23(8)
C(1)–Sn(1)–Cl(1)	89.33(10)	C–Sn(1)–Cl(1)	90.27(10)
O(1)–Sn(1)–Cl(1)	89.90(6)	C#1–Sn(1)–Cl(1)	89.73(10)
O(1)#1–Sn(1)–Cl(1)	90.10(6)	O(2)#1–Sn(1)–Cl(1)	91.77(8)
Cl(1)–Sn(1)–Cl(1)#1	180.00(3)	Cl(1)#1–Sn(1)–Cl(1)	180.0
O(1)–P(1)–N(2)	117.77(14)	O(2)–P(1)–N(3)	110.88(13)
O(1)–P(1)–N(3)	108.00(13)	O(2)–P(1)–N(2)	116.69(12)
N(2)–P(1)–N(3)	107.11(14)	N(3)–P(1)–N(2)	108.71(13)
O(1)–P(1)–N(1)	104.84(13)	O(2)–P(1)–N(1)	105.72(12)
N(2)–P(1)–N(1)	104.90(14)	N(3)–P(1)–N(1)	110.90(13)
N(3)–P(1)–N(1)	114.51(13)	N(2)–P(1)–N(1)	103.62(11)
P(1)–O(1)–Sn(1)	153.33(13)	P(1)–O(2)–Sn(1)	142.66(11)
C(2)–N(1)–P(1)	125.2(2)	C(1)–N(1)–P(1)	125.41(17)
C(2)–N(1)–H(1)	122.4	C(1)–N(1)–H(1A)	117.3
P(1)–N(1)–H(1)	122.4	P(1)–N(1)–H(1A)	117.3
C(9)–N(2)–C(10)	116.0(3)	C(8)–N(2)–P(1)	128.78(17)
C(9)–N(2)–P(1)	119.2(2)	C(8)–N(2)–H(2A)	115.6
C(10)–N(2)–P(1)	120.3(2)	P(1)–N(2)–H(2A)	115.6
C(16)–N(2)–C(17)	116.8(2)	C(12)–N(3)–P(1)	127.67(18)
C(16)–N(3)–P(1)	122.2(2)	C(12)–N(3)–H(3B)	116.2
C(17)–N(3)–P(1)	117.5(2)	P(1)–N(3)–H(3B)	116.2
Sn(1)–C(1)–H(1A)	109.5	Sn(1)–C–H(0A)	109.5
Sn(1)–C(1)–H(1B)	109.5	Sn(1)–C–H(0B)	109.5
H(1A)–C(1)–H(1B)	109.5	H(0A)–C–H(0B)	109.5
Sn(1)–C(1)–H(1C)	109.5	Sn(1)–C–H(0C)	109.5
H(1A)–C(1)–H(1C)	109.5	H(0A)–C–H(0C)	109.5
H(1B)–C(1)–H(1C)	109.5	H(0B)–C–H(0C)	109.5
O(2)–C(2)–N(1)	120.1(3)	O(1)–C(1)–N(1)	121.2(2)

The $P–N_{amide}$ bond lengths are longer than the $P–N_{amine}$ bond lengths, because of the resonance interaction of the N_{amide} with the C=O π system that cause a partial multiple bond character in $C–N_{amide}$ (the $C–N_{amide}$ bond lengths are shorter than the $C–N_{amine}$ bond lengths, Tables 3 and 4). All of these P–N bonds are shorter than the typical P–N single bond length (1.77 Å) [21]. This is likely due to the electrostatic effects (polar bonds) which overlap with P–N σ bond [22]. The environment of the nitrogen atoms is practically planar. In compound **1** the angles C(8)–N(2)–C(11), C(8)–N(2)–P(1) and C(11)–N(2)–P(1) are 110.8(3)°, 128.7(3)° and 120.4(3)°, respectively, with average 119.97°. The sum of surrounding angles around N(1) and N(3) atoms are 359.2° and 357.0°,respectively. Similar results were obtained for the nitrogen atoms of other structures that confirm the sp^2 hybridization for the N atoms, although due to the repulsion and steric interactions, some angles are greater, and the others are smaller than 120°.

The central Sn atom in compounds **1**–**4** has octahedron coordination. Identical ligands (the two methyl groups, the two phosphoramidates and the two chlorine atoms) are in *trans* positions with the bond angles of 180.0° around Sn atom. The different ligands are *cis* to each other and C–Sn–O, C–Sn–Cl and O–Sn–Cl bond angles are about 90°, Tables 3 and 4. The Sn–C bond lengths in **1**–**4** are [2.100(4), 2.113(4)], 2.111(4), 2.111(3) and 2.105(3) Å, respectively, that are quite close to those reported in the literature [23]. The Sn–Cl bond lengths in **1**–**4** are [2.5846(10), 2.5768(10)], 2.5658(8), 2.5750(9) and 2.570(2) Å lying in the normal covalent radii 2.37–2.60 Å [24]. The Sn–O bond lengths are [2.212(2), 2.203(2)], 2.223(2), 2.222(2) and 2.242(3) Å that are shorter than sum of the van der Waals radii of Sn and O atoms (3.70 Å) [25].

3. Experimental

3.1. X-ray measurements

X-ray data of compounds **1**–**3** were collected on a Bruker SMART 1000 CCD area detector [26] and for compound **4** on a Siemens P3/PC Siemens P3 four-circle

Table 5
Hydrogen bonds for complexes **1**–**4** (Å and °)

Compound	D–H–A	*d*(D–H) (Å)	*d*(H···A) (Å)	∠DHA (°)	*d*(D···A) (Å)
1	N(1)–H(1N)···Cl(1) [$-x$, $-y+1$, $-z+2$]	0.94	2.51	152	3.370(5)
	N(1′)–H(1N′)···Cl(1′) [$-x+1$, $-y+2$, $-z+1$]	0.97	2.45	153	3.351(5)
2	N(1)–H(1N)···Cl(1) [$-x$, $-y+1$, $-z+2$]	0.86	2.64	141	3.350(5)
3	N(1)–H(1)···Cl(1)	0.952	2.370	163.27	3.294(3)
4	N(1)–H(1A)···Cl(1)	0.880	2.386	159.88	3.227
	N(2)–H(2A)···O(1)	0.880	2.368	119.71	2.907
	N(3)–H(3B)···O(1) [$-x+1$, $-y+1$, $-z$]	0.880	2.214	150.97	3.014

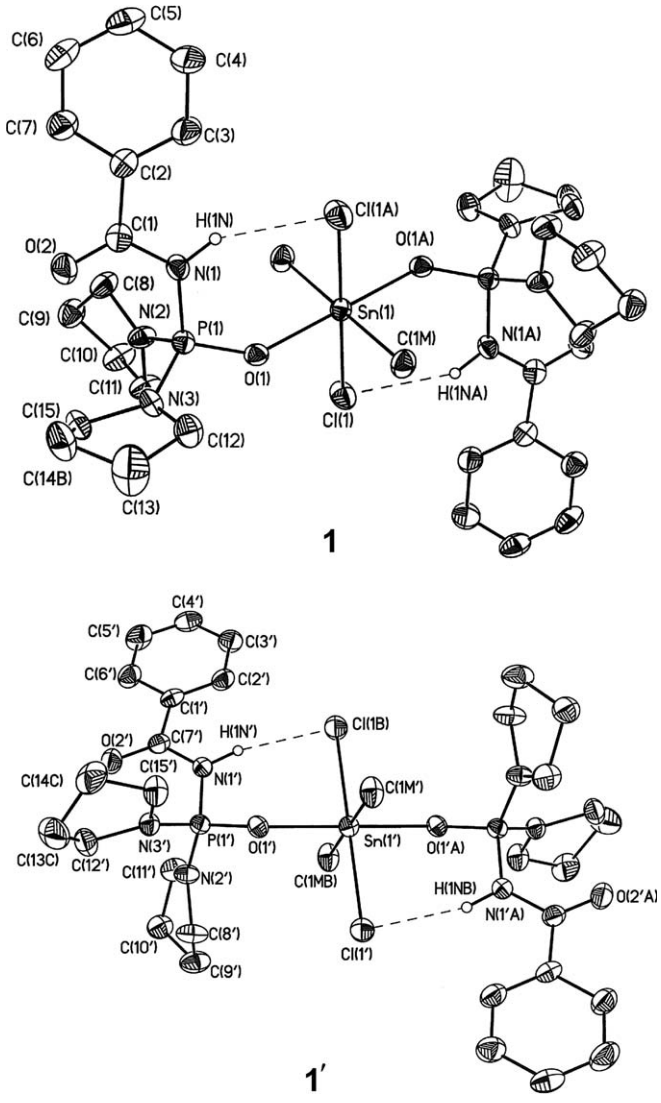


Fig. 1. Molecular structure and atom labeling scheme for the two independent molecules of complex **1** (50% probability ellipsoids).

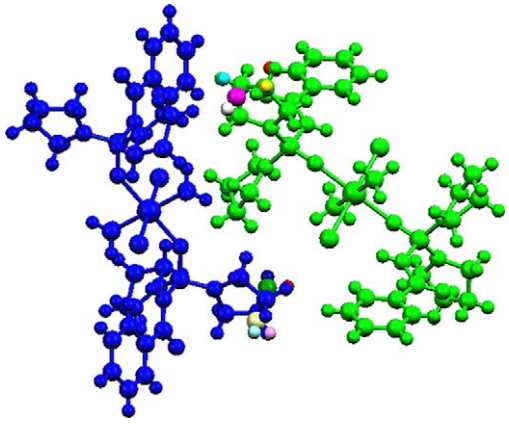


Fig. 2. Two conformers of compound **1** in the crystalline lattice in which the orientations of similar groups in the two molecules are different.

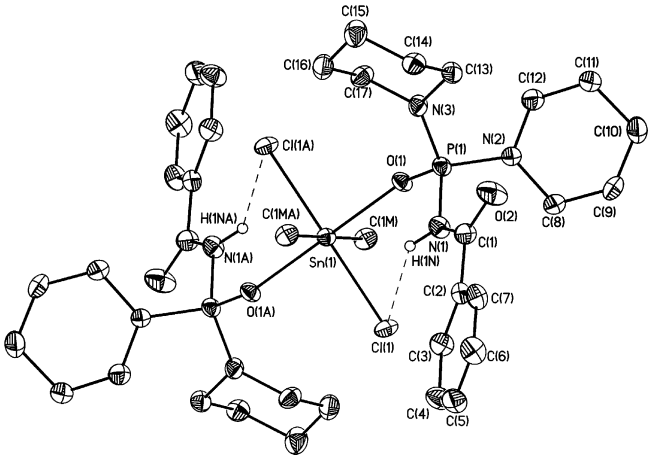


Fig. 3. Molecular structure and atom labeling scheme for complex **2** (50% probability ellipsoids).

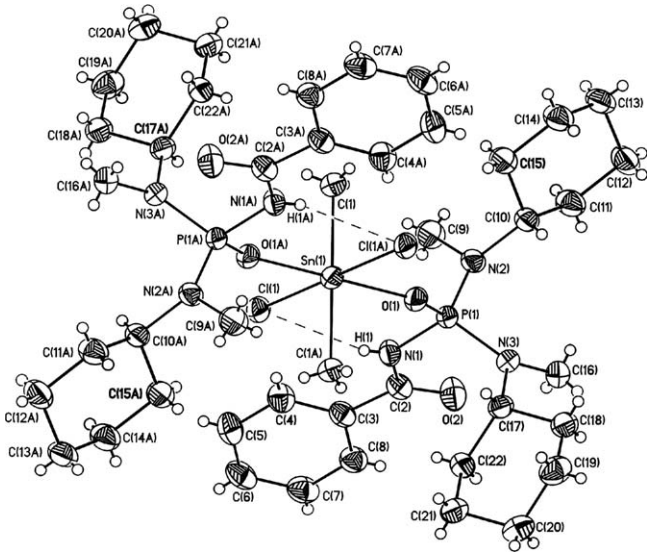


Fig. 4. Molecular structure and atom labeling scheme for complex **3** (50% probability ellipsoids).

diffractometer [27] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were refined with SHELXL-97 [28] by full-matrix least-squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program for compounds **1**–**3** [29].

3.2. Spectroscopic measurements

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal TMS and ^{31}P chemical shifts relative to 85% H_3PO_4 as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. Melting

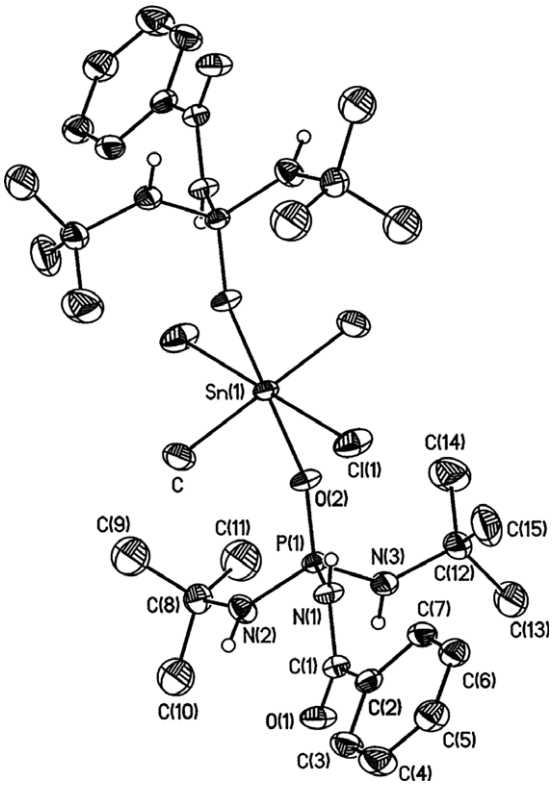


Fig. 5. Molecular structure and atom labeling scheme for complex **4** (50% probability ellipsoids).

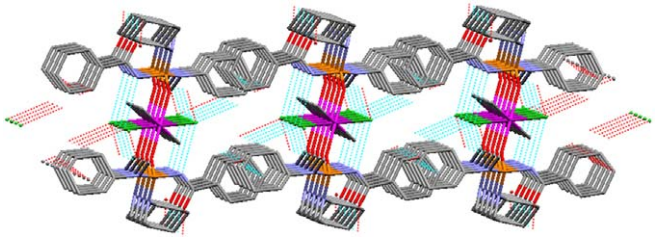


Fig. 6. A two-dimensional polymer (tubular array) obtained from intramolecular –Sn–Cl···H–N– hydrogen bonds and weak intermolecular C–H···O and C–H···Cl in the crystalline network of **3**.

points were obtained with an Electrothermal instrument. Ligands $C_6H_5C(O)NHP(O)(NC_4H_8)_2$ [19], $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$ [20], $C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$ [30] and $C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$ [16] for the synthesis of complexes **1**–**4** were prepared as the literature method.

3.3. Synthesis

3.3.1. Bis(N-benzoyl, N′,N″-bis(pyrrolidinyl) phosphoric triamide) dimethyl stannate(IV) dichloride (*1*)

N-Benzoyl, *N*′,*N*″-bis(pyrrolidinyl) phosphoric triamide (3.07 g, 10 mmol) was added to a solution of dimethyltin(IV) dichloride (1.10 g, 5 mmol) in methanol (35 mL) and stirred at room temperature. After 15 days, the solvent was evaporated to give a yellow powder. Recrystallization in methanol–acetonitrile produced single crystals of **1** (yield 1.84 g, 35%). M.p. 167 °C. ^{1}H NMR (d_6-DMSO): δ 0.90–1.12 [0.90 (d, $^2J(^{119}Sn,H) = 111.8$ Hz), 0.97 (d, $^2J(^{117}Sn,H) = 43.7$ Hz), 1.01 (s), 6H, CH_3], 1.74 (quin, $^3J(H,H) = 6.4$ Hz,16H, 8CH_2), 3.09–3.17 (m, 16H, 8CH_2), 7.45 (t, $^3J(H,H) = 7.6$ Hz, 4H, Ar-H), 7.56 (t, $^3J(H,H) = 7.6$ Hz, 2H, Ar-H), 7.88 (d, $^3J(H,H) = 7.6$ Hz, 4H, Ar-H), 9.13 (d, $^2J(PNH) = 6.6$ Hz, 2H, NH_{amide}). ^{13}C NMR (d_6-DMSO): δ 168.14 (s, C=O), 133.90 (d, $^3J(P,C) = 8.2$ Hz), 132.02 (s), 128.27 (s), 128.14 (s), 45.89 (d, $^2J(P,C) = 4.9$ Hz), 25.87 (d, $^3J(P,C) = 8.3$ Hz), 22.34 (d, $^1J(^{119/117}Sn,C) = 2832.3$ Hz). ^{31}P NMR (d_6-DMSO): δ 6.85 (m). IR (KBr): ν (cm^{-1}) = 3420 (w, NH), 3235 (m), 2865 (m), 1672 (s, C=O), 1444 (s), 1418 (s), 1249 (s), 1207 (s), 1115 (s, P=O), 1063 (s), 1014 (m), 864 (m, P–N_{amine}), 837 (m), 702 (s, P–N_{amide}), 577 (w, $(Sn–C)_{as}$), 527 (m, $(Sn–C)_s$), 480 (w, Sn–O). Anal. Calc. for $C_{32}H_{50}Cl_2N_6O_4P_2Sn$: C, 46.07; H, 6.04; N, 10.07. Found: C, 46.05; H, 6.03; N, 10.08%.

3.3.2. Bis(N-benzoyl, N′,N″-bis(pipperidinyl) phosphoric triamide) dimethyl stannate(IV) dichloride (*2*)

N-Benzoyl, *N*′,*N*″-bis(pipperidinyl) phosphoric triamide (3.35 g, 10 mmol) was added to a solution of dimethyltin(IV) dichloride (1.10 g, 5 mmol) in methanol (40 mL) and stirred at room temperature. After 16 days, the white precipitate was filtered and 15 mL of acetonitrile was added to the methanol solution. Single crystals of **2** were obtained after 6 days (yield 3.77 g, 68%). M.p. 169 °C. ^{1}H NMR (d_6-DMSO): δ 0.91–1.13 [0.91 (d, $^2J(^{119}Sn,H) = 112.4$ Hz), 0.98 (d, $^2J(^{117}Sn,H) = 40.7$ Hz), 1.02 (s), 6H, CH_3], 1.74 (quin, $^3J(H,H) = 6.4$ Hz, 16H, CH_2), 3.09–3.17 (m, 16H, CH_2), 7.45 (t, $^3J(H,H) = 7.4$ Hz, 4H, Ar-H), 7.56 (t, $^3J(H,H) = 7.4$ Hz, 2H, Ar-H), 7.88 (d, $^3J(H,H) = 7.6$ Hz, 4H, Ar-H), 8.43 (b, 1H, NH_{amide}), 9.07 (d, $^2J(PNH) = 6.1$ Hz, 1H, NH_{amide}). ^{13}C NMR (d_6-DMSO): δ 168.12 (s, C=O), 133.93 (d, $^3J(P,C) = 8.3$ Hz,), 131.98 (s), 128.24 (s), 128.11 (s), 44.98 (s), 25.79 (d, $^3J(P,C) = 4.8$ Hz), 22.15 (d, $^1J(^{119/117}Sn,C) = 2705.9$ Hz). ^{31}P NMR (d_6-DMSO): δ 10.17 (m). ^{1}H NMR ($CDCl_3$): δ 1.18–1.36 [1.18 (d, $^2J(^{119}Sn,H) = 88.7$ Hz), 1.23 (d, $^2J(^{117}Sn,H) = 41.1$ Hz), 1.27 (s), 6H, CH_3], 1.56 (m, 24H, CH_2), 3.20 (m, 16H, CH_2), 7.48 (t, $^3J(H,H) = 7.5$ Hz, 4H, Ar-H), 7.57 (t, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H), 7.87 (b, 1H, NH_{amide}), 7.95 (d, $^3J(H,H) = 7.5$ Hz, 4H, Ar-H), 8.69 (b, 1H, NH_{amide}). ^{13}C NMR ($CDCl_3$): δ 167.11 (d, $^2J(P,C) = 2.5$ Hz, C=O), 132.48 (d, $^3J(P,C) = 8.8$ Hz,), 132.25 (s), 128.32 (s), 127.32 (s), 45.43 (d, $^2J(P,C) = 3.2$ Hz), 25.64 (d, $^3J(P,C) = 4.8$ Hz), 22.06 (d, $^1J(^{119/117}Sn,C) = 2767.9$ Hz). ^{31}P NMR ($CDCl_3$): δ 10.46 (m). IR (KBr): ν (cm^{-1}) = 3250 (w, NH), 2930 (s), 1678 (s, C=O), 1444 (s), 1419 (s), 1337 (w), 1248 (m), 1162 (s), 1125 (s, P=O), 1073 (s), 959 (s), 860 (m), 838 (m, P–N_{amine}), 721 (m, P–N_{amide}), 559 (w, $(Sn–C)_{as}$), 506 (w, $(Sn–C)_s$), 471 (w, Sn–O). Anal. Calc. for $C_{36}H_{58}Cl_2N_6O_4P_2Sn$: C, 48.56; H, 6.57; N, 9.44. Found: C, 48.54; H, 6.57; N, 9.43%.

Table 6
P=O, P–N_{amide}, P–N_{amine} and C=O bond lengths (Å) in compounds **1**–**9**

No.	Compound	P=O	P–N_{amide}	P–N_{amine}	C=O	Reference
1	$SnCl_2(CH_3)_2[C_6H_5C(O)NHP(O)(NC_4H_8)_2]_2$	1.519(3), 1.516(3)	1.680(3), 1.687(3)	1.610(3), 1.615(3), 1.617(3), 1.608(3)	1.220(4), 1.218(4)	[a]
2	$SnCl_2(CH_3)_2[C_6H_5C(O)NHP(O)(NC_5H_{10})_2]_2$	1.505(3)	1.689(3)	1.626(3), 1.627(3)	1.218(4)	[a]
3	$SnCl_2(CH_3)_2[C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2]_2$	1.496(2)	1.692(3)	1.625(3), 1.633(3)	1.221(4)	[a]
4	$SnCl_2(CH_3)_2[C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2]_2$	1.493(2)	1.689(2)	1.619(2), 1.617(2)	1.225(3)	[a]
5	$SnCl_2(CH_3)_2[4\text{-}F\text{-}C_6H_4C(O)NHP(O)(NC_5H_{10})_2]_2$	1.5012(14)	1.6921(17)	1.6201(17), 1.6260(17)	1.222(2)	[9]
6	$C_6H_5C(O)NHP(O)(NC_4H_8)_2$	1.487(3)	1.679(4)	1.618(4), 1.615(4)	1.208(4), 1.217(5)	[19]
7	$C_6H_5C(O)NHP(O)(NC_5H_{10})_2$	1.460(12), 1.472(13), 1.425(12), 1.463(11)	1.671(13), 1.661(13), 1.685(14), 1.690(13)	1.614(13), 1.642(14), 1.619(17), 1.631(14), 1.646(14), 1.589(15), 1.624(13), 1.603(15)	1.240(17), 1.239(18), 1.228(18), 1.223(17)	[20]
8	$C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$	1.4842(12)	1.6980(14)	1.6344(14), 1.6368(14)	1.218(2)	[30]
9	$C_6H_5C(O)NHP(O)[NH\text{-}C(CH_3)_3]_2$	1.473(2), 1.476(2)	1.711(2), 1.704(2)	1.629(2), 1.629 (2), 1.619(3), 1.629 (2)	1.225(3), 1.232(3)	[16]

[a] This work.

3.3.3. Bis(*N*-benzoyl, *N*′,*N*″-bis(*N*-methylcyclohexyl) phosphoric triamide) dimethyl stannate(IV) dichloride (**3**)

N-Benzoyl, *N*′,*N*″-bis(*N*-methylcyclohexyl) phosphoric triamide (3.91 g, 10 mmol) was added to a solution of dimethyltin(IV) dichloride (1.10 g, 5 mmol) in methanol (45 mL) and stirred at room temperature. After 20 days, the solvent was concentrated and 10 mL of acetonitrile was added to the reaction vessel. The single crystals of **3** were obtained during 7 days by slow evaporation of the solvents (yield 3.73 g, 61%). M.p. 183 °C. ^{1}H NMR (d_6-DMSO): δ 0.89–1.04 [0.89 (d, $^2J(^{119}Sn,H) = 109.8$ Hz), 0.96 (d, $^2J(^{117}Sn,H) = 41.9$ Hz), 1.00 (s), 6H, CH_3], 1.12–1.99 (m, 44H, CH, CH_2), 2.53 (d, $^3J(PNCH) = 10.8$ Hz, 12H, CH_3), 7.46 (t, $^3J(H,H) = 7.3$ Hz, 4H, Ar-H), 7.55 (t, $^3J(H,H) = 7.3$ Hz, 2H, Ar-H), 7.87 (d, $^3J(H,H) = 7.3$ Hz, 4H, Ar-H), 8.73 (b, 1H, NH_{amide}), 9.04 (b, 1H, NH_{amide}). ^{13}C NMR (d_6-DMSO): δ 167.34 (d, $^2J(P,C) = 2.0$ Hz, C=O), 132.58 (d, $^3J(P,C) = 8.2$ Hz), 132.12 (s), 128.08 (s), 127.44 (s), 56.72 (s), 54.20 (d, $^2J(P,C) = 4.2$ Hz, *N*-CH_3), 30.41 (d, $^2J(P,C) = 3.9$ Hz, CH), 30.26 (d, $^3J(P,C) = 2.2$ Hz, CH_2), 27.61 (d, $^2J(P,C) = 4.1$ Hz, CH), 25.74 (d, $^3J(P,C) = 4.4$ Hz, CH_2), 25.15 (s), 24.72 (d, $^1J(^{117}Sn,C) = 566.4$ Hz), 23.77 (d, $^1J(^{119}Sn,C) = 565.2$ Hz). ^{31}P NMR (d_6-DMSO): δ 13.60 (m). ^{1}H NMR ($CDCl_3$): δ 1.02 (m, 4H), 1.17–1.35 [1.17 (d, $^2J(^{119}Sn,H) = 91.2$ Hz), 1.23 (d, $^2J(^{117}Sn,H) = 31.5$ Hz), 1.26 (s), 6H, CH_3], 1.47–1.87 (m, 30H), 2.18 (m, 4H), 2.67 (d, $^3J(PNCH) = 11.3$ Hz, 12H, CH_3), 3.40 (m, 4H), 7.47 (t, $^3J(H,H) = 7.5$ Hz, 4H, Ar-H), 7.56 (t, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H), 7.96 (d, $^3J(H,H) = 7.5$ Hz, 4H, Ar-H), 8.07 (b, 1H, NH_{amide}), 9.30 (b, 1H, NH_{amide}). ^{13}C NMR ($CDCl_3$): δ 167.44 (d, $^2J(P,C) = 2.5$ Hz, C=O), 132.60 (d, $^3J(P,C) = 8.6$ Hz), 132.17 (s), 128.30 (s), 127.37 (s), 57.92 (s), 54.99 (d, $^2J(P,C) = 4.7$ Hz, *N*-CH_3), 30.49 (d, $^2J(P,C) = 3.6$ Hz, CH), 30.31 (d, $^3J(P,C) = 2.1$ Hz, CH_2), 27.48 (d, $^2J(P,C) = 5.6$ Hz, CH), 25.53 (d, $^3J(P,C) = 2.1$ Hz, CH_2), 25.02 (s), 24.32 (d, $^1J(^{117}Sn,C) = 615.9$ Hz), 23.87 (d, $^1J(^{119}Sn,C) = 574.8$ Hz). ^{31}P NMR ($CDCl_3$): δ 14.02 (m). IR (KBr): ν (cm^{-1}) = 3425 (w, NH), 3205 (m), 2925 (s), 1679 (s, C=O), 1443 (s), 1418 (s), 1259 (m), 1153 (s, P=O), 1001 (s), 968 (s), 886 (m), 847 (m, P–N_{amine}), 707 (m, P–N_{amide}), 563 (w, $(Sn–C)_{as}$), 518 (w, $(Sn–C)_s$), 489 (w, Sn–O). Anal. Calc. for $C_{44}H_{74}Cl_2N_6O_4P_2Sn$: C, 52.71; H, 7.44; N, 8.38. Found: C, 52.70; H, 7.44; N, 8.36%.

3.3.4. Bis(*N*-benzoyl, *N*′,*N*″-bis(tert-butyl) phosphoric triamide) dimethyl stannate(IV) dichloride (**4**)

N-Benzoyl, *N*′,*N*″-bis(*tert*-butyl) phosphoric triamide (3.11 g, 10 mmol) was added to a solution of dimethyltin(IV) dichloride (1.10 g, 5 mmol) in methanol (30 mL) and stirred at room temperature. After 5 days, the solvent was evaporated and the white powder dissolved in methanol/acetonitrile solution. After 7 days, single crystals of **4** were obtained (yield 4.14 g, 78%). M.p. 235 °C. ^{1}H NMR (d_6-DMSO): δ 0.91–1.13 [0.91 (d, $^2J(^{119}Sn,H) = 110.9$ Hz), 0.98 (d, $^2J(^{117}Sn,H) = 42.6$ Hz), 1.02 (s), 6H, CH_3], 1.21 (s, 36H, CH_3), 4.00 (d, $^2J(PNH) = 6.6$ Hz, 4H, NH(amine)), 7.44 (t, $^3J(H,H) = 7.6$ Hz, 4H, Ar-H), 7.54 (t, $^3J(H,H) = 7.6$ Hz, 2H, Ar-H), 7.95 (d, $^3J(H,H) = 7.6$ Hz, 4H, Ar-H), 9.46 (d, $^2J(PNH) = 6.8$ Hz, 2H, NH_{amide}). ^{13}C NMR (d_6-DMSO): δ 168.15 (d, $^2J(P,C) = 1.9$ Hz, C=O), 134.07 (d, $^3J(P,C) = 7.8$ Hz), 131.79 (s), 128.01 (s), 127.93 (s), 50.32 (s), 31.21 (d, $^3J(P,C) = 5.0$ Hz), 22.42 (d, $^1J(^{119/117}Sn,C) = 586.5$ Hz). ^{31}P NMR (d_6-DMSO): δ 2.95 (m). IR (KBr): ν (cm^{-1}) = 3315 (m, NH), 3155 (m), 2960 (m), 1648 (s, C=O), 1488 (m), 1447 (s), 1424 (s), 1389 (s), 1274 (w), 1219 (s), 1150 (s, P=O), 1046 (m), 1023 (m), 879 (w, P–N_{amine}), 787 (m, P–N_{amide}), 680 (w), 567 (w, $(Sn–C)_{as}$), 543 (w, $(Sn–C)_s$), 479 (w, Sn–O). Anal. Calc. for $C_{32}H_{58}Cl_2N_6O_4P_2Sn$: C, 45.62; H, 6.94; N, 9.98. Found: C, 45.60; H, 6.93; N, 9.99%.

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Appendix A. Supplementary information

Crystallographic data for the structures **1**–**4** have been deposited with Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 292741 ($C_{32}H_{50}Cl_2N_6O_4P_2Sn_1$), CCDC 292742 ($C_{36}H_{58}Cl_2N_6O_4P_2Sn_1$), CCDC 292743 ($C_{44}H_{74}Cl_2N_6O_4P_2Sn_1$) and CCDC 286214 ($C_{32}H_{58}Cl_2N_6O_4P_2Sn_1$). Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: www:http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.032.

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