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Polyhedron 25 (2006) 711-721



Syntheses, spectroscopic characterization and crystal structures of some new phosphoramidates and an organotin(IV) complex of N-(4-fluorobenzoyl)-N',N''-bis(piperidinyl)phosphoric triamide

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Received 18 June 2005; accepted 25 July 2005 Available online 30 August 2005

Abstract

Some new phosphoramidates with formula 4-F-C₆H₄C(O)N(H)P(O)X₂, X = NC₄H₈ (1), NC₅H₁₀ (2), 4-CH₃-NC₅H₉ (3), NC₄H₈O (4), NC₆H₁₂ (5), N(CH₂CH₃)₂ (6), N(CH₂CH₃CH₃)₂ (7) were synthesized. The reaction of compound 2 with dimethyl-tin(IV) dichloride leads to an octahedral organotin(IV) complex, SnCl₂(CH₃)₂[4-F-C₆H₄C(O)N(H)P(O)(NC₅H₁₀)₂]₂ (8) with equal ligands in *trans* positions. These compounds were characterized by IR, ¹H, ¹³C, ³¹P, ¹¹⁹Sn NMR, mass spectroscopy and elemental analysis. The structures have been determined for compounds 1, 2, 4, 5 and 8. Compound 2 exists as four symmetrically independent molecules in the crystalline lattice. Compounds 1, 4 and 5 form dimmers via intermolecular $-P=O\cdots H-N-$ hydrogen bonds that in 1 is centrosymmetric. In compound 2, two dimmers were formed; each of them was produced between two adjacent independent molecules. In compounds 1, 2, 3, 4 and 8, containing five- and six-membered ring amine groups, ³*J*(P,C_{aliphatic}) > ²*J*(P,C_{aliphatic}). Compound 5 with seven-membered ring amine, similar to compounds 6 and 7 with acyclic aliphatic amines, shows that ²*J*(P,C_{aliphatic}) - ³*J*(P,C_{aliphatic}). Mass spectra of these compounds indicate the 4-F-C₆H₄CO⁺ and 4-F-C₆H₄CN⁺ fragments. © 2005 Elsevier Ltd. All rights reserved.

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

1. Introduction

The chemistry of phosphoramidates is recently developed due to the biological activity [1–3] and also the coordination chemistry [4–6] of these compounds. Some of them with $RC(O)N(H)P(O)R^{1}_{2}$ formula were used as O,O'-donor ligands for metal ions, particularly for rare earth metal cations [7,8]. Although the crystal structures of several phosphoramidates and their complexes are already known [4–6,9–12], there are little discussions about the substituent effects on the structural and NMR parameters. Among coordination compounds, the organometallic compounds of tin(IV) are very important antitumor agents [13,14]. Organotin(IV) compounds have been extensively used as wood preservatives, agrochemical fungicides and biocides [15,16]. The coordination compounds of organotin(IV) are a matter of interest in recent researches [17-20]. In our previous studies, we obtained some structures with two conformers in the lattice [21-23]. Cain et al. reported the crystal structure of compound $\{(5R,4S)-N-Pr-ephed$ rine $P(S)[NH(Si)(CH_3)_3]$ that has three independent molecules in the unit cell [24]. The first phosphoramidate with four crystallographically independent molecules in the crystalline network was $C_6H_5C(O)N(H)P(O)$ -(NC₅H₁₀)₂ [25] and in this work we report its analogous compound 4-F-C₆H₄C(O)N(H)P(O)(NC₅H₁₀)₂ (2). There are several articles that have been discussed

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^{0277-5387/}\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2005.07.035

on noticeable information on the coupling constants between ³¹P and ¹³C (or ¹H) nuclei [26,27]. Herein, we represent the synthesis of some new phosphoramidates with general formula 4-F-C₆H₄C(O)N(H)P(O)X₂, X = NC₄H₈ (1), NC₅H₁₀ (2), 4-NC₅H₉-CH₃ (3), NC₄H₈O (4), NC₆H₁₂ (5), N(CH₂CH₃)₂ (6), N(CH₂CH₂CH₃)₂ (7). Also, we studied the behavior of 2 as *O*-donor ligand to interaction with SnCl₂(CH₃)₂ and an octahedral organotin(IV) complex, SnCl₂(CH₃)₂[4-F-C₆H₄C(O)-N(H)P(O)(NC₅H₁₀)₂]₂ (8) was prepared. The structures of compounds 1, 2, 4, 5 and 8 were determined by X-ray crystallography. Furthermore, we discussed on structural, NMR and Mass spectral parameters in these compounds and their analogous derivatives.

2. Experimental

2.1. Materials

Dipropylamine (\geq 99%), morpholine (\geq 98%) (Merck) and 4-fluorobenzamide (98%), formic acid (98%), phosphorus pentachloride (\geq 98%), pyrrolidine (\geq 98%), piperidine (\geq 99.5%), hexemethyleneimine (\geq 97%), diethylamine (\geq 99.7%), dimethyltin dichloride (~95%) (Fluka) were used as supplied. In all reactions, the low temperature condition was used.

2.2. X-ray measurements

X-ray data of compounds 1, 2, 5 and 8 were collected on a Bruker SMART 1000 CCD [28] and for compound 4 on a Siemens P3/PC [29] single crystal diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were refined with SHELXL-97 [30] 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 [31].

2.3. Spectroscopic measurements

All reactions were performed under argon atmosphere and in dry solvents. ¹H, ¹³C, ³¹P and ¹¹⁹Sn NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ¹H and ¹³C chemical shifts were determined relative to internal TMS, ³¹P chemical shifts relative to 85% H₃PO₄ as external standard and ¹¹⁹Sn chemical shift relative to Sn(CH₃)₄ solution. Infrared (IR) spectra were recorded on a shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. High resolution mass spectra were obtained with a Shimadzu model QP-1100EX spectrometer (EI, 70 eV). 4-F- $C_6H_4C(O)NHP(O)Cl_2$ was prepared according to the literature method [32].

2.4. Syntheses

2.4.1. General procedure for synthesis of compounds 1-8

Compounds 1–7 were prepared by the reaction of 10 mmol *N*-(4-fluorobenzoyl) phosphoramidic dichloride with 40 mmol of corresponding amines in dry chloroform and stirred at -5 °C. After about 5 h, the solvent was removed and product was washed with H₂O and recrystallized from methanol/chloroform. Compound **8** was synthesized by the reaction of 20 mmol of **2** with 10 mmol dimethyltin(IV) dichloride in methanol at room temperature.

3. Results and discussion

3.1. NMR and IR study

Synthesis of compounds 1–7 were performed by the reaction of N-(4-fluorobenzoyl) phosphoramidic dichloride [32] with corresponding amines, Scheme 1. Compound 8 was obtained from the reaction of compound $\mathbf{2}$ with dimethyltin(IV) dichloride. ¹³C NMR spectra of compounds 1, 2, 3, 4 and 8, containing five- and sixmembered ring amine groups, show that ${}^{3}J(P,C_{aliphatic})$ is greater than ${}^{2}J(P,C_{aliphatic})$. For compound 5 with seven-membered ring amine, similar to compounds 6 and 7 with acyclic aliphatic amines, ${}^{2}J(P,C_{aliphatic}) >$ ${}^{3}J(P,C_{aliphatic})$. Compound 6 shows an opposite result for ${}^{2,3}J(\dot{P},C_{aliphatic})$ relative to compound 1 (with diethylamine group), Scheme 2. Also, it is observed from Table 1 that with increasing the ring size of amine groups in compounds 1–5, the ${}^{3}J(P,C_{aliphatic})$ becomes smaller and it varies from 8.0 Hz in 1 to 3.8 Hz in 5. These results are in good agreement with our previous studies on the similar compounds 9-12, Table 1. The carbon atoms of C=O groups in compounds 6, 7, 8 and 10 couple with their related phosphorus atoms with ${}^{2}J(P,C(O))$ coupling constant values in the range from 1.9 Hz in 6 and 8 to 3.9 Hz in 10. The *ipso* carbon atoms of phenyl rings in compounds 1-12 show ${}^{3}J(P,C_{aromatic})$ coupling constants in the range from 7.6 Hz in 3 to 8.9 Hz in 6 and 7.

¹³C NMR spectrum of compound **3** indicates eight peaks for the two unequivalent aliphatic rings of 4-methylpiperidinyl groups. The four doublet signals with two various ${}^{2}J(P,C_{aliphatic})$ [and also ${}^{3}J(P,C_{aliphatic})$] coupling constant values are related to the carbon atoms with two and three bond distances from phosphorus atom, Table 1 and Fig. 1.

The δ (³¹P) of compounds 1, 2 and 5 indicates that with increasing the ring size of amine groups, it shifts to down fields (Table 1). The phosphorus-31 chemical



Scheme 1. Preparation of compounds 1-7.



Scheme 2. The formula of compounds 1, 5-7.

shifts of compounds **1**, **2** and **5** with 4-fluorobenzoyl moiety are in upfields relative to their analogous compounds **10–12** with formula $C_6H_5C(O)N(H)P(O)R_2$ ($R = NC_4H_8$, NC_5H_{10} , NC_6H_{12}). The δ (³¹P) of compounds **2** and its organotin(IV) complex, **8**, are close to each other, 10.34 ppm in **2** and 10.15 ppm in **8**. ¹¹⁹Sn NMR of compound **8** shows a signal at –210.75 ppm for the Sn atom. ¹H NMR spectrum of this molecule indicates two separate signals for the NH protons

of two ligands. The fluorine substituent couple with aromatic carbon and proton atoms of phenyl ring and we observed ${}^{1-4}J(F,C_{aromatic})$ and ${}^{4}J(F,H_{aromatic})$ in compounds **1–8**.

IR spectra of compounds 1–8 show that the $v_{P=O}$; $v_{P-N(amine)}$; $v_{P-N(amide)}$ and $v_{C=O}$ frequencies are in the range from 1162 in 8 to 1215 in 1; 870 in 1 to 964 in 4; 752 (1) to 757 (5 & 8) and 1661 (5) to 1680 (8), respectively. The C=O frequency in structurally similar com-

Table 1

¹*i*tote ¹ ²*J*(P,C_{aliphatic}), ³*J*(P,C_{aliphatic}) and ³*J*(P,C_{aromatic}) (Hz), δ (³¹P) (ppm) for compounds 1–12 and m.p. (°C), yield (%) of 1–8

No.	Compound	$^{2}J(P,C_{aliphatic})$	$^{3}J(P,C_{aliphatic})$	$^{3}J(\mathbf{P},\mathbf{C}_{\mathrm{aromatic}})$	$\delta(^{31}P)$ M.p. (°C)	Yield (%)
1	$4\text{-}F\text{-}C_6H_4C(O)N(H)P(O)R_2^1$	5.0 (CH ₂)	8.0 (CH ₂)	8.5	7.05 181	88
2	$4\text{-}\text{F-}\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}_2^2$	0.0 (CH ₂)	4.8 (CH ₂)	8.7	10.34 194	83
3	$4\text{-}\text{F-}\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}_2^3$	3.4 (CH ₂), 1.9 (CH ₂)	5.8 (CH ₂), 4.8 (CH ₂)	7.6	10.39 189	79
4	$4-F-C_6H_4C(O)N(H)P(O)R_2^7$	$0.0 (CH_2)$	5.4 (CH ₂)	8.6	9.44 193	70
5 6	$4-F-C_6H_4C(O)N(H)P(O)R_2$ $4-F-C_2H_2C(O)N(H)P(O)[N(C_2H_2)_2]$	$4.3 (CH_2)$ 19 (C=O) 50 (CH_2)	$3.8 (CH_2)$	8./ 8.9	12.72 144	08 73
7	$4-F-C_6H_4C(O)N(H)P(O)[N(C_2H_7)_2]_2$	$2.4 (C=0), 4.5 (CH_2)$	$2.3 (CH_2)$	89	13 44 81	82
8	$Sn(CH_3)_2Cl_2[4-F-C_6H_4C(O)N(H)P(O)R_2^2]_2$	$1.9 (C=O), 2.6 (CH_2)$	$4.9 (CH_2)$	8.1	10.15 176	31
9 ^a	$C_6H_5C(O)N(H)P(O)R_2^1$	5.5 (CH ₂)	8.6 (CH ₂)	8.7	8.84	
10 ^b	$C_6H_5C(O)N(H)P(O)R_2^{\overline{2}}$	3.9 (C=O), 2.7 (CH ₂)	4.7 (CH ₂)	8.5	12.02	
11 ^b	$C_6H_5C(O)N(H)P(O)R_2^3$	$2.9 (CH_2), 0.0 (CH_2)$	4.9 (CH ₂), 5.1 (CH ₂)	8.6	12.04	
12 ^c	$C_6H_5C(O)N(H)P(O)R_2^3$	4.7 (CH ₂)	4.2 (CH ₂)	8.7	14.70	
· a T b T c T	he data of this compound are given in [23]. he data of these compounds are given in [25]. he data of this compound are given in [42].	N H ₃ C		N N		
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			35	30	25	-

Fig. 1. Selected region of ¹³C NMR spectrum of compound 3.

Table 2 Crystallographic data for **1**, **2** and **4**

	1	2	4
Empirical formula	$C_{15}H_{21}FN_3O_2P$	C ₁₇ H ₂₅ FN ₃ O ₂ P	C ₁₅ H ₂₁ FN ₃ O ₄ P
Formula weight	325.32	353.37	357.32
<i>T</i> (K)	120(2)	120(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	C2/c
Unit cell dimensions			
<i>a</i> (Å)	9.4043(19)	9.4800(11)	15.732(3)
b (Å)	9.4365(19)	17.5062(19)	10.740(2)
c (Å)	17.744(4)	22.439(2)	21.553(4)
α (°)	90	76.168(2)	90
β (°)	90.044(4)	84.962(3)	106.93(3)
γ (°)	90	84.366(3)	90
$V(\text{\AA}^3)$	1574.6(6)	3590.4(7)	3483.9(12)
Ζ	4	8	8
$D_{\rm calc} ({ m Mg}\ { m m}^{-3})$	1.372	1.307	1.362
Absorption coefficient (mm ⁻¹)	0.196	0.177	0.192
<i>F</i> (000)	688	1504	1504
Crystal size (mm ³)	$0.4 \times 0.5 \times 0.6$	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.36 \times 0.32$
θ Range for data collection (°)	2.30-28.99	0.94-26.00	3.30-28.06
Limiting indices	$-12 \leqslant h \leqslant 12, \ -12 \leqslant k \leqslant 12, \ -20 \leqslant l \leqslant 24$	$-11 \leqslant h \leqslant 11, \ -21 \leqslant k \leqslant 21, \ -27 \leqslant l \leqslant 27$	$0 \leq h \leq 20, \ 0 \leq k \leq 14, \ -28 \leq l \leq 27$
Reflections collected/unique (R_{int})	13097/4107 (0.0307)	25752/13810 (0.0412)	4311/4165 (0.0092)
Completeness to θ (%)	$(\theta = 28.99^{\circ})$ 98.0	$(\theta = 26.00^{\circ}) 97.7$	$(\theta = 28.06^{\circ})$ 98.2
Absorption correction	none	semi-empirical from equivalents	none
Maximum and minimum transmission	0.928 and 0.197	0.9654 and 0.9487	
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4107/0/199	13810/12/857	4165/0/253
Goodness-of-fit on F^2	1.000	1.020	1.025
Final R indices	$R_1 = 0.0410, wR_2 = 0.1093$	$R_1 = 0.0698, wR_2 = 0.1490$	$R_1 = 0.0488, wR_2 = 0.1178$
R indices (all data)	$R_1 = 0.0451, wR_2 = 0.1143$	$R_1 = 0.1258, wR_2 = 0.1705$	$R_1 = 0.0765, wR_2 = 0.1346$
Largest difference in peak and hole (e $Å^{-3}$)	0.957 and -0.329	0.654 and -0.516	0.251 and -0.228

pounds 1, 6 and also in 5, 7 (see Scheme 2) are very close to each other. The P=O stretching frequency in complex 8 (1162 cm⁻¹) is weaker than in its ligand 2 (1178 cm⁻¹), but for C=O frequency an opposite result was obtained (1680 cm⁻¹ in 8 and 1668 cm⁻¹ in 2). The two bands at 542 and 511 cm⁻¹ are related to the asymmetric and symmetric stretching frequencies of Sn–C bonds, respectively [33] and the band at 467 cm⁻¹ corresponds to the vibration of Sn–O bond [34].

3.2. X-ray crystallography investigation

Single crystals of compounds **1**, **2**, **4**, **5** and **8** were obtained from a solution of methanol and chloroform after slow evaporation at room temperature. The crystal data and the details of the X-ray analysis are given in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5. Molecular structures of these compounds are shown in Figs. 2–6.

The two aliphatic rings of pyrrolidine groups in compound 1 have puckered shape and they are not planar. Compound 2 with six-membered ring amine group exists as four symmetrically independent molecules in the crystal lattice. This is due to the differences in similar torsion angles of these four independent molecules. This phenomenon was also observed for compound $C_6H_5C(O)N(H)P(O)(NC_5H_{10})_2$ [25]. The complexation of compound **2** with dimethyltin dichloride (compound **8**) produced a coordination compound with two symmetrically equal phosphoramidate ligands, Fig. 6.

Compounds 1, 4 and 5 each contain one amidic hydrogen atom and form dimmers via intermolecular – $P=O\cdots H-N-$ hydrogen bonds that in 1 is a centrosymmetric dimmer (Table 6). In compound 2 (with four independent molecules in the unit cell), the two conformers labeled with P(1), P(1A) [and also the two others labeled with P(1B), P(1C)] are connected to each other via two different $-P=O\cdots H-N-$ hydrogen bonds and form a noncentrosymmetric dimmer. The earlier studied *N*-benzoyl, phosphoric triamides exist either in the form of dimmeric aggregates [35] or as polymeric chains [36].

In molecules 1, 2, 4, 5 and 8 the phosphoryl and the carbonyl groups are anti, Figs. 2–6. The phosphorus atoms in these structures have slightly distorted tetrahedral configuration. The bond angles around P(1) atoms

Table 3 Crystallographic data for **5** and **8**

	5	8
Empirical formula	$C_{19}H_{29}FN_{3}O_{2}P$	$C_{36}H_{56}Cl_2F_2N_6O_4P_2Sn$
Formula weight	381.42	926.40
<i>T</i> (K)	120(2)	120(2)
λ	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_{1}/c$
Unit cell dimensions		
a (Å)	23.030(4)	14.906(3)
b (Å)	9.2745(13)	8.6132(17)
c (Å)	20.585(3)	16.538(3)
α (°)	90	90
β (°)	116.684(4)	101.483(4)
γ (°)	90	90
$V(\text{\AA}^3)$	3928.6(11)	2080.8(7)
Ζ	8	2
$D_{\rm calc} ({ m Mg}{ m m}^{-3})$	1.290	1.479
Absorption coefficient (mm^{-1})	0.167	0.873
F(000)	1632	956
Crystal size (mm ³)	$0.23 \times 0.21 \times 0.18$	$0.45 \times 0.3 \times 0.15$
θ Range for data collection (°)	1.98–29.00	1.39-28.00
Limiting indices	$-29 \leqslant h \leqslant 31, -12 \leqslant k \leqslant 12, -26 \leqslant l \leqslant 27$	$-19 \leq h \leq 18, -11 \leq k \leq 9, -21 \leq l \leq 19$
Reflections collected/unique (R_{int})	13691/5065 (0.0281)	15430/4900 (0.0178)
Completeness to θ (%)	$(\theta = 29.00^{\circ}) 97.0$	$(\theta = 28.00^{\circ})$ 97.5
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.970 and 0.962	0.877 and 0.696
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5065/130/362	4900/0/243
Goodness-of-fit on F^2	1.018	1.001
Final R indices	$R_1 = 0.0948, wR_2 = 0.1608$	$R_1 = 0.0276, wR_2 = 0.0549$
R indices (all data)	$R_1 = 0.1676, wR_2 = 0.1782$	$R_1 = 0.0357, wR_2 = 0.0566$
Largest difference in peak and hole (e $Å^{-3}$)	0.842 and -0.688	1.274 and -0.509

Table 4 Selected bond lengths (Å) and angles (°) for compounds 1, 2, 4 and 5

	1	2	4	5
P(1)–O(1)	1.4863(10)	1.480(2)	1.4801(17)	1.472(2)
P(1) - N(1)	1.6899(11)	1.683(3)	1.6839(16)	1.675(3)
P(1)–N(2)	1.6239(12)	1.636(3)	1.6246(18)	1.634(3)
P(1) - N(3)	1.6390(12)	1.625(3)	1.6318(18)	1.626(4)
O(2)–C(1)	1.2207(16)	1.223(4)	1.212(2)	1.328(4)
N(1)–C(1)	1.3763(15)	1.378(4)	1.375(3)	1.365(4)
N(2)-C(8)	1.4841(16)	1.460(5)	1.468(3)	1.445(4)
F(1)-C(5)	1.3615(16)	1.366(4)	1.358(2)	1.321(4)
O(1) - P(1) - N(1)	104.66(5)	104.60(15)	104.63(9)	106.88(14)
O(1)-P(1)-N(2)	110.37(6)	118.86(16)	111.11(9)	109.89(19)
O(1) - P(1) - N(3)	119.59(6)	110.78(15)	118.30(11)	106.41(18)
N(2)-P(1)-N(1)	115.73(6)	105.13(16)	112.22(9)	116.41(19)
N(3)-P(1)-N(1)	102.89(6)	112.94(17)	106.52(9)	116.1(2)
N(2)-P(1)-N(3)	103.93(6)	104.64(16)	104.16(10)	100.7(3)
C(1)-N(1)-P(1)	125.81(9)	127.4(3)	127.28(14)	129.2(3)

Table 5 Selected bond lengths (Å) and angles (°) for compound **8**

P(1)–O(1)	1.5012(14)
P(1)–N(1)	1.6921(17)
P(1)–N(2)	1.6260(17)
P(1)–N(3)	1.6201(17)
O(2)–C(1)	1.222(2)
N(1)-C(1)	1.384(3)
F(1)-C(5)	1.355(2)
Sn(1)–C(18)	2.1238(19)
Sn(1)–O(1)	2.2176(13)
Sn(1)-Cl(1)	2.5617(6)
C(18)-Sn(1)-C(18)#1	180.000(1)
C(18)–Sn(1)–O(1)	87.51(7)
C(18)-Sn(1)-O(1)#1	92.49(7)
O(1)#1-Sn(1)-O(1)	180.0
C(18)-Sn(1)-Cl(1)	90.25(6)
C(18)#1–Sn(1)–Cl(1)	89.75(6)
O(1)-Sn(1)-Cl(1)	91.91(4)
O(1)#1-Sn(1)-Cl(1)	88.09(4)
Cl(1)#1-Sn(1)-Cl(1)	180.0
P(1)-O(1)-Sn(1)	145.42(9)

Symmetry code: #1: -x, -y + 2, -z + 2.

in these compounds are in the range from $119.59(6)^{\circ}$ in **1** to $100.7(3)^{\circ}$ in **5**, for the angles O(1)-P(1)-N(3) and N(2)-P(1)-N(3), respectively, Tables 4 and 5. 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**, **2**, **4**, **5** and **8** are 1.4863(10), [1.480(2), 1.479(2), 1.471(2), 1.475(3)], 1.4801(17), 1.472(2) and 1.5012(14) Å that are larger than the normal P=O bond length (1.45 Å) [37]. The P=O bond lengths in our previously reported structures are in the range from 1.4875(14) Å in **12** to 1.459(12) Å in **10** (Table 7). The P=O and P-N_{amide}

Fig. 2. Molecular structure and atom-labeling scheme for P(O)(4-F- $C_6H_4C(O)NH)(NC_4H_8)_2$, compound 1 (50% probability ellipsoids).

bond lengths in complex 8 is longer than those of ligand 2, but the C=O bond length in 8 is shorter than in 2, Table 7. The C=O bond length in compound 5 with seven-membered ring amine group has the longest, 1.328(4) Å, and in compound 4, 1.212(2) Å, has the lowest value.

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})



Fig. 3. Molecular structure and atom-labeling scheme for $P(O)(4-F-C_6H_4C(O)NH)(NC_5H_{10})_2$, compound 2 showing four crystallographically independent molecules in the lattice three of them have disordered forms (50% probability ellipsoids).

bond lengths are shorter than the C–N_{amine} bond lengths). All of these P–N bonds are shorter than the typical P–N single bond length (1.77 Å [37]). This is likely due to the electrostatic effects (polar bonds) which overlap with P–N σ bond [38]. The P–N bond lengths in the previously reported structures were in the range from 1.6916(16) Å (P–N_{amide} in **12**) to 1.590(15) Å (P–N_{amine} in **10**), respectively (Table 7).

The environment of the nitrogen atoms is practically planar. In compound 1 the angles C(11)-N(2)-C(8),



Fig. 4. Molecular structure and atom-labeling scheme for P(O)(4-F- $C_6H_4C(O)NH)(NC_4H_8O)_2$, compound 4 (50% probability ellipsoids).



Fig. 5. Molecular structure and atom-labeling scheme for P(O)(4-F- $C_6H_4C(O)NH)(NC_6H_{12})_2$, compound **5** (50% probability ellipsoids).

Table 6 Hydrogen bonds D–H···A for compounds 1, 2, 4, 5, and 8 (Å and °)



Fig. 6. Molecular structure and atom-labeling scheme for $Sn(CH_3)_2Cl_2[P(O)(4-F-C_6H_4C(O)NH)(NC_5H_{10})_2]_2$, compound **8** (50% probability ellipsoids).

C(11)–N(2)–P(1) and C(8)–N(2)–P(1) are 110.39(10)°, 126.80(9)° and 118.78(8)°, respectively, with average 118.7°. The sum of surrounding angles around N(1) and N(3) atoms are 359.99° and 351.69°, respectively. Similar results were obtained for the nitrogen atoms of other structures that confirm the sp² hybridization for the N atoms, although due to the repulsion and steric interactions, some angles are greater, and the others are smaller than 120°.

In compound **8**, the structure is symmetric and the central Sn atom has octahedron coordination. The two methyl groups (and also the two phosphoramidates and the two chlorine atoms) are in *trans* positions and the C(18)–Sn(1)–C(18)#1, O(1)–Sn(1)–O(1)#1 and Cl(1)–Sn(1)–Cl(1)#1 bond angles are 180.0° and the C–Sn–O, C–Sn–Cl and O–Sn–Cl bond angles are about 90°, Table 5. The Sn–C bond lengths (both are 2.1238(19) Å) are quite close to those reported in the literature [39]. The Sn–Cl bond lengths are 2.5617(6) Å lying in the normal covalent radii 2.37–2.60 Å [40]. The Sn–O bond lengths are 2.2176(13) Å that are shorter than sum of the van der Waals radii of Sn and O atoms (3.70 Å) [41].

Compound	D–H···A	d(D–H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{A})$	∠DHA
1	N1-H1N···O1 $[-x+1, -y+1, -z]$	0.845	2.001	2.842(2)	173.85
2	N1–H1N···O1A	0.86	1.96	2.818(4)	172
	N1A–H1NA···O1	0.91	1.99	2.886(4)	170
	N1C-H1C···O1B	0.75	2.17	2.912(4)	170
	N1B-H1B···O1C	0.85	2.07	2.916(4)	171
4	N1–H1A···O1 [$-x, y, -z + 1/2$]	0.86	2.06	2.904(3)	166
5	N1–H1N···O1 $[-x, -y+1, -z+1]$	0.82	2.02	2.820(4)	165
8	N1–H1N···Cl1 $[-x, -y+2, -z+2]$	0.90	2.50	3.320(2)	152

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Table 7 P=O, P-N_{amide}, P-N_{amine} and C=O bond lengths (Å) in compounds with five-, six- and seven-membered ring amine groups

No.	Compound	P=O	P-N _{amide}	P–N _{amine}	C=0
1	$4\text{-}\text{F-}\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^1_2$	1.4863(10)	1.6899(11)	1.6239(12), 1.6390(12)	1.2207(16)
2	$4\text{-}\text{F-}\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}^2_2$	1.480(2), 1.479(2), 1.471(2), 1.475(3)	1.683(3), 1.681(3), 1.670(3), 1.678(4)	1.625(3), 1.618(3) [conformer 1] 1.625(3), 1.633(3) [conformer 2] 1.636(3), 1.632(3) [conformer 3] 1.633(3), 1.626(3) [conformer 4]	1.223(4), 1.222(4), 1.222(4), 1.229(9), 1.238(10)
4	$4-F-C_{6}H_{4}C(O)N(H)P(O)R_{2}^{3}$	1.4801(17)	1.6839(16)	1.6246(18), 1.6318(18)	1.212(2)
5	$4\text{-}\text{F-}\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})\text{R}_2^4$	1.472(2)	1.675(3)	1.626(4), 1.634(3), 1.635(4), 1.641(4) [disordered form]	1.328(4), 1.312(4)
8	$Sn(CH_3)_2Cl_2[4\text{-}F\text{-}C_6H_4C(O)N(H)P(O)R^2{}_2]_2$	1.5012(14)	1.6921(17)	1.6260(17), 1.6201(17)	1.222(2)
9 ^a	$C_6H_5C(O)N(H)P(O)R_2^1$	1.487(3), 1.485(3)	1.679(4), 1.687(4)	1.618(4), 1.625(4) [conformer 1] 1.615(4), 1.618(3) [conformer 2]	1.217(5), 1.207(4)
10 ^b	$C_6H_5C(O)N(H)P(O)R_2^2$	1.465(12), 1.459(12), 1.461(13), 1.464(13)	1.672(13), 1.690(13), 1.691(14), 1.656(13)	1.614(13), 1.605(15) [conformer 1] 1.615(17), 1.590(15) [conformer 2] 1.644(14), 1.631(14) [conformer 3] 1.623(13), 1.647(14) [conformer 4]	1.235(17), 1.229(17), 1.230(17), 1.236(18)
12 ^c	$C_6H_5C(O)N(H)P(O)R_{2}^4$	1.4875(14)	1.6916(16)	1.6369(16), 1.6345(15)	1.227(2)
			N (N [·]	

^a The data of this compound are given in [23].
^b The data of these compounds are given in [25].
^c The data of this compound are given in [42].

Appendix A. Supplementary data

Spectroscopic data of compounds 1-8 can be obtained as supplementary materials. Crystallographic data for the structures in this paper have been deposited with Cambridge Crystallographic Data Center as CCDC supplementary publication nos. 259182 $(C_{15}H_{21}F_1N_3O_2P_1)$, CCDC 259186 $(C_{17}H_{25}F_1N_3O_2P_1)$, CCDC 259185 (C15H21F1N3O4P1), CCDC 259184 $(C_{19}H_{29}F_1N_3O_2P_1)$ and CCDC 259187 $(C_{36}H_{56}Cl_2 F_2N_6O_4P_2Sn_1$). Copies of the data may be obtained on application to 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2005.07.035.

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