Journal of Organometallic Chemistry 693 (2008) 2551–2560

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Self-assembly of di- and triorganotin(IV) complexes: Syntheses, characterization and crystal structures of 1D polymeric chain containing *O*,*O*-diethyl or *O*,*O*-diisopropyl phosphoric acid ligands

Rufen Zhang [a], Mingqing Yang [a], Chunlin Ma [a,b,*]

[a] Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China
[b] Department of Chemistry, Taishan University, Taian 271021, PR China

ARTICLE INFO

Article history:
Received 29 February 2008
Received in revised form 25 April 2008
Accepted 25 April 2008
Available online 6 May 2008

Keywords:
Self-assembly
Organotin(IV)
1D infinite chain
X-ray crystallography

ABSTRACT

A series of organotin(IV) complexes with *O*,*O*-diethyl phosphoric acid (L^1H) and *O*,*O*-diisopropyl phosphoric acid (L^2H) of the types: $[R_3Sn \cdot L]_n$ ($L = L^1$, R = Ph **1**, R = $PhCH_2$ **2**, R = Me **3**, R = Bu **4**; $L = L^2$, R = Ph **9**, R = $PhCH_2$ **10**, R = Me **11**, R = Bu **12**), $[R_2Cl\ Sn \cdot L]_n$ ($L = L^1$, R = Me **5**, R = Ph **6**, R = $PhCH_2$ **7**, R = Bu **8**; $L = L^2$, R = Me **13**, R = Ph **14**, R = $PhCH_2$ **15**, R = Bu **16**), have been synthesized. All complexes were characterized by elemental analysis, TGA, IR and NMR (^1H, ^{13}C, ^{31}P and ^{119}Sn) spectroscopy analysis. Among them, complexes **1**, **2**, **3**, **5**, **8**, **9** and **11** have been characterized by X-ray crystallography diffraction analysis. In the crystalline state, the complexes adopt infinite 1D infinite chain structures which are generated by the bidentate bridging phosphonate ligands and the five-coordinated tin centers.

1. Introduction

Recently, metal-directed self-assembly has become a powerful tool for the complexes possessing intrinsic physical and chemical properties that are promising for the creation of new materials and new metal-based drugs [1]. Among them, organotin(IV) complexes have been intensely studied owing to their potential biological activities as well as their wide industrial applications [2]. Many organotin(IV) carboxylates or substituted carboxylates have been prepared and structurally characterized [3]. In our previous work, through self-assembly of organotin(IV) moieties with appropriate multifunctional ligands we obtained numerous novel and interesting complexes. For example, we have reported the macrocycle containing six tin nuclei with *O*-mercaptobenzoic acid and the hexanuclear macrocycle containing a four-numbered Sn_2O_2 ring with *m*-mercaptobenzoic acid and 18-tin-nuclear 48-member macrocycle with 2-mercaptonicotinic acid [4a,4b]. We also have reported some organotin(IV) carboxylates containing 1D chain, 2D network and trinuclear macrocyclic structures with 2-pyrazinecarboxylic acid and triorganotin moieties based on mixed ligands of 2,3,4,5-tetrafluorobenzoic acid and 4,4′-bipy, triphenylphosphine oxide or phen [4c,4d].

Organotin(IV) derivatives that involve phosphates or phosphonates have also been reported in the literature [5]. As we known, the phosphorus moieties have wide agricultural applications because of their potent biocidal effect [6]. The self-assembly of the organotin(IV) moieties and phosphorus moieties in a single molecular could produce a still more powerful and lasting effective complex. Several model organotin(IV) derivatives that involve thiophosphorus acid have also been reported. Molloy et al. have reported the crystal structure of bis(dimethyldithiophosphinato)dimethyltin(IV) and bis(*O*,*O*′-diisopropyl dithiophosphato) diphenyltin(IV), and the two molecules are six-coordinated in a distorted octahedral geometry with the four sulfur atoms of the anisobidentate chelating dithiophosphinato ligands lying in a plane with the central tin atom [7]. Thus, it is interest to examine the structure of the oxygen phosphate ester ligand to test whether typical oxygen or sulfur behavior would predominate in determining the solid-state structure. In the paper, we report the syntheses of a series of organotin(IV) complexes with *O*,*O*-diethyl phosphoric acid (L^1H) and *O*,*O*-diisopropyl phosphoric acid (L^2H) of the types: $[R_3Sn \cdot L]_n$ ($L = L^1$, R = Ph **1**, R = $PhCH_2$ **2**, R = Me **3**, R = Bu **4**; $L = L^2$, R = Ph **9**, R = $PhCH_2$ **10**, R = Me **11**, R = Bu **12**), $[R_2Cl\ Sn \cdot L]_n$ ($L = L^1$, R = Me **5**, R = Ph **6**, R = $PhCH_2$ **7**, R = Bu **8**; $L = L^2$, R = Me **13**, R = Ph **14**, R = $PhCH_2$ **15**, R = Bu **16**) and characterize them by elemental, IR and NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn) analyses. X-ray crystallography analyses of the complexes **1**, **2**, **3**, **5**, **8**, **9** and **11** have also been given in present paper.

* Corresponding author. Address: Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China. Tel.: +86 635 8230660; fax: +86 538 6715521.
E-mail address: macl@lcu.edu.cn (C. Ma).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.04.036

2. Results and discussion

2.1. Syntheses of complexes 1–16

The triorganotin(IV) phosphates **1**–**4** and **9**–**12** were synthesized by the reaction of triorganotin(IV) chloride with *O*,*O*-diethyl phosphoric acid (L^1H) or *O*,*O*-diisopropyl phosphoric acid (L^2H) with the mole ratio of 1:1 when sodium ethoxide was added, and the synthesis procedures are given in Scheme 1. The diorganotin(IV) phosphates **5**–**8** and **13**–**16** were synthesized by the reaction of diorganotin(IV) dichloride with *O*,*O*-diethyl phosphoric acid (L^1H) or *O*,*O*-diisopropyl phosphoric acid (L^2H) with the mole ratio of 1:1. It is worth noting that, when the mole ratio is 1:2, we also obtained the complexes **5**–**8** and **13**–**16**. It is probable that the spatial resistances of the coordinated phosphate group are strong enough to prevent another ligand chelating to the central tin atom [8]. The synthesis procedures are given in Scheme 2.

2.2. Spectra

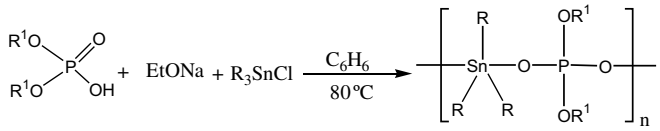
2.2.1. IR

Comparing the IR spectra of the free ligand with complex **1**–**16**, the band at 3100–3550 cm^{-1} which appear in the spectra of the free ligand as the ν(O–H) vibration, are absent in those of complexes **1**–**16**, thus indicating metal–ligand bond formation through these sites. The typical absorptions for P–O, O–C and Sn–C vibrations in these complexes are all located in the normal range of similar organotin(IV) complexes. The strong absorption appears at about 448–460 cm^{-1} in the respective spectra of complexes **1**–**16**, which is absent in the free ligand, is assigned to the Sn–O stretching mode of vibration. Some obvious differences among the spectra of the compounds are also observed. A strong band at about 270 cm^{-1} for **5**–**8** and **15**–**18** are assigned to ν(Sn–Cl) stretching mode of vibration.

2.2.2. NMR

^1H NMR data shows that the signal of the –OH proton in the spectrum of the ligand is absent in all of the complexes, indicating the removal of the –OH proton and the formation of Sn–O bonds. The structural changes occurring in the ligand upon deprotonation and coordination to the Sn atom should be reflected by the changes in the ^{13}C NMR spectra of our complexes. The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron cloud transfer from the ligand to the acceptor. In the ^{31}P NMR spectra, the chemical shift is observed at about 18 ppm. The downfield chemical shift in comparison to that of free acid indicates a considerable drift of electron density from the phosphorus to the tin atoms through the oxygen atoms [9].

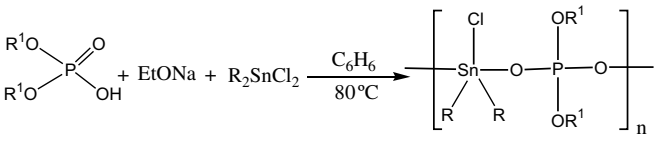
As reported in the literature, value of $\delta(^{119}Sn)$ in the ranges −210 to −400, −90 to −190 and 200 to −60 ppm has been associated with six-, five- and four-coordinate tin centers, respectively [10]. The ^{119}Sn NMR data of complexes **1**–**16** (from −140.0 to −173.0) show only one signal, typical of five-coordinated tin complexes.



R^1= -CH_2CH_3 R= Ph **1**, R= $PhCH_2$ **2**, R= CH_3 **3**, R= *n*-Bu **4**

R^1= -$CH(CH_3)_2$ R= Ph **9**, R= $PhCH_2$ **10**, R= CH_3 **11**, R= *n*-Bu **12**

Scheme 1.



R^1= -CH_2CH_3 R= CH_3 **5**, R= Ph **6**, R= $PhCH_2$ **7**, R= *n*-Bu **8**

R^1= -$CH(CH_3)_2$ R= CH_3 **13**, R= Ph **14**, R= $PhCH_2$ **15**, R= *n*-Bu **16**

Scheme 2.

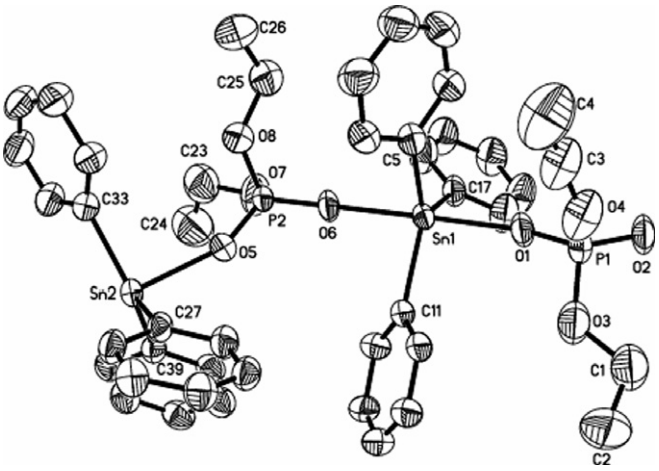


Fig. 1. Molecular structure of complex **1**.

2.3. Crystal structures of $\{[Ph_3SnO_2P(OC_2H_5)_2]_2\}_n$ 1, $[(PhCH_2)_3SnO_2P(OC_2H_5)_2]_n$ 2 and $\{[Me_3SnO_2P(OC_2H_5)_2]_2\}_n$ 3

The molecular structures are illustrated in Figs. 1–3, respectively. The 1D infinite chains are shown in Figs. 4–6, respectively. Selected bond lengths and angles are listed in Table 3. In the crystalline state, these complexes adopt an infinite 1D polymeric chain structures with a five-coordinated tin center, which are generated by the bidentate bridging phosphate ligands and the Sn center. The Sn atom exists in a ideal trigonal bipyramidal environment

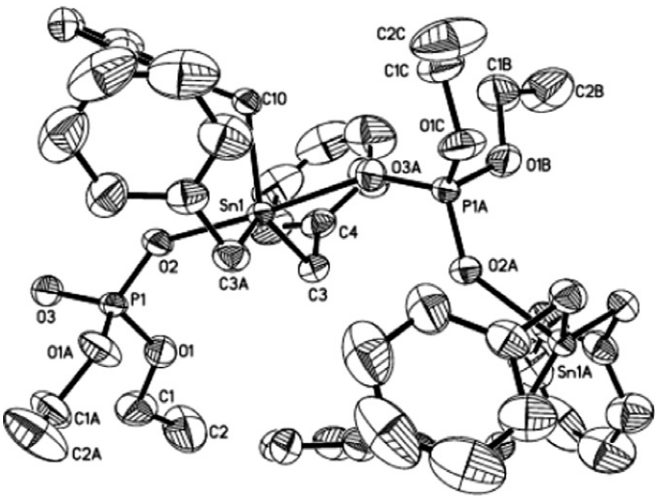


Fig. 2. Molecular structure of complex **2**.

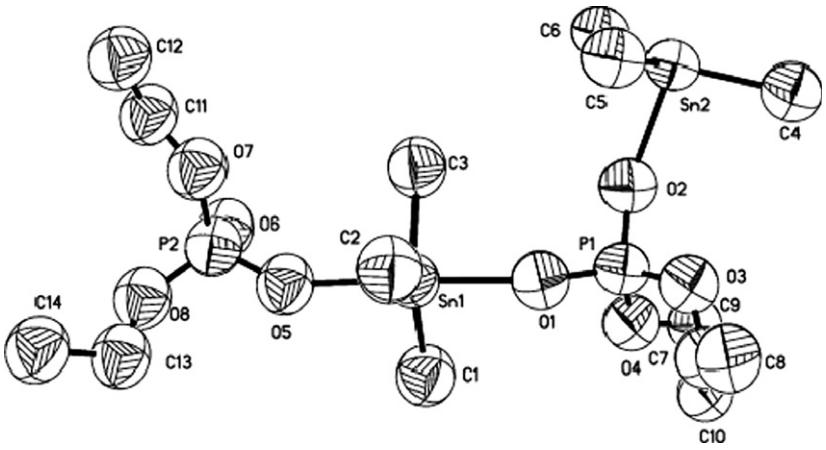


Fig. 3. Molecular structure of complex **3**.

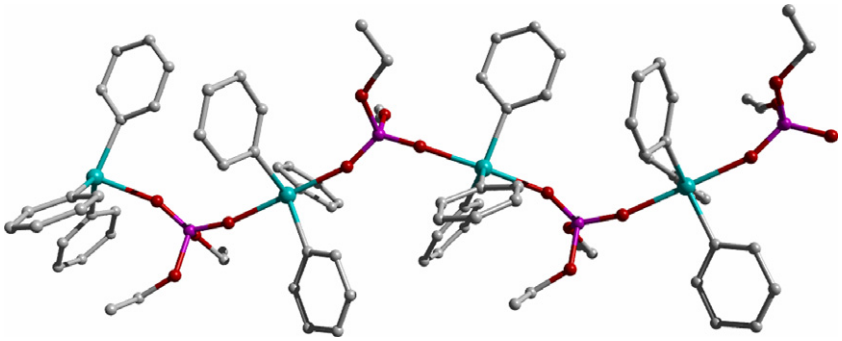


Fig. 4. 1D chain of complex **1**.

with two O atoms and three C atoms, which exhibits a *trans*-R_3SnO_2 geometry [11]. The axial positions are occupied by the O atoms of the ligands [axial angles: O(6)–Sn(1)–O(1) = 178.9(3)°, O(2)#1–Sn(2)–O(5) = 177.3(3)°, #1 x, $y+1$, z, for complex **1**; O(2)–Sn(1)–O(3)#2 = 176.14(16)°, #2 $x-1/2$, y, $-z+1/2$, for complex **2**; O(1)–Sn(1)–O(5) = 177.6(4)°, O(2)–Sn(2)–O(6)#1 = 176.0(5)°, #1 $-x+1$, $y-1/2$, $-z+1$, for complex **3**]. The O atoms of the phosphate bridges two Sn atoms and gives rise to the almost equal Sn–O bond lengths [Sn(1)–O(1) = 2.201(7) Å, Sn(1)–O(6) = 2.198(6) Å; Sn(2)–O(5) = 2.205(7) Å, Sn(2)–O(2)#1 = 2.183(7) Å, for complex **1**; Sn(1)–O(2) = 2.191(4) Å, Sn(1)–O(3)#2 = 2.286(4) Å, for complex **2**; Sn(1)–O(1) = 2.155(10) Å, Sn(1)–O(5) = 2.162(11) Å, Sn(2)–O(2) = 2.197(11) Å, Sn(2)–O(6)#1 = 2.209(11) Å, for complex **3**]. These Sn–O bond lengths are a little longer than the Sn–O covalent bond lengths [2.038–2.115 Å] [12]. The Sn–C bond lengths [2.045(13)–2.147(5) Å] are consistent with those reported in other organotin(IV) complexes. The phosphorus atoms, of which there is only one kind, are found at the center of a distorted tetrahedron with four oxygen atoms as nearest neighbors [5d].

2.4. Crystal structures of $\{[Me_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **5** and $\{[Bu_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **8**

The crystal structures are shown in Figs. 7 and 8. The 1D infinite zigzag chains are shown in Figs. 9 and 10, respectively. Selected bond lengths and angles are listed in Table 4. As can be seen from Figs. 7 and 8, only one Cl atom of the diorganotin dichloride was substituted by the O atoms of the ligand because of the spatial resistances [8,13]. The center tin atom is five-coordinated with the two O atoms occupying the axial sites [axial angles: O(1)–Sn(1)–O(5) = 174.0(4)°, O(6)#1–Sn(2)–O(2) = 172.0(4)°, #1 $x+1/2$, $-y+3/2$, z, for complex **5**; O(6)#1–Sn(1)–O(1) = 167.7(5)°, #1 $x+1$, y, z, O(2)–Sn(2)–O(5) = 170.6(5)°, for complex **8**]. One Cl atom and two C atoms define the equatorial plane. For the complex **5**, the sum of the angles subtended at the Sn(1) in the equatorial plane is 359.8°, so the atoms Sn(1), Cl(1), C(9) and C(10) are almost in the same plane; the sum of the angles of the Sn(2) in the equatorial plane is 359.9°, so the atoms Sn(2), Cl(2), C(11) and C(12) are almost coplanar. In the complex **8**, the sums of the angles of the tin atoms in the equatorial plane are 359.9° [Sn(1)] and 359.8° [Sn(2)], so that the atoms Sn(1), Cl(1), C(9), C(13) and Sn(2), Cl(2), C(17), C(21) are almost coplanar, respectively. The Sn–O bond lengths of the complexes **5** and **8** are similar to these of complexes **1**–**3**, which are a little longer than the Sn–O covalent bond lengths. The bond lengths of Sn–Cl [Sn(1)–Cl(1) = 2.351(7) Å, Sn(2)–Cl(2) = 2.399(7) Å, for complex **5**; Sn(1)–Cl(1) = 2.425(6) Å, Sn(2)–Cl(2) = 2.430(5) Å, for complex **8**] lie in the range of the normal covalent radii (2.30–2.60 Å) [14]. The phosphorus atoms are found at the center of a distorted tetrahedron with four oxygen atoms as nearest neighbors [5d].

2.5. Crystal structures of $\{[Ph_3SnO_2P(OC_3H_7)_2]_3\}_n$ **9** and $[Me_3SnO_2P(OC_3H_7)_2]_n$ **11**

The crystal structures are shown in Figs. 11 and 12. The 1D infinite zigzag chain of complex **11** is shown in Fig. 13. Selected bond lengths and angles are listed in Table 5. As can be seen form Figs. 11–13, the structure of complexes **9** and **11** are similar to the complexes **1**–**3**. The complexes **9** and **11** also adopt an infinite 1D polymeric chain structures with a five-coordinated tin center, which

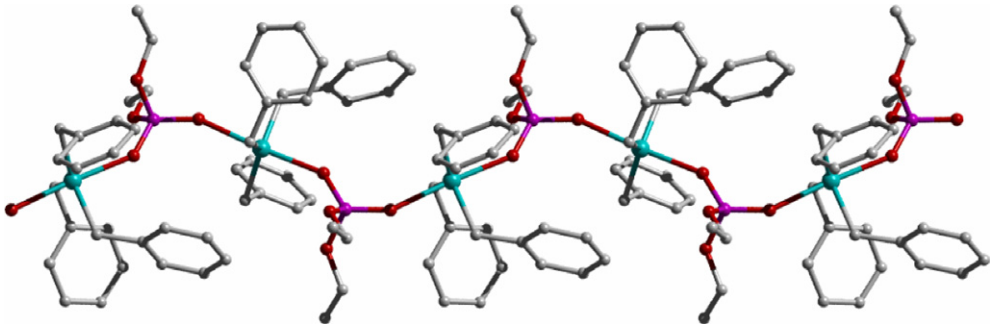


Fig. 5. 1D chain of complex **2**.

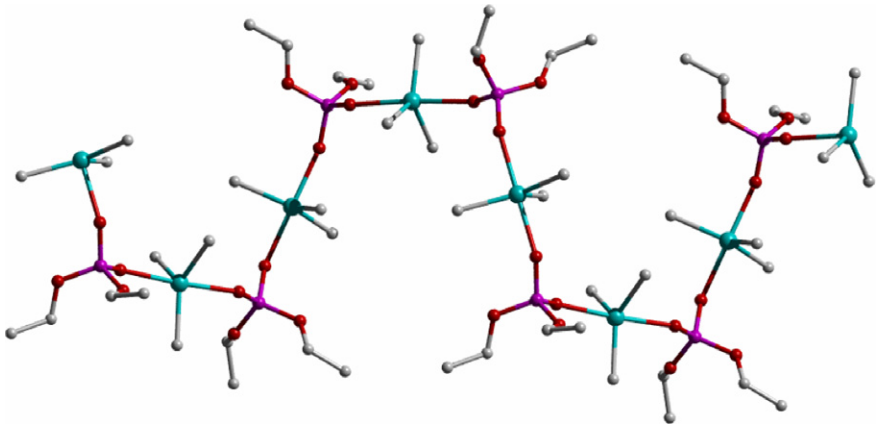


Fig. 6. 1D chain of complex **3**.

Table 1
Crystal data and structure refinement parameters for complexes **1**–**3** and **5**

	Complex **1**	Complex **2**	Complex **3**	Complex **5**
Empirical formula	$C_{44}H_{50}O_8P_2Sn_2$	$C_{25}H_{31}O_4PSn$	$C_{14}H_{38}O_8P_2Sn_2$	$C_{12}H_{32}Cl_2O_8P_2Sn_2$
Formula weight	1006.16	545.16	633.76	674.60
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*P*-1	*Pnma*	*P*21	*Pna*2(1)
a (Å)	9.8041(14)	12.2897(18)	9.9410(10)	18.984(2)
b (Å)	12.8982(18)	20.474(2)	14.3150(15)	7.809(2)
c (Å)	18.552(3)	10.2000(17)	9.9460(10)	17.292(2)
α (°)	100.616(5)	90	90	90
β (°)	93.739(5)	90	90.154	90
γ (°)	102.819(5)	90	90	90
V (Å^3)	2234.6(5)	2566.5(6)	1415.4(3)	2563.5(8)
Z	2	4	2	4
D_{calc} (Mg/m^3)	1.495	1.411	1.487	1.748
μ (mm^{-1})	1.238	1.084	1.905	2.312
F(000)	1016	1112	632	1328
Crystal size (mm)	0.40 × 0.36 × 0.28	0.46 × 0.40 × 0.32	0.58 × 0.52 × 0.45	0.18 × 0.15 × 0.10
Reflections collected	20781	10010	6626	11776
Unique reflections [R_{int}]	7739 [R_{int} = 0.1426]	2320 [R_{int} = 0.0290]	4505 [R_{int} = 0.0430]	4124 [R_{int} = 0.0722]
Data/restraints/parameters	7739/1034/504	2320/0/152	4505/623/235	4124/1140/254
Goodness-of-fit on F^2	1.001	1.000	1.027	1.070
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0693, wR_2 = 0.1162	R_1 = 0.0321, wR_2 = 0.0904	R_1 = 0.0780, wR_2 = 0.1816	R_1 = 0.0733, wR_2 = 0.1171
R indices (all data)	R_1 = 0.1916, wR_2 = 0.1549	R_1 = 0.0526, wR_2 = 0.1223	R_1 = 0.1802, wR_2 = 0.2349	R_1 = 0.1107, wR_2 = 0.1305

are generated by the bidentate bridging phosphate ligands and the Sn center. The primary bond lengths [Sn(1)–O(1) = 2.221(8), Sn(1)–O(2) = 2.198(8), Sn(1)–C(1) = 2.103(13), Sn(1)–C(7) = 2.113 (13), Sn(1)–C(13) = 2.121(13), for complex **9**; Sn(1)–O(1) = 2.223 (10), Sn(1)–O(2)#1 = 2.230(11), #1 $x - 1/2$, $-y + 1/2$, z, Sn(1)–C(7) = 2.040(17), Sn(1)–C(8) = 2.049(17), Sn(1)–C(9) = 2.043(17), for complex **11**] are nearly equal to these corresponding bond lengths of complexes **1**–**3**. The phosphorus atoms are also found at the center of a distorted tetrahedron with four oxygen atoms as nearest neighbors.

2.6. TGA studies

To study the stability of these polymers, thermogravimetric analysis (TGA) was performed for complex **1**–**16**. The TGA curve of these complex exhibits one primary continuous weight loss

Table 2
Crystal data and structure refinement parameters for complexes **8**, **9** and **11**

	Complex **8**	Complex **9**	Complex **11**
Empirical formula	$C_{24}H_{56}Cl_2O_8P_2Sn_2$	$C_{72}H_{87}O_{12}P_3Sn_3$	$C_9H_{23}O_4PSn$
Formula weight	842.91	1593.40	344.93
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	*P*-1	*P*2(1)/*c*	*Pna*2(1)
a (Å)	9.7868(17)	18.9483(10)	11.517(8)
b (Å)	10.3971(19)	12.0165(7)	9.515(7)
c (Å)	19.2134(13)	33.3415(18)	15.283(11)
α (°)	84.9330(10)	90	90
β (°)	89.9740(2)	98.026(2)	90
γ (°)	76.2970(10)	90	90
V (Å^3)	1891.6(5)	7517.2(7)	1675(2)
Z	2	4	4
D_{calc} (Mg/m^3)	1.480	1.408	1.368
μ (mm^{-1})	1.583	1.109	1.616
F(000)	856	3240	696
Crystal size (mm)	0.21 × 0.18 × 0.16	0.15 × 0.10 × 0.08	0.42 × 0.28 × 0.14
Reflections collected	8245	81841	7354
Unique reflections [R_{int}]	5587 [R_{int} = 0.0876]	12888 [R_{int} = 0.1291]	2307 [R_{int} = 0.0475]
Data/restraints/parameters	5587/545/351	12888/3684/812	2307/317/136
Goodness-of-fit on F^2	1.006	1.003	0.979
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0693, wR_2 = 0.1162	R_1 = 0.0321, wR_2 = 0.0904	R_1 = 0.0794, wR_2 = 0.1875
R indices (all data)	R_1 = 0.1916, wR_2 = 0.1549	R_1 = 0.0526, wR_2 = 0.1223	R_1 = 0.1478, wR_2 = 0.2573

Table 3
Selected bond lengths (Å) and angles (°) for complex **1**–**3**

$\{[Ph_3SnO_2P(OC_2H_5)_2]_2\}_n$ **1**			
Sn(1)–C(5)	2.099(13)	Sn(2)–C(27)	2.111(11)
Sn(1)–C(11)	2.112(11)	Sn(2)–C(33)	2.119(13)
Sn(1)–C(17)	2.099(13)	Sn(2)–C(39)	2.129(12)
Sn(1)–O(1)	2.201(7)	Sn(2)–O(2)#1	2.183(7)
Sn(1)–O(6)	2.198(6)	Sn(2)–O(5)	2.205(7)
P(1)–O(1)	1.479(7)	P(2)–O(5)	1.465(8)
P(1)–O(2)	1.452(7)	P(2)–O(6)	1.463(7)
P(1)–O(3)	1.584(10)	P(2)–O(7)	1.659(10)
P(1)–O(4)	1.442(12)	P(2)–O(8)	1.544(9)
C(5)–Sn(1)–C(11)	126.1(5)	C(27)–Sn(2)–C(33)	122.2(5)
C(5)–Sn(1)–C(17)	113.8(5)	C(27)–Sn(2)–C(39)	116.6(4)
C(17)–Sn(1)–C(11)	120.0(5)	C(33)–Sn(2)–C(39)	121.1(5)
O(6)–Sn(1)–O(1)	178.9(3)	O(2)#1–Sn(2)–O(5)	177.3(3)
$[(PhCH_2)_3SnO_2P(OC_2H_5)_2]_n$ **2**			
Sn(1)–C(3)	2.147(5)	Sn(1)–O(3)#2	2.286(4)
Sn(1)–C(3)#1	2.147(5)	O(1)–P(1)	1.565(4)
Sn(1)–C(10)	2.140(6)	O(2)–P(1)	1.500(4)
Sn(1)–O(2)	2.191(4)	O(3)–P(1)	1.471(4)
C(3)–Sn(1)–C(3)#1	127.2(3)	C(10)–Sn(1)–C(3)#1	116.03(14)
C(10)–Sn(1)–C(3)	116.03(14)	O(2)–Sn(1)–O(3)#2	176.14(16)
C(10)–Sn(1)–O(2)	94.5(2)	C(1)–O(1)–P(1)	124.1(4)
C(3)–Sn(1)–O(2)	92.05(16)	P(1)–O(2)–Sn(1)	141.2(3)
$\{[Me_3SnO_2P(OC_2H_5)_2]_2\}_n$ **3**			
Sn(1)–C(1)	2.062(13)	Sn(2)–C(4)	2.062(13)
Sn(1)–C(2)	2.078(13)	Sn(2)–C(5)	2.064(13)
Sn(1)–C(3)	2.045(13)	Sn(2)–C(6)	2.064(13)
Sn(1)–O(1)	2.155(10)	Sn(2)–O(2)	2.197(11)
Sn(1)–O(5)	2.162(11)	Sn(2)–O(6)#1	2.209(11)
O(1)–P(1)	1.468(8)	O(5)–P(2)	1.470(8)
O(2)–P(1)	1.495(8)	O(6)–P(2)	1.480(8)
O(3)–P(1)	1.472(8)	O(7)–P(2)	1.502(8)
O(4)–P(1)	1.494(8)	O(8)–P(2)	1.482(9)
C(1)–Sn(1)–C(2)	131.8(12)	C(4)–Sn(2)–C(5)	125.8(10)
C(3)–Sn(1)–C(1)	122.4(11)	C(4)–Sn(2)–C(6)	121.8(10)
C(3)–Sn(1)–C(2)	105.8(11)	C(5)–Sn(2)–C(6)	112.1(10)
O(1)–Sn(1)–O(5)	177.6(4)	O(2)–Sn(2)–O(6)#1	176.0(5)

Symmetry code for complex **1**: #1 *x*, *y* + 1, *z*. Symmetry code for complex **2**: #1 *x*, $-y + 1/2$, *z*; #2 $x - 1/2$, *y*, $-z + 1/2$. Symmetry code for complex **3**: #1 $-x + 1$, $y - 1/2$, $-z + 1$.

stages in the range of 200–350 °C (two typical TGA curves of complexes **1** and **5** are shown in Figs. 14 and 15, respectively). In general, all these complexes exhibit good thermal stability [15].

3. Conclusions

In summary, a series of organotin(IV) complexes based on *O*,*O*-dialkyl phosphoric acid have been synthesized and characterized. Both the spectra and crystal structures show that when the *O*,*O*-dialkyl phosphoric acid react with triorganotin(IV) chloride they can form 1D infinity chain through substituting the chloride atom; whereas when the *O*,*O*-dialkyl phosphoric acid react with diorganotin(IV) dichloride they also can form 1D infinity chain through substituting only one chloride atom because of the steric constraints. Comparing with the thiophosphates, the oxygenated derivatives have a greater propensity for employing the potentially bidentate phosphorus ligand fully, to chelate the central tin atoms or bind the tin atoms into an associated polymer. The geometry of the tin atom in each complex is five-coordinated and displays a trigonal bipyramid geometry. All these complexes exhibit good thermal stability from the TGA.

4. Experimental section

4.1. Materials and measurements

Triphenyltin(IV) chloride, tri-*n*-butyltin(IV) chloride, trimethyltin(IV) chloride, dimethyltin(IV) dichloride, di-*n*-butyltin(IV) dichloride, diphenyltin(IV) dichloride, *O*,*O*-diethyl phosphoric acid and *O*,*O*-diisopropyl phosphoric acid were commercially available. Tribenzyltin(IV) chloride and dibenzyltin(IV) dichloride were prepared by a standard method reported in literature [16]. The melting points were obtained with an X-4 digital micro-melting-point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-5700 spectrophotometer using KBr discs. ^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were obtained on a Varian Mercury Plus 400 MHz NMR spectrometer. The chemical shifts are reported in ppm with respect to the references and are quoted relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR. ^{31}P chemical shifts are quoted relative to 85% H_3PO_4 and ^{119}Sn chemical shifts are quoted relative to tetramethyltin. TGA was carried out with a Perkin–Elmer Pyris-1 instrument with a heating rate of 10 °C min^{-1} from 50 to 500 °C and with a 20.0 cm^3 min^{-1} nitrogen gas flow. Element analyses were performed with a PE-2400II apparatus.

4.1.1. $\{[Ph_3SnO_2P(OC_2H_5)_2]_2\}_n$ **1**

The *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) were added to the solution of benzene (30 ml) in standard Schlenk technique, and the mixture was stirred for 10 min. Triphenyltin(IV) chloride (0.385 g, 1 mmol) was then added to the mixture, and the reaction was refluxed for 12 h. After cooling down to the room temperature, the solution was filtered and the solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ether/petroleum to give colorless crystals of complex **1**. Yield, 78%. m.p. 201–203 °C. Anal. Calc. for $C_{44}H_{50}O_8P_2Sn_2$: C, 52.52; H, 5.01. Found: C, 52.15; H, 4.86%. IR (KBr, cm^{-1}): 2988, 1600, 1585, 1430, 1180, 1045, 825, 576, 456. ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (t, 12H, $-CH_3$), 1.30 (m, 8H, $-CH_2-$), 7.78–7.95 (m, 30H, Sn–C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 13.5 ($-CH_3$), 26.2 ($-CH_2-$), 129.5, 130.8, 131.1, 136.5, 137.2, 153.6 (Ar–C, $^1J_{Sn-C}$ = 572 Hz). ^{31}P NMR ($CDCl_3$, ppm): 18.7. ^{119}Sn NMR ($CDCl_3$, ppm): −163.1.

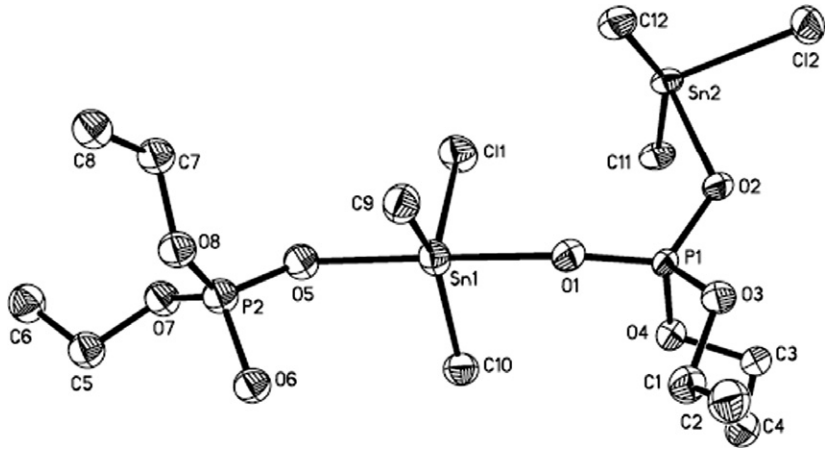


Fig. 7. Molecular structure of complex **5**.

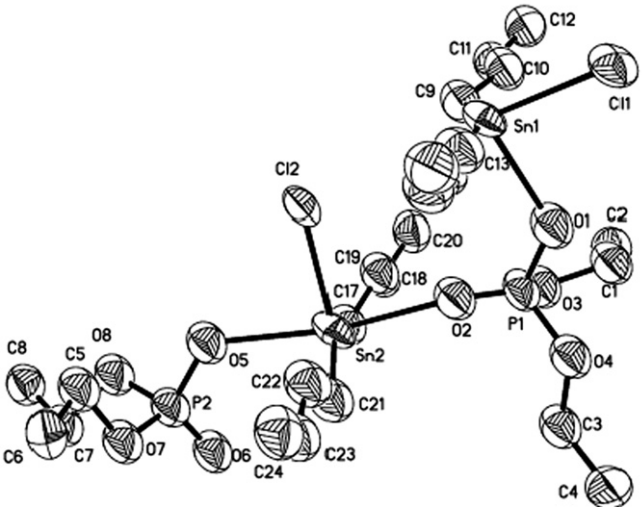


Fig. 8. Molecular structure of complex **8**.

4.1.2. $[(PhCH_2)_3SnO_2P(OC_2H_5)_2]_n$ **2**

Complex **2** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and tribenzyltin(IV) chloride (0.427 g, 1 mmol). Yield, 66%. m.p. 158–160 °C. Anal. Calc. for $C_{25}H_{31}O_4PSn$: C, 55.08; H, 5.73. Found: C, 55.39; H, 5.56%. IR (KBr, cm^{-1}): 2982, 1598, 1560, 1491, 1451, 1191, 1126, 1061, 830, 575, 450. ^1H NMR ($CDCl_3$, ppm): δ 0.89 (t, 6H, $-CH_3$), 1.29 (m, 4H, $-CH_2-$), 3.18 (s, 6H, $Sn-CH_2C_6H_5$), 7.30–7.51 (m, 15H, $-C_6H_5$). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6 ($-CH_3$), 26.1 ($-CH_2-$), 38.2 ($Sn-CH_2C_6H_5$, $^1J_{Sn-C}$ = 485 Hz), 117.1, 128.2, 130.3, 136.9, 138.5, 150.1 (Ar–C). ^{31}P NMR ($CDCl_3$, ppm): 18.2. ^{119}Sn NMR ($CDCl_3$, ppm): −158.2.

4.1.3. $\{[Me_3SnO_2P(OC_2H_5)_2]_2\}_n$ **3**

Complex **3** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and trimethyltin(IV) chloride (0.200 g, 1 mmol). Yield, 85%. m.p. 145–147 °C. Anal. Calc. for $C_{14}H_{38}O_8P_2Sn_2$: C, 26.53; H, 6.04. Found: C, 26.20; H, 5.83%. IR (KBr, cm^{-1}): 2985, 1387, 1201, 1156, 992, 827, 572, 451. ^1H NMR ($CDCl_3$, ppm): δ 0.91 (m, 30H, $-CH_3$), 1.31 (m, 8H, $-CH_2-$). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6 ($-CH_3$), 14.8 ($-CH_3$, $^1J_{Sn-C}$ = 465 Hz), 26.5 ($-CH_2-$). ^{31}P NMR ($CDCl_3$, ppm): 18.5. ^{119}Sn NMR ($CDCl_3$, ppm): −143.3.

4.1.4. $[n\text{-}Bu_3SnO_2P(OC_2H_5)_2]_n$ **4**

Complex **4** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and tri-*n*-butyltin(IV) chloride (0.325 g, 1 mmol). Yield, 72%. m.p. 123–125 °C. Anal. Calc. for $C_{16}H_{37}O_4PSn$: C, 43.37; H, 8.42. Found: C, 43.02; H, 8.25%. IR (KBr, cm^{-1}): 2983, 2959, 1230,

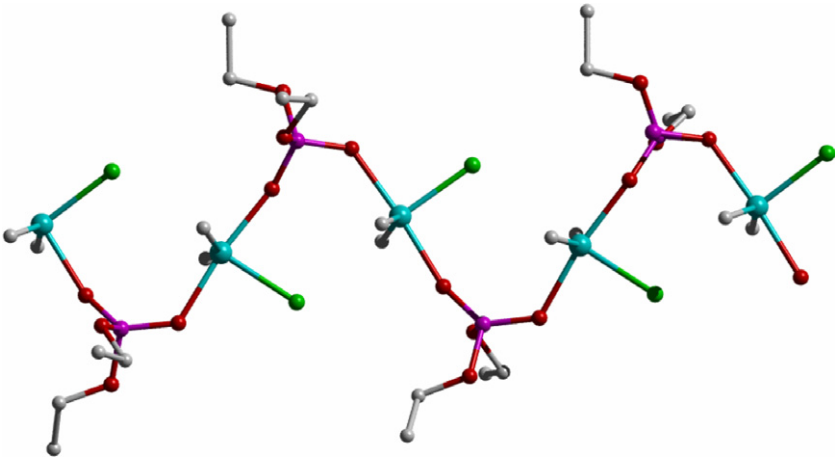


Fig. 9. 1D zigzag chain of complex **5**.

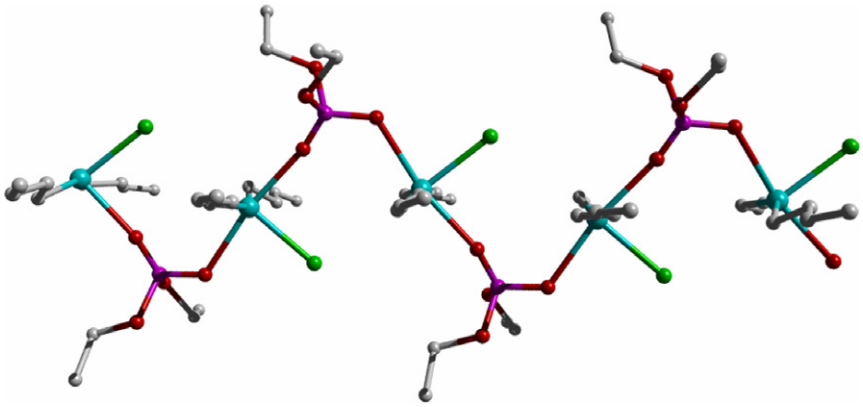


Fig. 10. 1D zigzag chain of complex **8**.

Table 4
Selected bond lengths (Å) and angles (°) for complex **5** and **8**

$\{[Me_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **5**			
Sn(1)–C(9)	2.104(16)	Sn(2)–C(11)	2.073(14)
Sn(1)–C(10)	2.126(15)	Sn(2)–C(12)	2.055(15)
Sn(1)–Cl(1)	2.351(7)	Sn(2)–Cl(2)	2.399(7)
Sn(1)–O(1)	2.200(9)	Sn(2)–O(2)	2.206(10)
Sn(1)–O(5)	2.211(11)	Sn(2)–O(6)#1	2.166(8)
P(1)–O(1)	1.528(6)	P(2)–O(5)	1.539(6)
P(1)–O(2)	1.525(6)	P(2)–O(6)	1.533(7)
P(1)–O(3)	1.556(6)	P(2)–O(7)	1.545(6)
P(1)–O(4)	1.546(6)	P(2)–O(8)	1.541(7)
C(9)–Sn(1)–C(10)	144.2(7)	C(12)–Sn(2)–C(11)	152.1(7)
C(9)–Sn(1)–Cl(1)	110.8(5)	C(11)–Sn(2)–Cl(2)	101.3(5)
C(10)–Sn(1)–Cl(1)	104.7(5)	C(12)–Sn(2)–Cl(2)	106.6(5)
O(1)–Sn(1)–O(5)	174.0(4)	O(6)#1–Sn(2)–O(2)	172.0(4)
$\{[Bu_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **8**			
Sn(1)–C(9)	2.073(19)	Sn(2)–C(17)	2.089(18)
Sn(1)–C(13)	2.028(19)	Sn(2)–C(21)	1.980(2)
Sn(1)–Cl(1)	2.425(6)	Sn(2)–Cl(2)	2.430(5)
Sn(1)–O(1)	2.377(13)	Sn(2)–O(2)	2.306(15)
Sn(1)–O(6)#1	2.289(14)	Sn(2)–O(5)	2.379(13)
P(1)–O(1)	1.418(13)	P(2)–O(5)	1.430(13)
P(1)–O(2)	1.230(15)	P(2)–O(6)	1.286(14)
P(1)–O(3)	1.580(13)	P(2)–O(7)	1.605(14)
P(1)–O(4)	1.568(14)	P(2)–O(8)	1.612(14)
C(13)–Sn(1)–C(9)	142.7(9)	C(21)–Sn(2)–C(17)	143.8(8)
C(9)–Sn(1)–Cl(1)	108.1(6)	C(17)–Sn(2)–Cl(2)	108.2(6)
C(13)–Sn(1)–Cl(1)	109.0(6)	C(21)–Sn(2)–Cl(2)	107.8(6)
O(6)#1–Sn(1)–O(1)	167.7(5)	O(2)–Sn(2)–O(5)	170.6(5)

Symmetry code for complex **5**: #1 $x + 1/2, -y + 3/2, z$. Symmetry code for complex **8**: #1 $x + 1, y, z$.

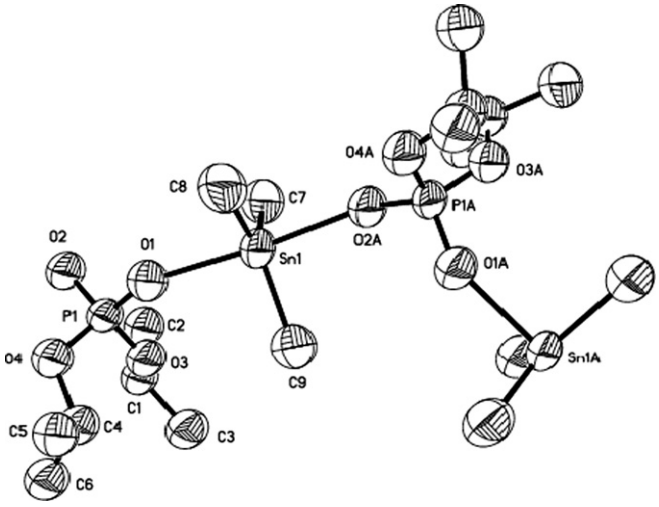


Fig. 12. Molecular structure of complex **11**.

1139, 1109, 1058, 832, 567, 450. ^{1}H NMR ($CDCl_3$, ppm): δ 0.91 (t, 15H, $-CH_3$), 1.28–1.41 (m, 22H, $-CH_2-$). ^{13}C NMR ($CDCl_3$, ppm): δ 13.8 ($-CH_3$), 14.6 ($-CH_2-$, $^1J_{Sn-C}$ = 502 Hz), 26.8 ($-CH_2-$), 30.1 ($-CH_2-$). ^{31}P NMR ($CDCl_3$, ppm): 17.8. ^{119}Sn NMR ($CDCl_3$, ppm): −148.5.

4.1.5. $\{[Me_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ ***5***

Complex **5** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and dimethyltin(IV) dichloride (0.220 g,

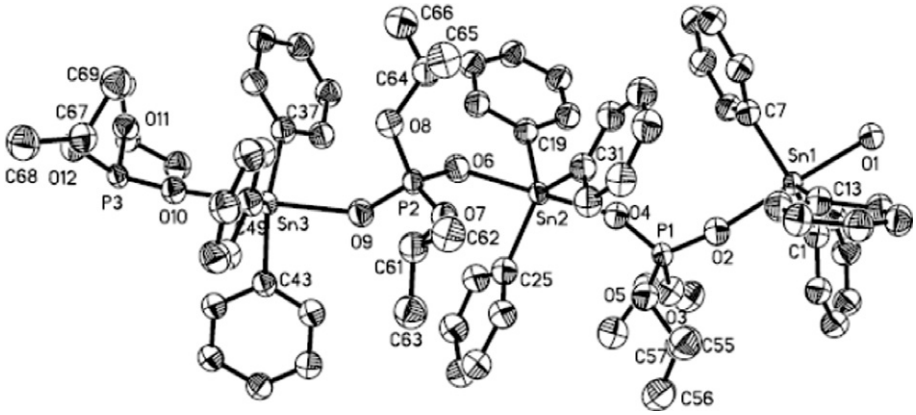


Fig. 11. Molecular structure of complex **9**.

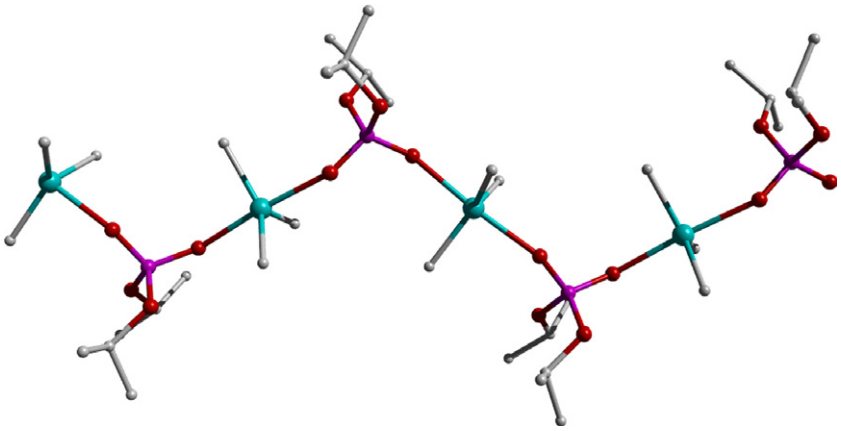


Fig. 13. 1D chain of complex **11**.

Table 5
Selected bond lengths (Å) and angles (°) for complex **9** and **11**

$\{[Ph_3SnO_2P(OC_3H_7)_2]_3\}_n$ **9**			
Sn(1)–C(1)	2.103(13)	Sn(2)–C(19)	2.123(12)
Sn(1)–C(7)	2.113(13)	Sn(2)–C(25)	2.101(12)
Sn(1)–C(13)	2.121(13)	Sn(2)–C(31)	2.107(13)
Sn(1)–O(1)	2.221(8)	Sn(2)–O(4)	2.221(8)
Sn(1)–O(2)	2.198(8)	Sn(2)–O(6)	2.229(8)
Sn(3)–C(37)	2.123(12)	P(1)–O(2)	1.458(8)
Sn(3)–C(43)	2.128(12)	P(1)–O(3)	1.548(9)
Sn(3)–C(49)	2.121(12)	P(1)–O(4)	1.484(8)
Sn(3)–O(9)	2.208(7)	P(1)–O(5)	1.559(9)
Sn(3)–O(10)	2.213(7)	P(2)–O(6)	1.480(8)
P(2)–O(7)	1.554(8)	P(2)–O(8)	1.576(8)
P(2)–O(9)	1.488(8)	P(3)–O(1)#1	1.485(8)
P(3)–O(10)	1.482(8)	P(3)–O(11)	1.568(8)
C(1)–Sn(1)–C(7)	118.4(5)	C(25)–Sn(2)–C(19)	117.8(5)
C(1)–Sn(1)–C(13)	119.7(5)	C(25)–Sn(2)–C(31)	126.9(5)
C(7)–Sn(1)–C(13)	121.8(5)	C(31)–Sn(2)–C(19)	115.2(5)
O(2)–Sn(1)–O(1)	178.0(3)	O(4)–Sn(2)–O(6)	178.5(3)
C(37)–Sn(3)–C(43)	121.1(5)	C(49)–Sn(3)–C(43)	114.8(5)
C(49)–Sn(3)–C(37)	124.1(5)	O(9)–Sn(3)–O(10)	176.7(3)
$[Me_3SnO_2P(OC_3H_7)_2]_n$ **11**			
Sn(1)–C(7)	2.040(17)	Sn(1)–O(2)#1	2.230(11)
Sn(1)–C(8)	2.049(17)	P(1)–O(1)	1.440(9)
Sn(1)–C(9)	2.043(17)	P(1)–O(2)	1.449(9)
Sn(1)–O(1)	2.223(10)	P(1)–O(3)	1.441(9)
P(1)–O(4)	1.470(10)		
C(7)–Sn(1)–C(8)	117.0(13)	O(1)–Sn(1)–O(2)#1	175.4(5)
C(7)–Sn(1)–C(9)	112.5(14)	O(1)–P(1)–O(2)	113.0(7)
C(9)–Sn(1)–C(8)	130.3(12)	O(1)–P(1)–O(3)	110.1(7)

Symmetry code for complex **9**: #1 $x+1, y, z$. Symmetry code for complex **11**: #1 $x-1/2, -y+1/2, z$.

1 mmol). Yield, 80%. m.p. 207–209 °C. Anal. Calc. for $C_{12}H_{32}Cl_2O_8P_2Sn_2$: C, 21.36; H, 4.78. Found: C, 21.67; H, 4.95%. IR (KBr, cm^{-1}): 2980, 1255, 1168, 1112, 1066, 820, 663, 563, 449, 265. ^1H NMR ($CDCl_3$, ppm): δ 0.90 (m, 24H, $-CH_3$), 1.31 (m, 8H, $-CH_2-$). ^{13}C NMR ($CDCl_3$, ppm): δ 13.7 ($-CH_3$), 14.5 ($-CH_3$, $^1J_{Sn-C}$ = 460 Hz), 27.2 ($-CH_2-$). ^{31}P NMR ($CDCl_3$, ppm): 18.2. ^{119}Sn NMR ($CDCl_3$, ppm): −140.5.

*4.1.6. $\{[Ph_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **6***

Complex **6** was synthesized by the same procedure as **1** with *O,O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and diphenyltin(IV) dichloride (0.344 g, 1 mmol). Yield, 77%. m.p. 221–223 °C. Anal. Calc. for $C_{32}H_{40}Cl_2O_8P_2Sn_2$: C, 41.64; H, 4.37. Found: C, 41.29; H, 4.18%. IR (KBr, cm^{-1}): 2985, 1637, 1590, 1158, 1110, 1073, 835, 580, 457, 267. ^1H NMR ($CDCl_3$, ppm): δ 0.88 (t, 12H, $-CH_3$), 1.29 (m, 8H, $-CH_2-$), 7.81–7.96 (m,

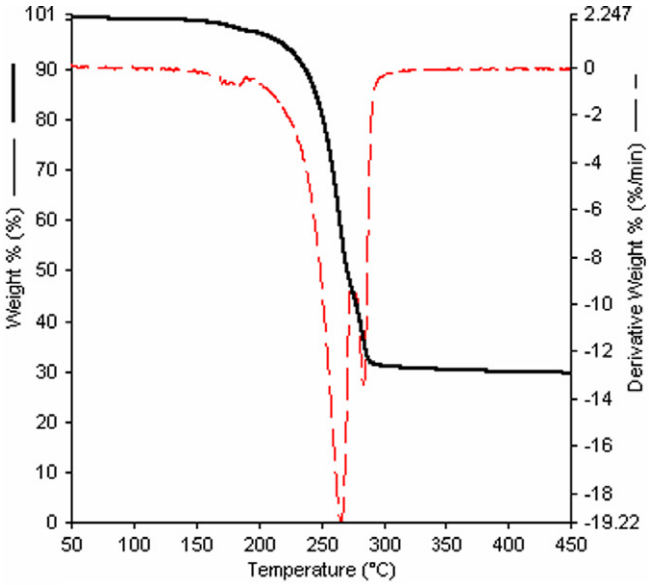


Fig. 14. TGA curve of complex **1**.

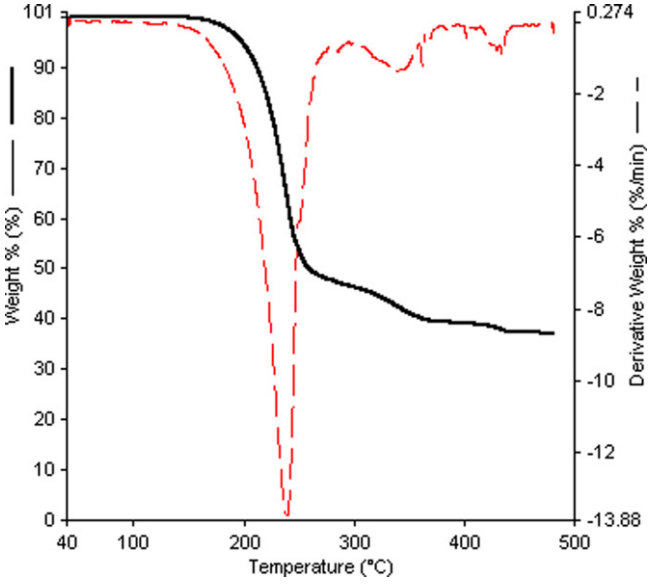


Fig. 15. TGA curve of complex **5**.

20H, Sn–C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6 (–CH_3), 26.8 (–CH_2–), 128.8, 130.3, 131.2, 138.4, 138.6, 149.2 (Ar–C, $^1J_{Sn-C}$ = 580 Hz). ^{31}P NMR ($CDCl_3$, ppm): 18.0. ^{119}Sn NMR ($CDCl_3$, ppm): −172.6.

4.1.7. $\{[(PhCH_2)_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **7**

Complex **7** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and dibenzyltin(IV) dichloride (0.372 g, 1 mmol). Yield, 75%. m.p. 213–215 °C. Anal. Calc. for $C_{36}H_{48}Cl_2O_8P_2Sn_2$: C, 44.16; H, 4.94. Found: C, 44.53; H, 4.76%. IR (KBr, cm^{-1}): 2986, 1620, 1595, 1220, 1078, 826, 578, 459, 273. ^{1}H NMR ($CDCl_3$, ppm): δ 0.89 (t, 12H, –CH_3), 1.28 (m, 8H, –CH_2–), 3.17 (s, 8H, Sn–$CH_2C_6H_5$), 7.31–7.50 (m, 20H, –C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 13.8 (–CH_3), 26.2 (–CH_2–), 38.2 (Sn–$CH_2C_6H_5$, $^1J_{Sn-C}$ = 487 Hz), 117.0, 128.0, 131.2, 135.8, 139.2, 152.0 (Ar–C). ^{31}P NMR ($CDCl_3$, ppm): 18.3. ^{119}Sn NMR ($CDCl_3$, ppm): −166.5.

4.1.8. $\{[n\text{-}Bu_2ClSnO_2P(OC_2H_5)_2]_2\}_n$ **8**

Complex **8** was synthesized by the same procedure as **1** with *O*,*O*-diethyl phosphoric acid (0.154 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and di-*n*-butyltin(IV) dichloride (0.304 g, 1 mmol). Yield, 72%. m.p. 177–179 °C. Anal. Calc. for $C_{24}H_{56}Cl_2O_8P_2Sn_2$: C, 34.20; H, 6.70. Found: C, 33.90; H, 6.96%. IR (KBr, cm^{-1}): 2983, 2968, 2930, 1320, 1255, 1100, 829, 569, 452, 270. ^{1}H NMR ($CDCl_3$, ppm): δ 0.90 (t, 24H, –CH_3), 1.30–1.40 (m, 32H, –CH_2–). ^{13}C NMR ($CDCl_3$, ppm): δ 13.7 (–CH_3), 14.6 (–CH_2–, $^1J_{Sn-C}$ = 511 Hz), 26.9 (–CH_2–), 31.3 (–CH_2–). ^{31}P NMR ($CDCl_3$, ppm): 18.2. ^{119}Sn NMR ($CDCl_3$, ppm): −146.9.

4.1.9. $\{[Ph_3SnO_2P(OC_3H_7)_2]_3\}_n$ **9**

Complex **9** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and triphenyltin(IV) chloride (0.385 g, 1 mmol). Yield, 77%. m.p. 186–188 °C. Anal. Calc. for $C_{72}H_{87}O_{12}P_3Sn_3$: C, 54.27; H, 5.50. Found: C, 54.59; H, 5.23%. IR (KBr, cm^{-1}): 3001, 2932, 1635, 1586, 1430, 1099, 1075, 823, 575, 454. ^{1}H NMR ($CDCl_3$, ppm): δ 0.89 (d, 36H, –CH_3), 1.76 (m, 6H, CH), 7.80–8.01 (m, 45H, Sn–C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 23.6(–CH_3), 28.9 (CH), 127.8, 130.8, 131.0, 136.6, 137.2, 153.5 (Ar–C, $^1J_{Sn-C}$ = 571 Hz). ^{31}P NMR ($CDCl_3$, ppm): 18.5. ^{119}Sn NMR ($CDCl_3$, ppm): −163.0.

4.1.10. $[(PhCH_2)_3SnO_2P(OC_3H_7)_2]_n$ **10**

Complex **10** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and tribenzyltin(IV) chloride (0.427 g, 1 mmol). Yield, 79%. m.p. 175–177 °C. Anal. Calc. for $C_{27}H_{35}O_4PSn$: C, 56.57; H, 6.15. Found: C, 56.23; H, 5.90%. IR (KBr, cm^{-1}): 2996, 1640, 1610, 1429, 1208, 1132, 1003, 820, 570, 450. ^{1}H NMR ($CDCl_3$, ppm): δ 0.90 (d, 12H, –CH_3), 1.75 (m, 2H, CH), 3.20 (s, 6H, Sn–$CH_2C_6H_5$), 7.33–7.56 (m, 15H, –C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 23.5 (–CH_3), 28.7 (CH), 38.2 (Sn–$CH_2C_6H_5$, $^1J_{Sn-C}$ = 486 Hz), 117.6, 129.3, 129.8, 137.7, 138.5, 151.2 (Ar–C). ^{31}P NMR ($CDCl_3$, ppm): 18.2. ^{119}Sn NMR ($CDCl_3$, ppm): −158.9.

4.1.11. $[Me_3SnO_2P(OC_3H_7)_2]_n$ **11**

Complex **11** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and trimethyltin(IV) chloride (0.200 g, 1 mmol). Yield, 85%. m.p. 153–155 °C. Anal. Calc. for $C_9H_{23}O_4PSn$: C, 31.34; H, 6.72. Found: C, 31.69. H, 6.51%. IR (KBr, cm^{-1}): 2986, 1438, 1427, 1383, 1186, 1175, 1069, 821, 569, 448. ^{1}H NMR ($CDCl_3$, ppm): δ 0.91 (m, 21H, –CH_3), 1.74 (m, 2H, CH). ^{13}C NMR ($CDCl_3$, ppm): δ 14.8 (–CH_3, $^1J_{Sn-C}$ = 463 Hz), 23.5 (–CH_3), 28.7 (CH). ^{31}P NMR ($CDCl_3$, ppm): 18.2. ^{119}Sn NMR ($CDCl_3$, ppm): −143.0.

4.1.12. $[n\text{-}Bu_3SnO_2P(OC_3H_7)_2]_n$ **12**

Complex **12** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and tri-*n*-butyltin(IV) chloride (0.325 g, 1 mmol). Yield, 75%. m.p. 119–121 °C. Anal. Calc. for $C_{18}H_{41}O_4PSn$: C, 45.88; H, 8.77. Found: C, 45.57; H, 8.59%. IR (KBr, cm^{-1}): 2990, 2977, 1372, 1369, 1208, 1198, 1001, 830, 783, 573, 455. ^{1}H NMR ($CDCl_3$, ppm): δ 0.89 (t, 21H, –CH_3), 1.29–1.38 (m, 18H, –CH_2–), 1.75 (m, 2H, CH). ^{13}C NMR ($CDCl_3$, ppm): δ 13.7(–CH_3), 14.7 (–CH_2–, $^1J_{Sn-C}$ = 504 Hz), 23.6 (–CH_3), 28.7 (CH), 31.0 (–CH_2–). ^{31}P NMR ($CDCl_3$, ppm): 17.8. ^{119}Sn NMR ($CDCl_3$, ppm): −148.3.

4.1.13. $\{[Me_2ClSnO_2P(OC_3H_7)_2]_2\}_n$ **13**

Complex **13** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and dimethyltin(IV) dichloride (0.220 g, 1 mmol). Yield, 82%. m.p. 183–185 °C. Anal. Calc. for $C_{16}H_{40}Cl_2O_8P_2Sn_2$: C, 26.30; H, 5.52. Found: C, 26.00; H, 5.25%. IR (KBr, cm^{-1}): 2999, 2986, 1300, 1170, 1100, 819, 566, 451, 263. ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (m, 36H, –CH_3), 1.75 (m, 4H, CH). ^{13}C NMR ($CDCl_3$, ppm): δ 14.9(–CH_3, $^1J_{Sn-C}$ = 463 Hz), 23.6 (–CH_3), 28.8 (CH). ^{31}P NMR ($CDCl_3$, ppm): 17.9. ^{119}Sn NMR ($CDCl_3$, ppm): −140.7.

4.1.14. $\{[Ph_2ClSnO_2P(OC_3H_7)_2]_2\}_n$ **14**

Complex **14** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and diphenyltin(IV) dichloride (0.344 g, 1 mmol). Yield, 76%. m.p. 209–211 °C. Anal. Calc. for $C_{36}H_{48}Cl_2O_8P_2Sn_2$: C, 44.16; H, 4.94. Found: C, 44.52; H, 4.67%. IR (KBr, cm^{-1}):2990, 1630, 1599, 1320, 1207, 1113, 822, 575, 455, 268. ^{1}H NMR ($CDCl_3$, ppm): δ 0.91 (d, 24H, –CH_3), 1.74 (m, 4H, CH), 7.81–8.03 (m, 20H, Sn–C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 23.5(–CH_3), 28.9 (CH), 128.9, 131.3, 131.5, 139.2, 139.9, 151.7 (Ar–C, $^1J_{Sn-C}$ = 573 Hz). ^{31}P NMR ($CDCl_3$, ppm): 18.3. ^{119}Sn NMR ($CDCl_3$, ppm): −173.0.

4.1.15. $\{[(PhCH_2)_2ClSnO_2P(OC_3H_7)_2]_2\}_n$ **15**

Complex **15** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and dibenzyltin(IV) dichloride (0.372 g, 1 mmol). Yield, 83%. m.p. 198–200 °C. Anal. Calc. for $C_{40}H_{56}Cl_2O_8P_2Sn_2$: C, 46.41; H, 5.45. Found: C, 46.07; H, 5.18%. IR (KBr, cm^{-1}): 2987, 1625, 1587, 1300, 1198, 1103, 829, 570, 452, 273. ^{1}H NMR ($CDCl_3$, ppm): δ 0.92 (d, 24H, –CH_3), 1.76 (m, 4H, CH), 3.18 (s, 8H, Sn–$CH_2C_6H_5$), 7.32–7.49 (m, 20H, –C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 23.6 (–CH_3), 28.7 (CH), 38.3 (Sn–$CH_2C_6H_5$, $^1J_{Sn-C}$ = 490 Hz), 117.0, 128.6, 129.0, 137.5, 138.2, 152.3 (Ar–C). ^{31}P NMR ($CDCl_3$, ppm): 18.5. ^{119}Sn NMR ($CDCl_3$, ppm): −166.6.

4.1.16. $\{[n\text{-}Bu_2ClSnO_2P(OC_3H_7)_2]_2\}_n$ **16**

Complex **16** was synthesized by the same procedure as **1** with *O*,*O*-diisopropyl phosphoric acid (0.182 g, 1 mmol) and EtONa (0.068 g, 1 mmol) and di-*n*-butyltin(IV) dichloride (0.304 g, 1 mmol). Yield, 70%. m.p. 170–172 °C. Anal. Calc. for $C_{28}H_{64}Cl_2O_8P_2Sn_2$: C, 37.41; H, 7.17. Found: C, 37.02; H, 7.45%. IR (KBr, cm^{-1}): 2989, 2979, 1340, 1310, 1200, 1138, 1009, 825, 571, 451, 272. ^{1}H NMR ($CDCl_3$, ppm): δ 0.89 (t, 36H, –CH_3), 1.30–1.37 (m, 24H, –CH_2–), 1.76 (m, 4H, CH). ^{13}C NMR ($CDCl_3$, ppm): δ 13.5(–CH_3), 14.4 (–CH_2–, $^1J_{Sn-C}$ = 506 Hz), 23.7 (–CH_3), 28.8 (CH), 32.6 (–CH_2–). ^{31}P NMR ($CDCl_3$, ppm): 17.9. ^{119}Sn NMR ($CDCl_3$, ppm): −141.5.

4.2. Crystal structures of complexes **1**–**3**, **5**, **8**, **9** and **11**

Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined

against F^2 by full-matrix least squares using SHELXS-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Tables 1 and 2.

Acknowledgement

We thank the National Natural Science Foundation of China for the financial support of this research (Grant No. 20741008).

Appendix A. Supplementary material

CCDC 644062, 643935, 661000, 643933, 656164, 643931 and 643936 contain the supplementary crystallographic data for **1**, **2**, **3**, **5**, **8**, **9** and **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.036.

References

[1] (a) P.J. Langley, J. Hulliger, Chem. Soc. Rev. 28 (1999) 279–291;
(b) C. Janiak, Dalton Trans. (2003) 2781–2804;
(c) G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murry, J.D. Cashion, Science 298 (2002) 1762–1765;
(d) V. Chandrasekhar, S. Nagendran, V. Baskar, Coord. Chem. Rev. 235 (2002) 1–52;
(e) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder, Coord. Chem. Rev. 183 (1999) 117–138;
(f) S. Kitagawa, R. Kitaura, Comment Inorg. Chem. 23 (2002) 101–126;
(g) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. 116 (2004) 1490–1592.
[2] (a) R.R. Holmes, Acc. Chem. Res. 22 (1989) 190–197;
(b) R. García-Zarracino, H. Höpfl, J. Am. Chem. Soc. 127 (2005) 3120–3130;
(c) G. Prabusankar, R. Murugavel, Organometallics 23 (2004) 5644–5647;
(d) L. Pellerito, L. Nagy, Coord. Chem. Rev. 224 (2002) 111–150;
(e) M. Gielen, Coord. Chem. Rev. 151 (1996) 41–51;
(f) S.W. Ng, J.M. Hook, M. Gielen, Appl. Organomet. Chem. 14 (2000) 481–494.
[3] (a) V. Chandrasekhar, R.O. Day, R.R. Holmes, Inorg. Chem. 24 (1985) 1970–1971;
(b) R.O. Day, V. Chandrasekhar, K.C.K. Swamy, J.M. Holmes, D.S. Burton, R.R. Holmes, Inorg. Chem. 27 (1988) 2877–2887;
(c) V. Chandrasekhar, S. Nagendran, V. Baskar, Coord. Chem. Rev. 235 (2002) 1–52;
(d) G.L. Zheng, J.F. Ma, Z.M. Su, L.K. Yan, J. Yang, Y.Y. Li, J.F. Liu, Angew. Chem. Int. Ed. 43 (2004) 2409–2411;
(e) V. Chandrasekhar, K. Gopal, P. Sasikumar, R. Thirumoorthi, Coord. Chem. Rev. 249 (2005) 1745–1765.
[4] (a) C.L. Ma, Q.F. Zhang, R.F. Zhang, D.Q. Wang, Chem. Eur. J. 12 (2006) 420–428;
(b) C.L. Ma, Q. Jiang, R.F. Zhang, D.Q. Wang, Dalton Trans. (2003) 2975–2978;
(c) C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang, Dalton Trans. (2004) 1832–1840;
(d) C.L. Ma, J.S. Sun, R.F. Zhang, J. Organomet. Chem. 691 (2006) 5873–5886.
[5] (a) V. Chandrasekhar, V. Baskar, A. Steiner, S. Zacchini, Organometallics 21 (2002) 4528–4532;
(b) V. Chandrasekhar, V. Baskar, R. Boomishankar, K. Gopal, S. Zacchini, J.F. Bickley, A. Steiner, Organometallics 22 (2003) 3710–3716;
(c) V. Chandrasekhar, V. Baskar, A. Steiner, S. Zacchini, Organometallics 23 (2004) 1390–1395;
(d) K.C. Molloy, M.B. Hossain, D. Van der Helm, D. Cunningham, J.J. Zuckerman, Inorg. Chem. 20 (1981) 2402–2407;
(e) K.C. Molloy, F.A.K. Nasser, C.L. Barnes, D.V.D. Helm, J.J. Zuckerman, Inorg. Chem. 21 (1982) 960–964;
(f) J.P. Ashmore, T. Chives, K.A. Kerr, J.H.G. Van Roode, Inorg. Chem. 16 (1977) 191–196;
(g) F. Weller, J. Organomet. Chem. 322 (1987) 185–192.
[6] (a) J.L. Lefferts, K.C. Molly, J.J. Zuckerman, I. Haiduc, C. Guta, D. Ruse, Inorg. Chem. 19 (1980) 1662–1670;
(b) A.J. Crowe, P.J. Smith, Inorg. Chim. Acta 93 (1984) 179–184;
(c) M. Gielen, Appl. Organometal. Chem. 16 (2002) 481–494.
[7] (a) K.C. Molly, M.B. Hossain, D. Van Der Helm, J.J. Zuckerman, I. Haiduc, Inorg. Chem. 18 (1979) 3507–3511;;
(b) K.C. Molly, M.B. Hossain, D. Van Der Helm, J.J. Zuckerman, F.P. Mullins, Inorg. Chem. 20 (1981) 2172–2177.
[8] (a) Z.H. Chohan, R.A. Howie, J.L. Wardell, J. Organomet. Chem. 577 (1999) 140;
(b) C.L. Ma, Q. Jiang, R.F. Zhang, Appl. Organometal. Chem. 17 (2003) 623–630.
[9] T.N. Srivastava, J.D. Singh, S.K. Srivastava, Polyhedron 9 (7) (1990) 943–948.
[10] J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem. 315 (3) (1986) 299–308.
[11] (a) C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang, Eur. J. Inorg. Chem. (2005) 3024–3033;
(b) C.L. Ma, J.K. Li, R.F. Zhang, D.Q. Wang, J. Organomet. Chem. 691 (2006) 1713–1721.
[12] (a) J.S. Casas, A. Castineriros, E.G. Martines, A.S. Gonzales, A. Sanches, J. Sordo, Polyhedron 16 (1997) 795–800;
(b) M. Hill, M.F. Mahon, K.C. Molloy, J.Chem. Soc. Dalton Trans. (1996) 1857;
(c) S. Bhandari, M.F. Mahon, K.C. Molloy, J.Chem. Soc. Dalton Trans. (1999) 1951.
[13] (a) A.P.G. de Sousa, R.M. Silva, A. Cesar, J.L. Wardell, J.C. Huffman, A. Abras, J. Organomet. Chem. 605 (2000) 82–88;
(b) C.L. Ma, J.H. Zhang, F. Li, R.F. Zhang, Eur. J. Inorg. Chem. (2004) 2775–2783.
[14] F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rogers, D.G. Watson, Acta Crystallogr. B 35 (1979) 2331–2339.
[15] C.L. Ma, G.R. Tan, R.F. Zhang, Inorg. Chem. Commun. 9 (2006) 882–886.
[16] K. Sisido, Y. Takeda, Z. Kinugawa, J. Am. Chem. Soc. 83 (1961) 538–541.