




Reactions of 4-diphenylphosphino benzoic acid with organotin oxides and -oxy-hydroxide

RAMAKIRUSHNAN SURIYA NARAYANAN^a, PAKKIRISAMY THILAGAR^b,
JOYDEV ACHARYA^c, PAWAN KUMAR^c, DODDAPUNENI KRISHNA RAO^a,
VADAPALLI CHANDRASEKHAR^{a,c,*} and ANUKUL JANA^{a,*} 

^aTata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad, Telangana 500 107, India

^bDepartment of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, Karnataka 560 012, India

^cDepartment of Chemistry, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208 016, India
E-mail: vc@iitk.ac.in; ajana@tifrh.res.in

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Abstract. The reactions of *p*-diphenylphosphinobenzoic acid (LCOOH) with various organotin precursors have been carried out. Accordingly, the reaction of $[n\text{-BuSn}(\text{O})(\text{OH})_n]$ with LCOOH afforded the hexameric compound, $[n\text{-BuSn}(\text{O})\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-PPh}_2]_6$ (**1**). On the other hand, the reaction of LCOOH with $[n\text{-Bu}_2\text{SnO}]_n$ gave the tetrameric compound $[\{n\text{-Bu}_2\text{SnO}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-PPh}_2\}_2\text{O}]_2$ (**2**). The 1-D coordination polymers $[\text{R}_3\text{SnO}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-P}(\text{O})\text{Ph}_2]_n$, $[\text{R} = n\text{-Bu}$ (**3**), $\text{R} = \text{Ph}$ (**4**)] were prepared in the reaction of $[n\text{-Bu}_3\text{Sn}]_2\text{O}$ or $[\text{Ph}_3\text{Sn}]_2\text{O}$ with LCOOH. The compounds **1–4** were structurally characterized by multinuclear NMR spectroscopic and single crystal X-ray diffraction studies.

Keywords. Organostannoxane; multisite coordination ligand; organotin compounds; 1-D coordination polymer.

1. Introduction

The modular design of clusters, cages and coordination polymers remains an exciting goal for researchers owing to the novel structural and applicative aspects.^{1,2} Organotin carboxylates offer an opportunity to design functional molecules since a reasonable stoichiometric control exists in the product formation involving the reaction of an organotin oxide/oxide-hydroxide with carboxylic acids. A precise control of structure is thereby possible with the additional advantage that most of these compounds can be obtained in a simple one-pot reaction between the organotin precursors and carboxylic acids.^{3–9} Utilizing this strategy, various organostannoxanes were synthesised that possessed diverse functional groups ranging from being electroactive to photoactive.^{10,11} We have been interested to use this well-tested methodology to assemble coordination ligands supported on organostannoxane frameworks.¹²

In one such endeavour, we have shown that phosphine containing organostannoxanes could be successfully utilized to support palladium nanoparticles. Such hybrid systems were also shown to be catalytically active for various organic transformations.^{13–15} However, in these studies we were unable to structurally characterize the parent ligand. With this in mind and also to modulate the nuclearity and structural topology of such phosphine-containing organostannoxanes, we have carried out the reactions *p*-diphenylphosphinobenzoic acid (LCOOH) with various organotin precursors which resulted in the isolation of $[n\text{-BuSn}(\text{O})\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-PPh}_2]_6$ (**1**), $[\{n\text{-Bu}_2\text{SnO}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-PPh}_2\}_2\text{O}]_2$ (**2**) and $[\text{R}_3\text{SnO}_2\text{C}-\text{C}_6\text{H}_4\text{-}p\text{-P}(\text{O})\text{Ph}_2]_n$, $[\text{R} = n\text{-Bu}$ (**3**), $\text{R} = \text{Ph}$ (**4**)]. While **1** and **2** are molecular compounds possessing a drum (prismane) and a ladder structure respectively, **3** and **4** are coordination polymers. The synthesis and structural characterization of **1–4** are described, herein.

*For correspondence

2. Experimental

2.1 Materials and physical measurements

$[n\text{-BuSn(O)OH}]_n$, $(n\text{-Bu}_2\text{SnO})_n$, $(n\text{-Bu}_3\text{Sn})_2\text{O}$, $(\text{Ph}_3\text{Sn})_2\text{O}$ and 4-(diphenylphosphino)benzoic acid were purchased from Sigma Aldrich and were used as such without further purification. Solvents were stored over appropriate reagents and distilled under nitrogen prior to use. Melting points were measured using a JSGW apparatus and are uncorrected. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyser. ^1H , ^{13}P and ^{119}Sn NMR were recorded on a JEOL-JNM LAMBDA 400 model NMR spectrometer or on a Bruker-NanoBay 300 MHz NMR spectrometer. The chemical shifts are referenced with respect to tetramethylsilane (^1H), 85% H_3PO_4 (^{31}P) and tetramethyltin (^{119}Sn), respectively.

2.2 Synthetic procedures of compounds 1–4

Appropriate organotin precursors (1 equiv.) and *p*-(diphenylphosphino)benzoic acid (1 or 2 equiv.) were taken together in toluene (80 mL) and heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean–Stark apparatus. The reaction mixture was filtered and evaporated to afford a solid which was identified as the title products.

2.2a Compound 1: $[n\text{-BuSn(O)OH}]_n$ (0.30 g, 1.44 mmol) and *p*-(diphenylphosphino)benzoic acid (0.44 g, 1.44 mmol). Yield: 0.70 g (95.0%). M.p.: >290 °C dec. ^1H NMR (400.0 MHz, CDCl_3): 0.81 (t, 18H), 1.32 (m, 12H), 1.50 (m, 12H), 1.73 (m, 12H), 7.23 (m, 60H), 7.91 (m, 24H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.0 MHz, CDCl_3): –4.6 (s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (150.0 MHz, CDCl_3): –481.0 (s) ppm. Anal. Calcd. for $\text{C}_{152}\text{H}_{154}\text{O}_{18}\text{P}_6\text{Sn}_6$ (including two molecules of toluene): C, 57.65; H, 4.90%. Found: C, 57.41; H, 4.87%. Crystals suitable for X-ray diffraction study were obtained from the solution of **1** in toluene.

2.2b Compound 2: $[n\text{-Bu}_2\text{Sn(O)}]_n$ (0.10 g, 0.40 mmol) and *p*-(diphenylphosphino)benzoic acid (0.12 g, 0.40 mmol). Yield: 0.20 g (91.7%). ^1H NMR (300.1 MHz, C_6D_6): 0.81 (t, 24H), 1.32 (m, 16H), 1.50 (m, 16H), 1.73 (m, 16H), 7.23 (m, 40H), 7.91 (m, 16H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): –5.1 (s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.9 MHz, C_6D_6): –241.1 (s) and –253.2 (s) ppm. Anal. Calcd. for $\text{C}_{108}\text{H}_{128}\text{O}_{10}\text{P}_4\text{Sn}_4$: C, 59.3; H, 5.91%. Found: C, 57.7; H, 6.08%. Suitable crystals for single crystal X-ray diffraction were obtained from the solution of **2** in dichloromethane.

2.2c Compound 3: $(n\text{-Bu}_3\text{Sn})_2\text{O}$ (0.50 g, 0.84 mmol) and *p*-(diphenylphosphino)benzoic acid (0.51 g, 1.68 mmol). Yield: 1.00 g (92.6%). ^1H NMR (300.1 MHz, CDCl_3): 0.81 (t, 9H), 1.32 (m, 6H), 1.50 (m, 6H), 1.73 (m, 6H), 7.23 (m, 10H), 7.91 (m, 4H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): 28.7(s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.9 MHz, CDCl_3): 91.4(s) ppm. Anal. Calcd. for $\text{C}_{33}\text{H}_{47}\text{O}_3\text{PSn}$: C, 61.79; H,

7.39%. Found: C, 59.59; H, 6.83%. Crystals suitable for X-ray diffraction were obtained from the solution of **3** in chloroform.

2.2d Compound 4: $(\text{Ph}_3\text{Sn})_2\text{O}$ (0.50 g, 0.70 mmol) and *p*-(diphenylphosphino)benzoic acid (0.42 g, 1.4 mmol). Yield: 0.90 g (91.6%). M.p.: ^1H NMR (400.0 MHz, CDCl_3): 7.22–7.96 (m, 29H) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.0 MHz, CDCl_3): 29.9(s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (150.0 MHz, CDCl_3): –117.1(s) ppm. Anal. Calcd. for $\text{C}_{61}\text{H}_{50}\text{O}_3\text{PSn}_2$: C, 66.64; H, 4.58%. Found: C, 66.53; H, 4.55%. Crystals suitable for X-ray diffraction were obtained from the mother liquor of **4** in benzene.

2.3 X-ray crystallography

Single crystal X-ray data of **1**, **3** and **4** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography.¹⁶ Data integration and reduction were processed with SAINT software.¹⁷ An empirical absorption correction was applied to the collected reflections with SADABS¹⁸ using XPREP. Diffraction data of **2** was collected at low temperature (120 K) using Rigaku diffractometer with Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$. Data integration and reduction were processed with CrysAlisPro software.¹⁹ An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro. The structure was solved by intrinsic phasing method using SHELXT²⁰ program and refined by full matrix least-squares method based on F^2 by using SHELXL²¹ program through Olex2 interface.²² One of the disordered butyl group in compound **1** was treated with PART instruction and refined.²³ All the crystallographic figures were been created by using Diamond 3.2k software.²⁴ The crystal and refinement parameters for **1–4** were given in Table 1.

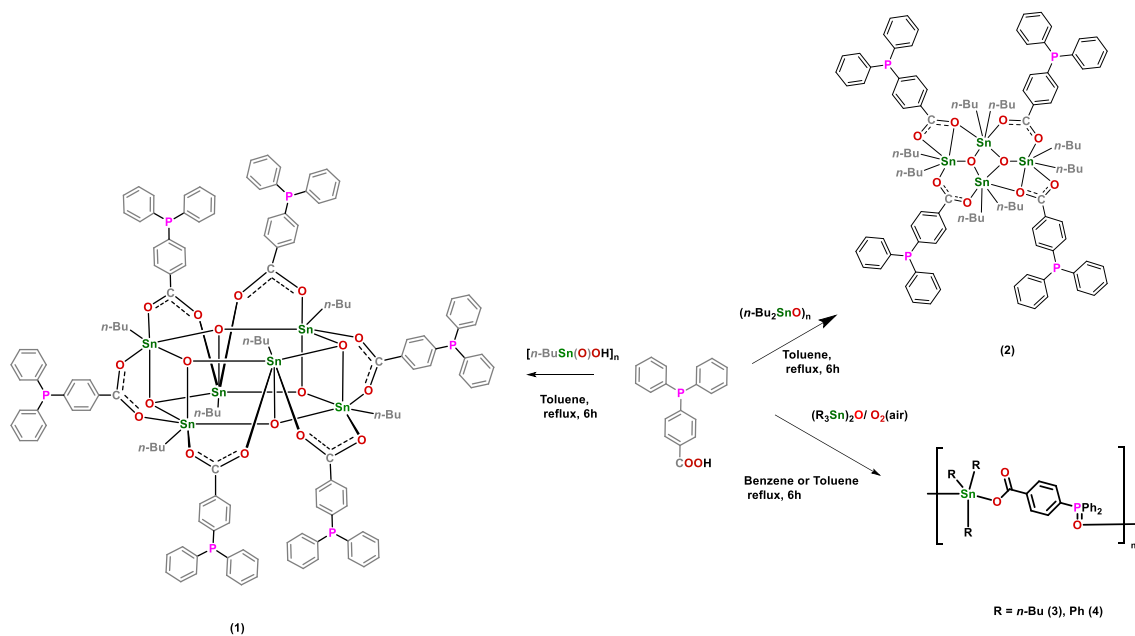
3. Results and Discussion

3.1 Synthesis and characterization

The reaction of the organotin oxide-hydroxide *n*-BuSn(O)OH with any carboxylic acid, RCOOH, in a 6:6 ratio is known to afford the hexameric drum-like cage $[n\text{-BuSn(O)O}_2\text{CR}]_6$.^{3,4} The core of this cage is made up of a Sn_6O_6 framework which is supported by bidentate carboxylate ligands. Similarly, the reaction of $[n\text{-Bu}_2\text{Sn(O)}]_n$ with any simple mono carboxylic acid, in a 4:4 ratio tends to form a tetraorganotin ladder compound $[[n\text{-Bu}_2\text{SnO}_2\text{CR}]_2\text{O}]_2$. We were interested to utilize this modular approach for preparing the designer multi-site coordinating ligands. Accordingly, the reaction of RCOOH (R = *p*-PPh₂–C₆H₄) with $[n\text{-BuSn(O)OH}]_n$ / $[n\text{-Bu}_2\text{Sn(O)}]_n$

Table 1. Crystal and refinement data for compounds 1–4.

Identification code	1	2	3	4
Empirical formula	C ₁₈₀ H _{188.4} O ₁₈ P ₆ Sn ₆	C ₁₁₀ H _{129.3} Cl ₂ O ₁₀ P ₄ Sn ₄	C ₃₁ H ₃₅ O ₃ PSn	C ₄₀ H ₃₂ O ₃ PSn
Formula weight	3537.66	2280.97	605.25	710.31
Temperature/K	100.15	120.01(2)	100.15	100.15
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> ₂ /n	<i>P</i> ₂ /n
<i>a</i> /Å	15.107(3)	15.4459(4)	8.4888(6)	9.7963(10)
<i>b</i> /Å	15.848(3)	16.2557(4)	18.6449(11)	17.8148(18)
<i>c</i> /Å	18.143(3)	22.4373(5)	19.1859(12)	18.998(2)
α /°	73.128(3)	70.155(2)	90	90
β /°	81.315(3)	87.784(2)	102.518(3)	95.181(2)
γ /°	83.206(3)	87.939(2)	90	90
Volume/Å ³	4096.4(12)	5293.6(2)	2964.4(3)	3302.0(6)
Z	1	2	4	4
ρ_{calc} g/cm ³	1.434	1.431	1.356	1.429
μ /mm ⁻¹	1.023	1.100	0.944	0.860
<i>F</i> (000)	1802.0	2327.0	1240.0	1444.0
Crystal size/mm ³	0.2 × 0.12 × 0.1	0.33 × 0.22 × 0.17	0.21 × 0.18 × 0.15	0.34 × 0.25 × 0.17
2 θ range for data collection/°	8.212 to 49.99	5.28 to 52.998	4.868 to 51.992	4.306 to 56.76
Index ranges	-17 ≤ <i>h</i> ≤ 17, -18 ≤ <i>k</i> ≤ 16, -21 ≤ <i>l</i> ≤ 21	-19 ≤ <i>h</i> ≤ 19, -20 ≤ <i>k</i> ≤ 20, -28 ≤ <i>l</i> ≤ 28	-10 ≤ <i>h</i> ≤ 8, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23	-12 ≤ <i>h</i> ≤ 9, -20 ≤ <i>k</i> ≤ 23, -23 ≤ <i>l</i> ≤ 25
Reflections collected	20910	76679	41203	21124
Independent reflections	14076 [<i>R</i> _{int} = 0.0440, <i>R</i> _{sigma} = 0.0965]	21909 [<i>R</i> _{int} = 0.0387, <i>R</i> _{sigma} = 0.0415]	5822 [<i>R</i> _{int} = 0.0708, <i>R</i> _{sigma} = 0.0396]	8016 [<i>R</i> _{int} = 0.0478, <i>R</i> _{sigma} = 0.0571]
Data/restraints/parameters	14076/36/988	21909/2/1198	5822/0/328	8016/48/299
Goodness-of-fit on <i>F</i> ²	1.003	1.103	1.048	1.072
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0554, <i>wR</i> ₂ = 0.1185	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.0987	<i>R</i> ₁ = 0.0327, <i>wR</i> ₂ = 0.0712	<i>R</i> ₁ = 0.0727, <i>wR</i> ₂ = 0.1523
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0853, <i>wR</i> ₂ = 0.1367	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.1076	<i>R</i> ₁ = 0.0427, <i>wR</i> ₂ = 0.0780	<i>R</i> ₁ = 0.1028, <i>wR</i> ₂ = 0.1888
Largest diff. peak/hole / e Å ⁻³	1.50/-0.84	1.37/-1.18	1.03/-0.63	1.39/-2.27



Scheme 1. Synthesis of organostannoxane compounds **1–4**.

in a 1:1 stoichiometry was carried out. In accordance with our expectation the hexameric and tetrameric cages $[n\text{-BuSn}(\text{O})_2\text{C}-\text{C}_6\text{H}_4-p\text{-PPh}_2]_6$ (**1**) and $[(n\text{-Bu}_2\text{SnO}_2\text{C}-\text{C}_6\text{H}_4-p\text{-PPh}_2)_2\text{O}]_2$ (**2**) were obtained in nearly quantitative yields (Scheme 1). Presence of a characteristic single peak at -481.0 ppm in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra for compound **1** and two signals at -241.1 and -251.2 ppm for compound **2**, respectively, confirmed their formation.^{3,4,10–15} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** and **2** showed singlets at -4.6 ppm and -5.0 ppm (in C_6D_6), respectively. These chemical shifts are comparable to the parent ligand, 4-diphenylphosphino benzoic acid (-4.2 ppm) indicating that the phosphine units in the organostannoxane drum are present in a similar chemical environment as in the parent ligand.^{13–15}

When we attempted the 1:2 reactions of $(n\text{-Bu}_3\text{Sn})_2\text{O}/(\text{Ph}_3\text{Sn})_2\text{O}$ with 4-diphenylphosphino benzoic acid instead of the monomeric products, we obtained the 1D-coordination polymers, $[\text{R}_3\text{SnO}_2\text{C}-\text{C}_6\text{H}_4-p\text{-P}(\text{O})\text{Ph}_2]_n$, $[\text{R} = n\text{-Bu}$ (**3**), $\text{R} = \text{Ph}$ (**4**)]. During the course of the reaction the $-\text{PPh}_2$ group of the 4-diphenylphosphino benzoic acid has been found to be oxidized to the $-\text{P}(\text{O})\text{Ph}_2$ group. The $\text{P}=\text{O}$ unit of the latter assists in the coordination polymer formation. This is evidenced by the $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR shift values of $29.0(\text{s})$, $-117.1(\text{s})$, respectively, for $\text{P}=\text{O}$ moiety and five coordinate tin atom.

3.2 X-ray crystallographic structural analysis

The molecular structure of compound **1** is shown in Figure 1(a) revealing a dendrimer-type architecture

containing a central stannoxane core from which emerge six radial arms containing the PPh_2 groups. (Figure 1(b)). The Sn_6O_6 core of the stannoxane cage is comprised of two puckered Sn_3O_3 rings that are fused with each other. This results in the formation of six Sn_2O_2 four-membered rings which are present in the side of the organostannoxane core (Figure 1(b)). Since the carboxylate ligands are involved in a bridging (isobidentate and anisobidentate) coordination mode with alternate tin atoms of the stannoxane core, the phosphine units are automatically organized in the periphery of the stannoxane core. Each tin atom in **1** is six-coordinate (5O, 1C) in a distorted octahedral geometry (Figure 1(c)). The average Sn–O bond distance is $2.115(2)$ Å. The average O–Sn–O bond angles involving the four-membered distannoxane ring is $\sim 78.0^\circ$ while the corresponding angle in the six-membered Sn_3O_3 ring is $\sim 104.8^\circ$. Selected bond parameters of **1** are given in Table 2.

The molecular structure of **2** resembles the typical *tetraorganotin ladder* structural form. Here, a central $(n\text{-Bu}_2\text{Sn})_2-\mu(\text{O})_2$ unit is flanked on either side by two $(n\text{-Bu}_2\text{SnO}_2\text{C}-\text{C}_6\text{H}_4-p\text{-PPh}_2)$ moieties to form a ladder-type architecture *via* the bridging carboxylate group of the $\text{O}_2\text{C}-\text{C}_6\text{H}_4-p\text{-PPh}_2$ unit (iso bidentate and anisobidentate modes). Each tin atom in **2** is six-coordinated (4O, 2C) in a distorted octahedral geometry (Figure 2(c)). The average Sn–O bond distance for $\text{Sn1A}-\text{O}$ bonds is $2.144(3)$ Å and $2.180(3)$ Å for $\text{Sn2A}-\text{O}$ bonds. The average $\text{Sn1}-\text{O1}-\text{Sn1}^*$, $\text{Sn1}-\text{O1}-\text{Sn2}$ and $\text{O1}-\text{Sn1}-\text{O1}^*$ bond angles are $102.8(1)^\circ$, $120.4(1)^\circ$ and $77.1(4)^\circ$ respectively (Table 3).

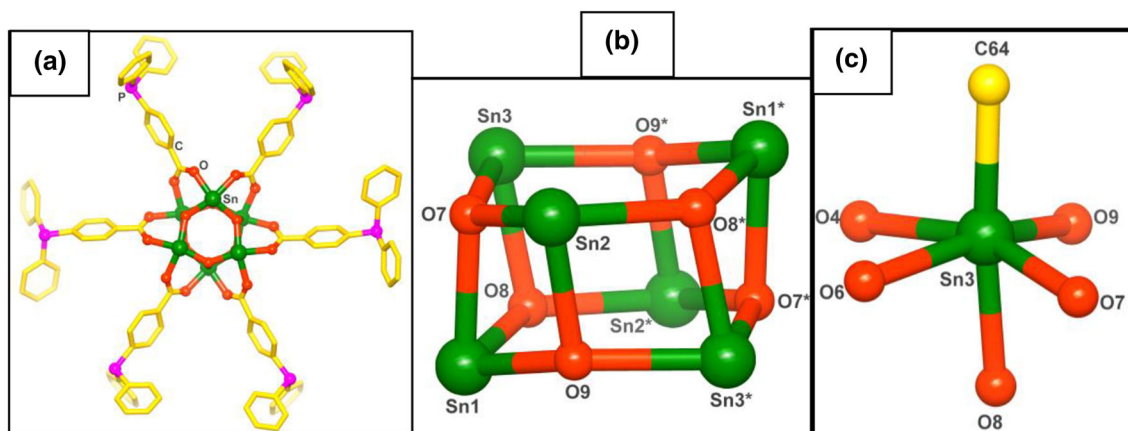


Figure 1. (a) Molecular structure of the organostannoxane drum **1**. (b) A view of Sn₆O₆ core of **1**. (c) Coordination environment around a tin atom (Sn3) and selected bond parameters.

Table 2. Selected bond parameters for compound **1**.

Bond Lengths (Å)	Bond Angles (°)
Sn1–O1 2.157(3); Sn1–O7 2.094(3)	O7–Sn1–C1 176.3(2); O9–Sn1–O8 ^{#1} 105.06(1)
Sn1–O9 2.086(3); Sn2–O2 2.165(3)	O9–Sn2–C24A 177.4(3); O7–Sn2–O8 103.8(1)
Sn2–O3 2.175(3); Sn2–O7 2.072(3)	O8–Sn3–C64 174.5(2); O9–Sn3–O7 ^{#1} 105.4(1)
Sn3–O4 2.162(3); Sn3–O6 2.145(3)	Sn1–O9–Sn3 130.5(2); Sn2–O8–Sn1 ^{#1} 132.6(2)
Sn3–O8 2.096(3); Sn1–O5 ^{#1} 2.143(3)	Sn2–O7–Sn3 ^{#1} 132.5(2); C18–P1–C9 102.1(3)
Sn1–O8 ^{#1} 2.086(3); Sn3–O7 ^{#1} 2.083(3)	C32–P2–C41 102.0(2); C52–P3–C58 104.6(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$.

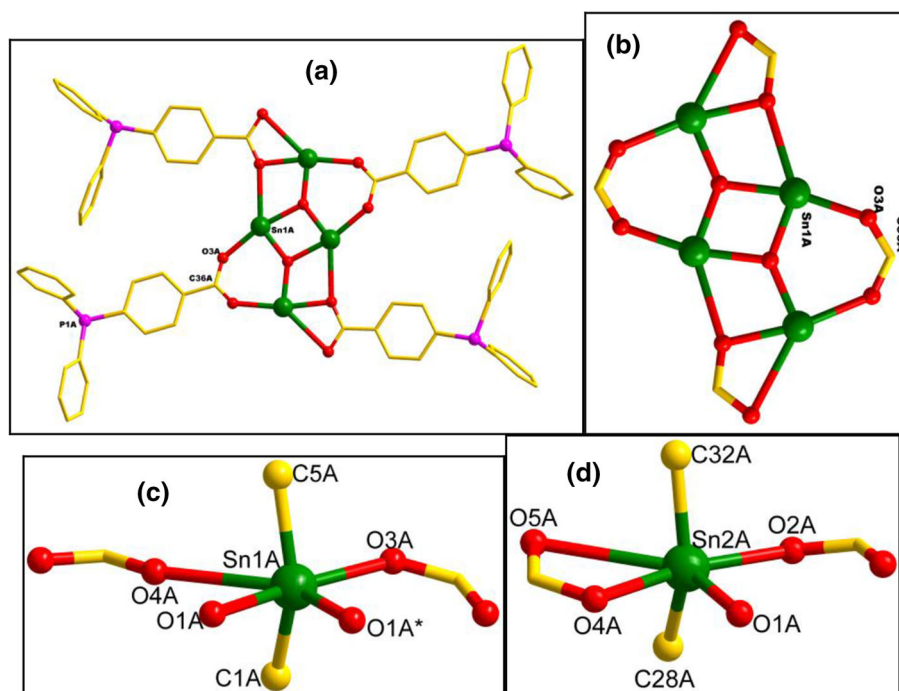


Figure 2. (a) Molecular structure of the organostannoxane ladder **2**. (b) A view of Sn₄O₄ core of **2**. (c) Coordination environment around a tin atoms (Sn1A and Sn2A) and selected bond parameters.

Table 3. Selected bond parameters for compound **2**.

Bond Lengths (Å)	Bond Angles (°)
Sn(1A)–O(1A) 2.033(3)	O(1A)–Sn(1A)–O(1A) ^{#1} 77.14(11)
Sn(1A)–O(1A) ^{#1} 2.170(3)	O(1A) ^{#1} –Sn(1A)–O(3A) 167.76(11)
Sn(1A)–O(3A) 2.230(3)	O(1A)–Sn(1A)–O(3A) 90.90(11)
Sn(1A)–C(5A) 2.123(4)	O(1A)–Sn(1A)–C(5A) 108.17(14)
Sn(1A)–C(1A) 2.126(4)	O(1A)–Sn(1A)–C(1A) 108.06(14)
Sn(2A)–O(1A) 2.038(3)	C(5A)–Sn(1A)–O(1A) ^{#1} 94.46(14)
Sn(2A)–O(4A) 2.186(3)	C(5A)–Sn(1A)–O(3A) 86.71(15)
Sn(2A)–O(2A) 2.264(3)	C(5A)–Sn(1A)–C(1A) 143.64(17)
Sn(2A)–O(5A) 2.233(3)	C(1A)–Sn(1A)–O(1A) ^{#1} 96.30(15)
Sn(2A)–C(28A) 2.134(4)	C(1A)–Sn(1A)–O(3A) 89.84(16)
Sn(2A)–C(32A) 2.121(4)	O(1A)–Sn(2A)–O(4A) 79.55(10)
P(1A)–C(49A) 1.828(5)	O(1A)–Sn(2A)–O(2A) 90.28(10)
P(1A)–C(43A) 1.833(5)	O(1A)–Sn(2A)–C(28A) 110.40(14)
P(1A)–C(40A) 1.833(4)	O(1A)–Sn(2A)–C(32A) 107.88(15)
	O(4A)–Sn(2A)–O(2A) 169.36(10)
	C(28A)–Sn(2A)–O(4A) 97.01(14)
	C(28A)–Sn(2A)–O(2A) 83.53(14)
	C(32A)–Sn(2A)–O(4A) 94.83(14)
	C(32A)–Sn(2A)–O(2A) 91.24(14)
	C(32A)–Sn(2A)–C(28A) 141.35(18)

Symmetry transformations used to generate equivalent atoms: #1 –X,1–Y,1–Z.



Figure 3. (a) Molecular structure of the organostannoxane 1-D coordination polymer **3**. (b) Coordination environment around a tin atom (Sn1).

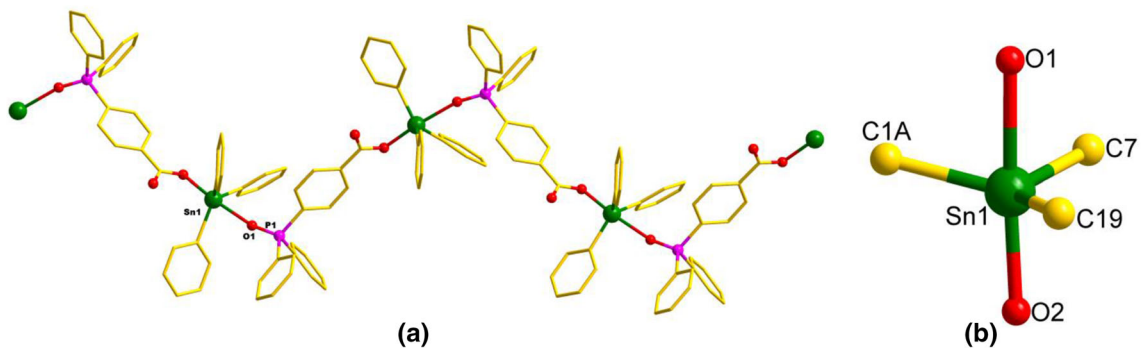


Figure 4. (a) Molecular structure of the organostannoxane 1-D coordination polymer **4**. Hydrogen atoms and disordered part of the phenyl rings are omitted for clarity. (b) Coordination environment around a tin atom (Sn1) in **4**.

Table 4. Selected bond parameters for compound **3**.

Bond Lengths (Å)	Bond Angles (°)
Sn(1)–O(1) 2.1894(18)	O(1)–Sn(1)–O(3) 175.31(6)
Sn(1)–O(3) 2.4295(18)	C(9)–Sn(1)–O(1) 98.60(9)
Sn(1)–C(9) 2.138(3)	C(9)–Sn(1)–O(3) 86.00(8)
Sn(1)–C(5) 2.141(3)	C(9)–Sn(1)–C(5) 117.44(11)
Sn(1)–C(1) 2.136(3)	C(5)–Sn(1)–O(1) 87.91(9)
P(1)–O(3) 1.4973(18)	C(5)–Sn(1)–O(3) 89.14(9)
P(1)–C(20) 1.801(3)	C(1)–Sn(1)–O(1) 93.99(9)
P(1)–C(26) 1.803(3)	C(1)–Sn(1)–O(3) 84.08(9)
P(1)–C(13) 1.805(3)	C(1)–Sn(1)–C(9) 124.63(11)
	C(1)–Sn(1)–C(5) 116.71(11)

Table 5. Selected bond parameters for compound **4**.

Bond Lengths (Å)	Bond Angles (°)
Sn(1)–C(19) 2.1243(16)	C(19)–Sn(1)–O(2) 89.18(12)
Sn(1)–O(2) 2.126(4)	C(19)–Sn(1)–C(7) 115.00(8)
Sn(1)–C(7) 2.1302(17)	O(2)–Sn(1)–C(7) 99.35(13)
Sn(1)–C(1A) 2.2336(18)	C(19)–Sn(1)–C(1A) 119.05(7)
Sn(1)–O(1) 2.413(5)	O(2)–Sn(1)–C(1A) 106.46(14)
P(1)–O(1) 1.451(5)	C(7)–Sn(1)–C(1A) 119.46(7)
P(1)–C(21) 1.804(2)	C(19)–Sn(1)–O(1) 82.63(12)
P(1)–C(33) 1.806(2)	O(2)–Sn(1)–O(1) 171.80(17)
P(1)–C(27) 1.809(2)	C(7)–Sn(1)–O(1) 84.50(13)
	C(1A)–Sn(1)–O(1) 77.49(13)

The molecular structures of compounds **3** and **4** are shown in Figures 3 and 4, respectively. In these compounds the R₃Sn [R = *n*-Bu (**3**), Ph(**4**)] unit is coordinated by the oxygen atoms arising from the carboxylate and the P=O moiety in opposite directions resulting a 1-D coordination polymer. In these compounds the tin atoms are pentacoordinated (3C, 2O) in a trigonal bipyramidal geometry. In compound **3**, the Sn–O bonds of 2.189(4) Å and 2.429(5) Å are correspond to the Sn–O–C(=O) and Sn–O=P types respectively (Table 4). The average Sn–C bond distance is 2.138(3) Å. In compound **4**, the Sn–O bonds of 2.126(4) Å and 2.413(5) Å belong to the Sn–O–C(=O) and Sn–O=P types respectively. The average Sn–C bond distance is 2.162(5) Å (Table 5).

4. Conclusions

We have utilized the *organostannoxane* synthesis approach to prepare functional compounds containing multi-site coordinating periphery. Thus, compounds containing six and four –PPh₂ units have been readily prepared. In an effort to prepare analogous compounds containing triorgano groups, we observed an unexpected oxidation of the PPh₂ groups to P(O)Ph₂ groups.

The resulting coordination action of the phosphine oxide along with the carboxylate unit affords a one-dimensional coordination polymer.

Supplementary Information (SI)

CCDC 1830820–1830824 containing crystal data of the compounds (**1–4**) can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK, (Fax: +44- (0)1223-336033 or Email: deposit@ccdc.cam.ac.uk); website: www.ccdc.cam.ac.uk/data_request/cif.

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