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Synthesis of monoorganotin(IV) chloride complexes of cis-1,2-bis(diphenylphosphino)ethylene: Solution and solid state structures

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Abstract

Organotin(IV) complexes of the type $[RSnCl_3(cis-Ph_2PCH=CHPPh_2)]$ [R = Me (**1**), ^{n}Bu (**2**), Ph (**3**)] were prepared by the reaction of $RSnCl_3$ with the rigid bisphosphine ligand, cis-1,2-bis(diphenylphosphino)ethylene in dichloromethane. The complexes have been characterized both in solution and the solid state. Low temperature ^{31}P and ^{119}Sn NMR studies indicate two different phosphorus environments. The crystal structures indicate a weak but chelating mode of coordination of the two phosphorus atoms to tin, leading to a distorted octahedral geometry. In solution the complexes **1**–**3** undergo a redistribution reaction to form $[SnCl_4(cis-Ph_2PCH=CHPPh_2)]$ (**4**) as one of the products. In order to confirm the redistribution, complex **4** has been prepared separately and characterized both structurally and spectrally.
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1. Introduction

The utility of organotin halides to study the fundamentally important Lewis acid–base model and reactivity of organotin species had been the subject of several investigations [1–3]. In contrast to the availability of the large amount of structural data with O-, N- and S-donor ligands [4], the structurally characterized organotin complexes containing direct Sn–P bonds are still rare [5–7]. Several NMR (^{31}P and ^{119}Sn) investigations of the complexes of organotin acceptors, R_nSnCl_{4-n} (n = 1, 2) and mono- and bis-phosphines have been carried out suggesting coordination of phosphorus to tin [3,8–11]. On the other hand structural characterizations have revealed the presence of a Sn–O–P link, generated by the aerial oxidation of the bisphosphine

when 1,2-bis(diphenylphosphino)ethane (dppe) was allowed to react with R_2SnCl_2 (R = Me, ^{n}Bu, Ph [12] and Bz [13]). In the case of highly Lewis acidic $RSnCl_3$ (R = Me, ^{n}Bu and Ph), despite the satisfactory spectroscopic evidence for the formation of Sn–P bond, no product could be characterized structurally from the reaction with bis(diphenlyphosphino)methane (dppm) or dppe [12]. Although the importance of organotin halide–phosphine complexes has been realized in the catalysis of ring opening of α,β-epoxyketones [14], the lack of structural understanding is perhaps responsible for not using organotin–phosphine complexes as potential catalysts. The difference in reactivity between cis-1,2-bis(diphenylphosphino)ethylene (cis-dppen) and its saturated analogue, dppe with various transition metals has been observed in a number of studies [15–18]. The purpose of the present study is to investigate the interaction of the rigid bisphosphine cis-dppen with monoorganotin chlorides. Herein

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we report the synthesis, solution and solid state structures of a series of monoorganotin chloride, $RSnCl_3$ (R = Me, ^nBu, Ph) complexes containing *cis*-dppen.

2. Experimental

All solvents were dried and distilled prior to use using standard methods [19]. Reactants and reagents were obtained from Aldrich Chemical Company and used without further purification. The IR spectra in the interval of 4000–400 cm^{-1} were recorded on a Perkin–Elmer 1720X FT-IR spectrometer. The ^1H, $^{31}P-\{^1H\}$ and $^{119}Sn-\{^1H\}$ NMR spectra were recorded on Bruker DPX 400 MHz or DRX 500 MHz instrument referenced relative to residual solvent, 85% H_3PO_4 and $Sn(CH_3)_4$, respectively. Mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II instrument using the solution of the complexes in a mixture of methanol and dichloromethane. Elemental analyses were performed at the Ecole d'ingénieurs de Fribourg, Switzerland.

2.1. Synthesis

2.1.1. [MeSnCl₃(cis-Ph₂PCH=CHPPh₂)] (1)

Methyltin trichloride (0.121 g, 0.5 mmol) in dichloromethane (5 ml) was added dropwise to a solution (5 ml) of *cis*-dppen (0.20 g, 0.5 mmol) also in dichloromethane. The resulting clear colourless solution was stirred for 3 h and the solvent reduced to 5 ml. Upon addition of *n*-pentane (15 ml) a white crystalline solid precipitated. It was filtered and recrystallized by vapour diffusion of *n*-pentane into a dichloromethane solution, to obtain single crystals. Yield 0.25 g, 79%. Mp: 147–148 °C. Anal. Calc. for $C_{27}H_{25}Cl_3P_2Sn$: C, 50.95; H, 3.96. Found: C, 50.64; H, 3.92%. IR (cm^{-1}): 3035, 2992, 1483, 1436, 1190, 1147, 1096, 1025, 998, 758, 753, 742, 721, 696, 686, 548, 531, 510, 474, 465. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.57 (t, 3H, Sn–CH₃), [$^2J(^{119}Sn-^1H)$: 114.6], [$^2J(^{117}Sn-^1H)$: 109.8]; 7.42–7.53, 7.62–7.70 (m, 22H, P–CH=CH and P–C₆H₅). ^{31}P NMR (162 MHz, CD_2Cl_2): δ –25.92 (br), –26.58 (s). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 601 [M – Cl]$^+$ (4), 917 [M*]$^+$ (22), 883 [M* – Cl]$^+$ (100) where M* = [$(SnCl_4)_2$(*cis*-dppen)].

2.1.2. [ⁿBuSnCl₃(cis-Ph₂PCH=CHPPh₂)] (2)

Compound **2** was obtained as for **1** by using *n*-butyltin trichloride (0.142 g, 0.5 mmol) and *cis*-dppen (0.2 g, 0.5 mmol). Single crystals were obtained by vapour diffusion of *n*-pentane into a dichloromethane solution. Yield 0.27 g, 78%. Mp: 159–160 °C. Anal. Calc. for $C_{30}H_{31}Cl_3P_2Sn$: C, 53.10; H, 4.60. Found: C, 52.95; H, 4.61%. IR (cm^{-1}): 3056, 2951, 2924, 2867, 1482, 1435, 1156, 1142, 1123, 1095, 1072, 1026, 997, 751, 743, 725, 714, 690, 550, 518, 478. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.89 (t, 3H, CH₃–, *J* = 7.2); 1.39 (sex, 2H, –CH₂–, *J* = 7.5), 1.78 (qt, 2H, –CH₂–, *J* = 7.5), 2.19 (br, 2H, –CH₂–Sn); 7.38–7.48, 7.53–7.71 (m, 22H, P–CH=CH and

P–C₆H₅). ^{31}P NMR (162 MHz, CD_2Cl_2): δ –24.64 (br), –26.60 (s). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 643 [M – Cl]$^+$(14), 917 [M*]$^+$ (1), 883 [M* – Cl]$^+$(100) where M* = [$(SnCl_4)_2$(*cis*-dppen)].

2.1.3. [PhSnCl₃(cis-Ph₂PCH=CHPPh₂)] (3)

Compound **3** was obtained by following the same procedure as **1** by using phenyltin trichloride (0.152 g, 0.5 mmol) and *cis*-dppen (0.2 g, 0.5 mmol) to yield a colourless precipitate. Single crystals were obtained when a chloroform solution of the compound was kept at –5 °C for several days. Yield 0.25 g, 71%. Mp 160–162 °C. Anal. Calc. for $C_{32}H_{27}Cl_3P_2Sn$: C, 55.02; H, 3.90. Found: C, 54.94; H, 3.86%. IR (cm^{-1}): 3050, 2983, 1572, 1477, 1482, 1435, 1188, 1159, 1097, 997, 746, 735, 689, 550, 517, 480, 440. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.49, 7.54–7.65, 7.79–7.87 (m, 27H, P–CH=CH, P–C₆H₅ and Sn–C₆H₅). ^{31}P NMR (162 MHz, $CDCl_3$): δ –26.71 (br), –26.96 (s, [$^1J(^{119}Sn-^{31}P)$: 677.0], [$^1J(^{117}Sn-^{31}P)$: 646.2]). Mass spectrum (ESI) {*m/z* [assignment] (%)}: 663 [M – Cl]$^+$ (1), 883 [M* – Cl]$^+$ (100) where M* = [$(SnCl_4)_2$(*cis*-dppen)].

2.1.4. [SnCl₄(cis-Ph₂PCH=CHPPh₂)] (4)

To a solution of *cis*-dppen (0.2 g, 0.5 mmol) in dichloromethane (10 ml), a solution of $SnCl_4$ (0.06 ml, 0.5 mmol) in dichloromethane (10 ml) was added. The resulting clear solution was stirred for 8 h whereupon the solution became slightly turbid. The solvent was reduced to 10 ml and addition of *n*-pentane (20 ml) caused the precipitation of the product as a yellowish white solid. It was filtered and recrystallized by vapour diffusion of *n*-pentane into a dichloromethane solution to obtain single crystals. Yield 0.26 g (79%). Mp: 179–180 °C. Anal. Calc. for $C_{26}H_{22}Cl_4P_2Sn$: C, 47.54; H, 3.38. Found. C, 47.76; H, 3.40%. IR (cm^{-1}): 3056, 3001, 1482, 1435, 1263, 1189, 1162, 1098, 1025, 997, 749, 727, 688, 552, 518, 499, 478, 462. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.51–7.55, 7.60–7.64, 7.79–7.85 (m, 20H, P–C₆H₅), 7.96 (dd, 2H, P–CH=CH, $^3J(^{31}P-^1H)$ = 14.0, [$^3J(^{119}Sn-^1H)$: 45.2], [$^3J(^{117}Sn-^1H)$: 43.2]). ^{31}P NMR (162 MHz, CD_2Cl_2): δ –26.60 (s), [$^1J(^{119}Sn-^{31}P)$: 717.4], [$^1J(^{117}Sn-^{31}P)$: 685.9]. ^{119}Sn NMR (186 MHz, CD_2Cl_2) : δ –628 (t). Mass spectrum (APCI) {*m/z* [assignment] (%)}: 655 [M]$^+$(30), 586 [M – 2Cl]$^+$ (100).

2.2. X-ray crystallography

The intensity data were collected at 173 K (–100 °C) on a Stoe Mark I-Image Plate Diffraction System (complex **2**) and a Stoe Mark II-Image Plate Diffraction System [20] (complexes **1**, **3** and **4**) using Mo Kα graphite monochromated radiation. The structures were solved by direct methods using the program SHELXS-97 [21]. The refinement and all further calculations were carried out using SHELXL-97 [22]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using
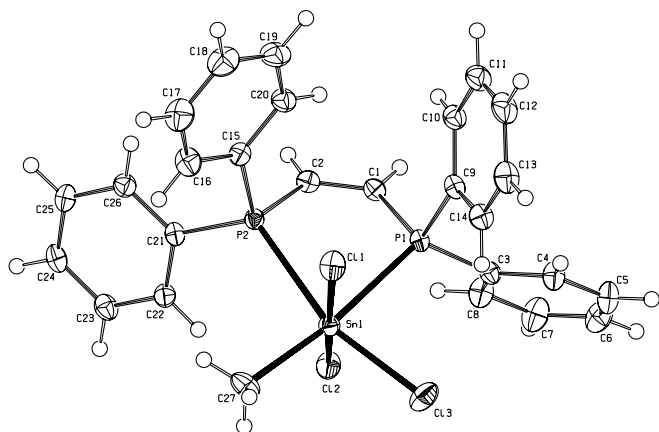
Fig. 1. Molecular structure of **1** with atom numbering scheme at 50% probability ellipsoids.
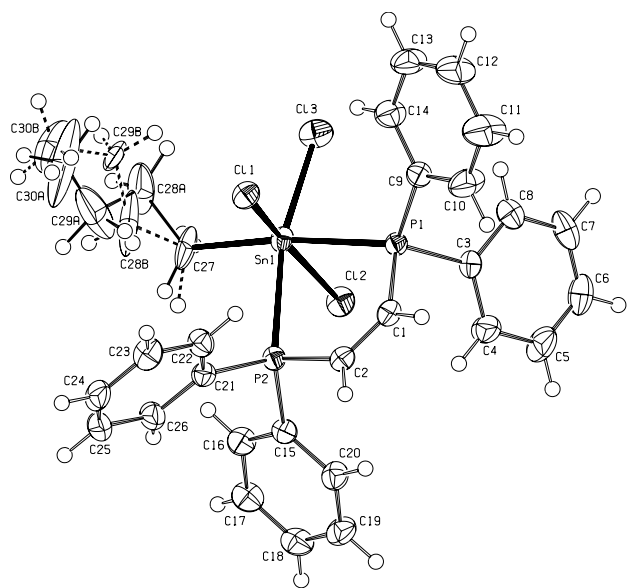

Fig. 2. Molecular structure of **2** with atom numbering scheme. The disordered ^{n}Bu group is shown with dashed bonds.
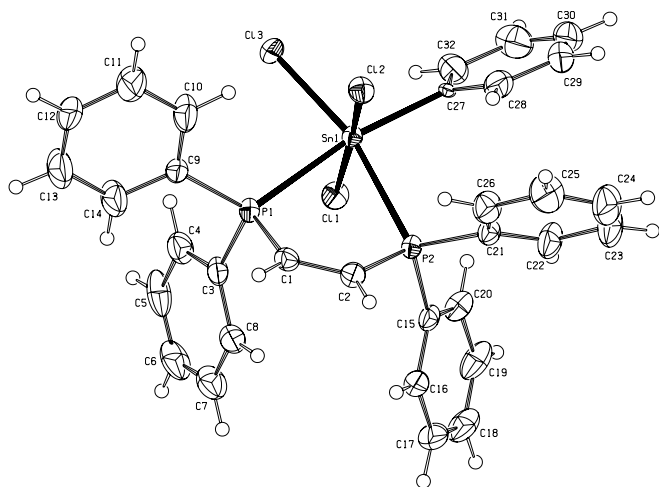

Fig. 3. Molecular structure of **3** with atom numbering scheme. The two CHCl₃ solvent molecules have been omitted for clarity.
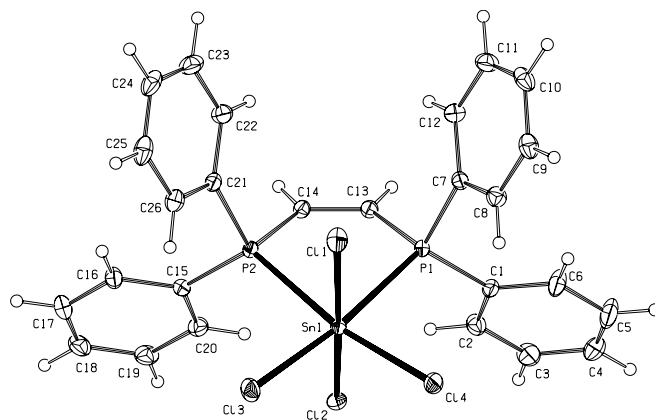

Fig. 4. Molecular structure of **4** with atom numbering scheme. The CH₂Cl₂ solvent molecule has been omitted for clarity.

weighted full-matrix least-squares on F^2. The *n*-butyl chain in **2** was found to be disordered over two positions A & B (occupancies 0.526 / 0.474). Semi-empirical absorption corrections were applied using the MULscanABS routine in PLATON [23]; transmission factors for **1** ($T_{min}/T_{max} = 0.563/0.779$), **2** ($T_{min}/T_{max} = 0.769/0.804$), **3** ($T_{min}/T_{max} = 0.683/0.763$) and **4** ($T_{min}/T_{max} = 0.517/0.902$). Further crystallographic data are given in Table 2. The molecular structure and crystallographic numbering schemes are illustrated in the PLATON drawings (Figs. 1–4).

3. Results and discussion

3.1. Synthesis

The reaction of *cis*-dppen with RSnCl₃ (R = Me, ^{n}Bu or Ph) in dichloromethane yielded colourless derivatives, **1–3,** in good yields. Rigorous exclusion of oxygen was not necessary as sufficiently pure products were obtained even in aerobic conditions. The products in the solid state are highly stable to air and moisture and oxidizes slowly in solution. They are moderately soluble in chlorinated solvents, acetone and DMSO but insoluble in diethyl ether, aliphatic hydrocarbons and water. It is to be noted that the crystallizations of the complexes were facile in contrast to the dppm or dppe derivatives [12]. The stability of these complexes can be attributed to the chelate effect of the ligand as well as to the electronegative effects of the three chlorine atoms.

3.2. Spectroscopy

In the IR spectra the absence of any significantly strong band in the region around 1190–1150 cm^{-1} assignable to the v(P=O) [12], indicates that the ligand in the products remain unoxidised. The ^{1}H NMR spectrum of **1** shows a sharp singlet at 1.57 ppm for the methyl group bonded to tin with satellites due to coupling with nuclei ^{119}Sn [^2J(^{119}Sn–^{1}H): 114.6 Hz] and ^{117}Sn [^2J(^{117}Sn–^{1}H): 109.8 Hz]. The ^{1}H NMR spectrum of **2** exhibits a broad

resonance centered at 2.19 ppm for the CH_2 group attached to tin, while the other signals due to *n*-butyl group are sharp. The resonance due to the protons of the phenyl group attached to tin in **3** and the –CH=CH– protons in all the complexes are merged with the other aromatic protons of the ligand.

The ^{31}P NMR of all the complexes at 300 K in CD_2Cl_2 exhibit two resonances in the region of −24.64 to −26.96 ppm; the low intensity signal around −26 ppm appears sharp and the high intensity signal is broad. Upon lowering the temperatures to 200 K, the major resonance gives rise to a quartet with the corresponding tin satellites. The spectral parameters have been obtained by solving the spectra for an ABX spin system and are listed in Table 1. The ^{31}P NMR spectra represent the AB part while the ^{119}Sn NMR spectra form the X part. The ^{31}P NMR chemical shifts occur upfield to that of the free ligand (δ −21.95, CD_2Cl_2), the coupling constants *J* (Sn–P_A) and *J* (Sn–P_B) (see Table 1) agree well with values reported in the literature [6,11]. As observed previously [24], the reason for the rather surprising upfield coordination shift in the ^{31}P NMR spectra remains unclear. One can expect either four or six line pattern in the X part of the ABX spectra, depending upon the ratio of the coupling constant to the chemical shift [25]. The ^{119}Sn NMR spectra at lower temperatures exhibit six lines for **1** and **3** whereas **2** shows a four line pattern. The chemical shifts (Table 1) are in the range reported previously for six coordinate geometry around tin [26].

The hexacoordinate complexes of the type discussed above can have two configurations **I** and **II** (vide infra). Only configuration **I** can give rise to two different phosphorus environments leading to an ABX type spectrum. The low temperature (200 K) ^{31}P NMR spectra are consistent with form **I**. The absence of tin satellites for the major peak at ambient temperature ^{31}P NMR spectra shows that some kind of exchange is occurring at this temperature. Ligand dissociation has been widely observed in the adducts of

Table 1
Low temperature ^{31}P and ^{119}Sn NMR spectral data[a] (δ in ppm and *J* in Hz) (for A, B and X notations see figure below)

	δ_A (^{31}P)	δ_B (^{31}P)	δ_X (^{119}Sn)	J_{A-B}	J_{A-X}	J_{B-X}
1[b]	−24.09	−31.32	−462.5	307	2419	1283
2[b]	−23.07	−30.24	−456.3	292	2344	1530
3[c]	−25.02	−32.51	−510.1	306	2327	1156

[a] ABX system solved according to reference [25].
[b] In CD_2Cl_2, 202.45 MHz (^{31}P NMR), 186.40 MHz (^{119}Sn NMR) at 200 K.
[c] In $CDCl_3$, 202.45 MHz (^{31}P NMR), 186.40 MHz (^{119}Sn NMR) at 225 K.

tin(IV) halides or organotin(IV) halides with phosphine ligands [24,27] and found to be the major cause for room temperature line broadening in the ^{31}P NMR spectra. In order to confirm the ligand dissociation, the ^{31}P NMR spectra were measured at higher temperatures. At 308 K, the broad peak sharpened and moved to a position around −22 ppm (free ligand −21.95 ppm in CD_2Cl_2 at 300 K), indicating that the dissociation is complete at higher temperatures.


I   **II**
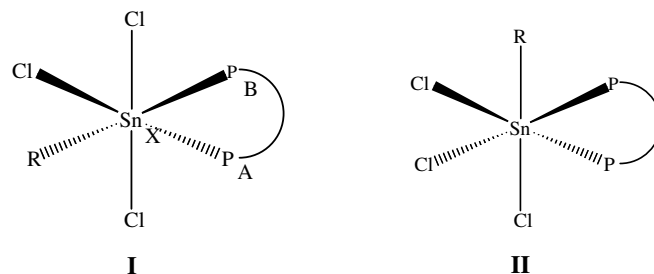
The minor signal in the ^{31}P NMR spectra is observed upfield (−26.6 ppm) to that of the free ligand. Tin satellites could be observed for this peak in the spectrum of **3**, while for **1** and **2** the signal intensity is too low to observe

Table 2
Crystal data and refinement details for **1**–**4**

Compound	**1**	**2**	**3** · 2CHCl$_3$	**4** · CH$_2$Cl$_2$
Empirical formula	$C_{27}H_{25}Cl_3P_2Sn$	$C_{30}H_{31}Cl_3P_2Sn$	$C_{32}H_{27}Cl_3P_2Sn$, 2(CHCl$_3$)	$C_{26}H_{22}Cl_4P_2Sn$, CH$_2$Cl$_2$
Formula weight	636.45	678.53	937.25	741.79
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Cc*	*P*2$_1$/*c*	*Pbca*	*P*2$_1$/*c*
a (Å)	17.6425(13)	11.1115(8)	15.6807(7)	13.0900(9)
b (Å)	9.5408(5)	13.0577(8)	21.9531(10)	11.0710(7)
c (Å)	15.9723(11)	20.5792(14)	22.7673(9)	21.2812(13)
β (°)	98.768(6)	101.109(9)	90	104.283(5)
V (Å^3)	2657.1(3)	2929.9(3)	7837.4(6)	2988.7(3)
Z	4	4	8	4
Absorption coefficient (mm^{-1})	1.399	1.274	1.372	1.515
Collected reflections	16 536	22 631	45 870	27 530
Independent reflections	6918	5679	6968	8070
$R_{(int)}$	0.0211	0.0388	0.0823	0.0416
R_1 (Observed data)	0.0166	0.0261	0.0550	0.0293
wR_2 (all data)	0.0456	0.0601	0.1153	0.0702

satellites. Change in temperature did not affect this signal as it remains sharp between 300 and 200 K. On the basis of J(P–Sn) coupling constants and the sharp feature, the signal has been attributed to the presence of [SnCl$_4$(*cis*-dppen)] due to a redistribution reaction in solution.

$$2RSnCl_3(cis\text{-dppen}) \rightarrow SnCl_4(cis\text{-dppen})$$
$$+ R_2SnCl_2(cis\text{-dppen})$$
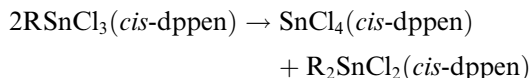
In order to support the above formulation [SnCl$_4$(*cis*-dppen)] was prepared separately and its ^{31}P NMR chemical shift recorded. A sharp signal at −26.6 ppm with tin satellites was observed. The same signals were observed in the solution of **1**–**3**. When the reaction mixture containing RSnCl$_3$ and *cis*-dppen was stirred for more than 24 h at room temperature a large amount of [SnCl$_4$(*cis*-dppen)] could be isolated, indicating the facile nature of the disproportionation. Mass spectra of complexes **1**–**3** which show, in addition to molecular peaks, a signal with 100% intensity at *m/z* 883 for [M*−Cl]$^+$, where M* = [(SnCl$_4$)$_2$(*cis*-dppen)] (mass = 917) indicate the formation of the species M* under ESI conditions. We have recently demonstrated through computational studies that the disproportionation reactions of organotin(IV) trihalides are energetically favourable [28]. Experimentally, the formation of [SnCl$_4$(Bu$_3$P)] has been observed previously for the reaction of PhSnCl$_3$ with Bu$_3$P [3,10]. Comparison of the spectroscopic data of the three complexes at 300 K shows that both redistribution and dissociation is faster for **3** than for **1** or **2**. Although we could not isolate [R$_2$SnCl$_2$(*cis*-dppen)] complexes, their presence are indicated as low intensity signals in ^{1}H, ^{31}P (∼−21.5 ppm at 300 K) and ^{119}Sn (∼−485 ppm at 200 K). The latter signals assignable to tin in an octahedral environment occur considerably upfield to the ^{119}Sn shifts, 6.0, −6.1 and −65 ppm reported previously for MeSnCl$_3$, ^{n}BuSnCl$_3$ and PhSnCl$_3$, respectively [29].

3.3. Crystal and molecular structures

The solid state structures of **1**–**3** were determined by single-crystal X-ray diffraction and are shown in Figs. 1–3. Selected bond distances and angles are listed in Table 2. The asymmetric units of **1** and **2** contain a molecule of the complex, while for **3** the asymmetric unit is composed of a molecule of the complex and two molecules of chloroform solvent. The molecular structures of the complexes are similar regardless of the nature of the organic group attached to tin. Therefore a general description for these compounds is given.

The geometry around the Sn atoms is distorted octahedral with the C atom of the tin bound organic group, one Cl atom and two P atoms of the chelating bisphosphine forming the equatorial plane, while the other two Cl atoms are axially disposed. The P(1)–Sn(1)–P(2) bite angle is the smallest amongst the *cis* angles, being equal to 75.46(1)°, 77.09(2)° and 74.80(4)° for **1**, **2** and **3,** respectively. In all

three complexes, the C=C distance is similar to the distance of 1.334(6) Å [30] observed in the free ligand. This precludes any π bonding interactions with tin. The Sn–C bond lengths in **1** and **2** [2.133(2) and 2.177(3) Å, respectively] are quite close to the values reported in the literature [31]. In complex **3**, however, the same distance [2.20(4) Å] is longer. As expected the rigid bisphosphine forms a chelate with the Sn *albeit* with a slight distortion. The Sn(1)–P(1) distances for complexes **1**–**3** [respectively, 2.667(1), 2.694(1) and 2.704(1) Å] are shorter than the Sn(1)–P(2) distances [respectively, 2.758(1), 2.753(1) and 2.723(1) Å]. The disparity in the Sn–P bond lengths with the ligand present in the chelating mode could be due to the *trans* influences of the ligands attached to Sn. The shorter Sn(1)–P(1) distance being the bond *trans* to the carbon

Table 3
Selected interatomic distances (Å) and angles (°) in **1**–**3**

	1	**2**	**3**
Interatomic distances			
Sn(1)–Cl(1)	2.4615(5)	2.4817(7)	2.4399(13)
Sn(1)–Cl(2)	2.5053(5)	2.4621(7)	2.4962(13)
Sn(1)–Cl(3)	2.4219(5)	2.4360(8)	2.4233(12)
Sn(1)–C(27)	2.133(2)	2.177(3)	2.202(4)
Sn(1)–P(1)	2.6686(5)	2.6945(7)	2.7036(13)
Sn(1)–P(2)	2.7578(5)	2.7526(7)	2.7231(13)
P(1)–C(1)	1.8081(18)	1.802(3)	1.806(5)
P(1)–C(3)	1.8128(19)	1.813(3)	1.805(6)
P(1)–C(9)	1.8028(19)	1.819(3)	1.814(5)
P(2)–C(2)	1.8054(18)	1.806(3)	1.796(5)
P(2)–C(15)	1.810(2)	1.810(3)	1.811(5)
P(2)–C(21)	1.8160(18)	1.820(3)	1.803(5)
C(1)–C(2)	1.338(2)	1.327(4)	1.337(7)
Bond angles			
C(27)–Sn(1)–Cl(3)	102.96(7)	99.08(11)	101.07(12)
C(27)–Sn(1)–Cl(1)	92.97(7)	98.63(8)	93.77(12)
Cl(3)–Sn(1)–Cl(1)	93.833(19)	95.78(2)	90.90(5)
C(27)–Sn(1)–Cl(2)	94.39(8)	94.55(8)	93.06(12)
Cl(3)–Sn(1)–Cl(2)	91.713(19)	92.65(3)	91.74(5)
Cl(1)–Sn(1)–Cl(2)	169.561(17)	163.01(3)	172.07(5)
C(27)–Sn(1)–P(1)	170.26(7)	171.83(11)	169.60(12)
Cl(3)–Sn(1)–P(1)	85.945(17)	89.00(2)	89.11(4)
Cl(1)–Sn(1)–P(1)	90.311(16)	79.22(2)	88.13(4)
Cl(2)–Sn(1)–P(1)	81.260(16)	86.22(2)	84.44(4)
C(27)–Sn(1)–P(2)	95.57(7)	94.85(11)	94.90(12)
Cl(3)–Sn(1)–P(2)	161.408(17)	166.04(2)	163.52(4)
Cl(1)–Sn(1)–P(2)	86.643(16)	82.92(2)	92.11(4)
Cl(2)–Sn(1)–P(2)	85.290(16)	85.34(2)	83.29(4)
P(1)–Sn(1)–P(2)	75.465(14)	77.09(2)	74.80(4)
C(9)–P(1)–C(1)	108.88(9)	105.05(13)	104.1(3)
C(9)–P(1)–C(3)	106.22(9)	105.12(12)	107.0(3)
C(1)–P(1)–C(3)	103.68(9)	102.03(12)	105.5(3)
C(9)–P(1)–Sn(1)	111.90(6)	119.24(9)	121.86(18)
C(1)–P(1)–Sn(1)	105.72(6)	106.07(9)	104.79(17)
C(3)–P(1)–Sn(1)	119.78(6)	117.35(9)	112.08(19)
C(2)–P(2)–C(15)	105.55(8)	105.63(12)	107.7(2)
C(2)–P(2)–C(21)	105.50(8)	102.66(12)	104.1(2)
C(15)–P(2)–C(21)	106.94(8)	106.33(12)	105.6(2)
C(2)–P(2)–Sn(1)	103.55(6)	105.38(9)	104.69(17)
C(15)–P(2)–Sn(1)	113.87(6)	116.03(9)	117.20(17)
C(21)–P(2)–Sn(1)	120.10(6)	119.16(9)	116.54(18)
C(2)–C(1)–P(1)	123.55(14)	126.0(2)	122.8(4)
C(1)–C(2)–P(2)	123.04(13)	123.9(2)	123.1(4)

Table 4
Selected interatomic distances (Å) and angles (°) in **4**

Bond lengths

Cl(1)–Sn(1)	2.4102(6)	Cl(2)–Sn(1)	2.4138(5)
Cl(3)–Sn(1)	2.3745(6)	Cl(4)–Sn(1)	2.3812(6)
P(1)–Sn(1)	2.6537(5)	P(2)–Sn(1)	2.6780(5)
C(1)–P(1)	1.808(2)	C(15)–P(2)	1.812(2)
C(7)–P(1)	1.801(2)	C(21)–P(2)	1.802(2)
C(13)–P(1)	1.802(2)	C(14)–P(2)	1.804(2)
C(13)–C(14)	1.329(3)		

Bond angles

Cl(1)–Sn(1)–Cl(2)	171.89(2)	Cl(3)–Sn(1)–Cl(1)	92.67(2)
Cl(4)–Sn(1)–Cl(1)	92.58(2)	Cl(3)–Sn(1)–Cl(2)	91.89(2)
Cl(4)–Sn(1)–Cl(2)	93.40(2)	Cl(3)–Sn(1)–Cl(4)	98.27(2)
Cl(1)–Sn(1)–P(1)	88.025(19)	Cl(1)–Sn(1)–P(2)	87.138(19)
Cl(2)–Sn(1)–P(1)	86.490(18)	Cl(2)–Sn(1)–P(2)	85.904(18)
Cl(3)–Sn(1)–P(1)	171.573(19)	Cl(3)–Sn(1)–P(2)	93.268(19)
Cl(4)–Sn(1)–P(1)	90.090(19)	Cl(4)–Sn(1)–P(2)	168.463(19)
P(1)–Sn(1)–P(2)	78.374(16)	C(7)–P(1)–Sn(1)	114.03(7)
C(13)–P(1)–Sn(1)	105.24(7)	C(1)–P(1)–Sn(1)	118.45(7)
C(21)–P(2)–Sn(1)	113.47(7)	C(14)–P(2)–Sn(1)	104.39(7)
C(15)–P(2)–Sn(1)	120.66(7)		

attached to Sn, while the longer Sn(1)–P(2) distance is *trans* to a chloride. The Sn–P distances are significantly longer than the sum of the covalent radii of atoms (2.51 Å) but shorter than the sum of the van der Waals radii (3.9 Å) [32]. The Sn-Cl distances lie in the range of 2.422(1)–2.505(1) Å, which is within the range of 2.37–2.60 Å observed previously [33]. The Sn(1)–Cl(3) bond, which lies *trans* to the phosphorus, is shorter than the other two bonds, Sn(1)–Cl(1) and Sn(1)–Cl(2) (Table 3).

The crystal structure of [SnCl₄(*cis*-dppen)] (**4**) has been determined for comparison purposes. Fig. 4 shows the molecular structure and Table 4 contains selected bond distances and angles. The asymmetric unit contains a molecule of the complex along with a molecule of dichloromethane solvent. The central tin atom is coordinated to the bidentate ligand and four chloro ligands in a slightly distorted octahedral geometry. The Sn–P distances [2.654(1) and 2.678(1) Å] are comparable to the same distance in other structurally characterized phosphine complexes of SnCl₄, such as *cis*-[SnCl₄{Et₂P(CH₂)₂PEt₂}] [2.648(5) Å] [24]. The *trans* influence, manifested in the variation of the Sn–Cl bond lengths (Table 4), agrees well with the pattern found in most adducts of SnX₄ (X = Cl, Br, I) with soft donor ligands [2,27,34–36]. As expected the P(1)–Sn(1)–P(2) bite angle [78.37(2)°] is again the smallest amongst the *cis* angles, but similar to what one would expect for such a chelating structure; for example, *cis*-[SnCl₄{Et₂P(CH₂)₂PEt₂}] [80.49(7)°] and *cis*-[SnF₄{Et₂P-(CH₂)₂PEt₂}] [80.70(4)°] [24]. The C=C distance [1.329(3) Å] of the ligand has not been altered significantly after complexation and is comparable to the same distance observed in complexes **1**–**3**.

4. Conclusion

We have prepared and characterized a series of mono-organotin(IV) complexes containing the rigid bisphosphine ligand, *cis*-dppen. The phosphine chelates to tin in an unsymmetrical fashion to form octahedral complexes. The two different Sn–P bond lengths observed in the solid state corroborate well with the low temperature ³¹P NMR spectra which exhibit two different *J*(Sn–P) values in all the organotin complexes. In solution these complexes undergo facile redistribution to form [SnCl₄(*cis*-dppen)]. The formation of the above stable crystalline complexes suggests that although the Sn–P coordination is weaker the rigidity of the bisphosphine can help in stabilizing the complexes resisting, to some extent, both oxidation and dissociation of the ligand.

Appendix A. Supplementary material

CCDC 627633, 627634, 627635 and 627636 contain the supplementary crystallographic data for **1**, **2**, **3** · 2CHCl₃, **4** · CH₂Cl₂. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.036.

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