

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 $[\text{R}_2\text{SnCl}_2(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ [R = Me (**1**), ⁿBu (**2**), Ph (**3**)] were prepared by the reaction of R_2SnCl_2 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 ³¹P and ¹¹⁹Sn 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 $[\text{SnCl}_4(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ (**4**) as one of the products. In order to confirm the redistribution, complex **4** has been prepared separately and characterized both structurally and spectrally.

Keywords: Organotin(IV) complexes; Bisphosphine complexes; NMR spectroscopy; Ligand scrambling

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 (³¹P and ¹¹⁹Sn) investigations of the complexes of organotin acceptors, $\text{R}_n\text{SnCl}_{4-n}$ ($n = 1, 2$) and mono- and bisphosphines 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, ⁿBu, Ph [12] and Bz [13]). In the case of highly Lewis acidic R_2SnCl_2 (R = Me, ⁿBu 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(diphenylphosphino)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, $R\text{SnCl}_3$ ($R = \text{Me}$, $n\text{Bu}$, 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 $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Perkin–Elmer 1720X FT-IR spectrometer. The ^1H , $^{31}\text{P}\text{--}\{^1\text{H}\}$ and $^{119}\text{Sn}\text{--}\{^1\text{H}\}$ NMR spectra were recorded on Bruker DPX 400 MHz or DRX 500 MHz instrument referenced relative to residual solvent, 85% H_3PO_4 and $\text{Sn}(\text{CH}_3)_4$, 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. $[\text{MeSnCl}_3(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ (**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 $\text{C}_{27}\text{H}_{25}\text{Cl}_3\text{P}_2\text{Sn}$: 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-CH_3), [$^2J(^{119}\text{Sn-}^1\text{H})$: 114.6], [$^2J(^{117}\text{Sn-}^1\text{H})$: 109.8]; 7.42–7.53, 7.62–7.70 (m, 22H, P-CH=CH and $\text{P-C}_6\text{H}_5$). ^{31}P NMR (162 MHz, CD_2Cl_2): δ -25.92 (br), -26.58 (s). Mass spectrum (ESI) $\{m/z$ [assignment] (%) $\}$: 601 $[\text{M} - \text{Cl}]^+$ (4), 917 $[\text{M}^*]^+$ (22), 883 $[\text{M}^* - \text{Cl}]^+$ (100) where $\text{M}^* = [(\text{SnCl}_4)_2(\text{cis-dppen})]$.

2.1.2. $[\text{BuSnCl}_3(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ (**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 $\text{C}_{30}\text{H}_{31}\text{Cl}_3\text{P}_2\text{Sn}$: 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, CH_3 -, $J = 7.2$); 1.39 (sex, 2H, $-\text{CH}_2$ -, $J = 7.5$), 1.78 (qt, 2H, $-\text{CH}_2$ -, $J = 7.5$), 2.19 (br, 2H, $-\text{CH}_2\text{-Sn}$); 7.38–7.48, 7.53–7.71 (m, 22H, P-CH=CH and

$\text{P-C}_6\text{H}_5$). ^{31}P NMR (162 MHz, CD_2Cl_2): δ -24.64 (br), -26.60 (s). Mass spectrum (ESI) $\{m/z$ [assignment] (%) $\}$: 643 $[\text{M} - \text{Cl}]^+$ (14), 917 $[\text{M}^*]^+$ (1), 883 $[\text{M}^* - \text{Cl}]^+$ (100) where $\text{M}^* = [(\text{SnCl}_4)_2(\text{cis-dppen})]$.

2.1.3. $[\text{PhSnCl}_3(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ (**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 $\text{C}_{32}\text{H}_{27}\text{Cl}_3\text{P}_2\text{Sn}$: 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 , $\text{P-C}_6\text{H}_5$ and $\text{Sn-C}_6\text{H}_5$). ^{31}P NMR (162 MHz, CDCl_3): δ -26.71 (br), -26.96 (s), [$^1J(^{119}\text{Sn-}^{31}\text{P})$: 677.0], [$^1J(^{117}\text{Sn-}^{31}\text{P})$: 646.2]. Mass spectrum (ESI) $\{m/z$ [assignment] (%) $\}$: 663 $[\text{M} - \text{Cl}]^+$ (1), 883 $[\text{M}^* - \text{Cl}]^+$ (100) where $\text{M}^* = [(\text{SnCl}_4)_2(\text{cis-dppen})]$.

2.1.4. $[\text{SnCl}_4(\text{cis-Ph}_2\text{PCH=CHPh}_2)]$ (**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 $\text{C}_{26}\text{H}_{22}\text{Cl}_4\text{P}_2\text{Sn}$: 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, $\text{P-C}_6\text{H}_5$), 7.96 (dd, 2H, P-CH=CH , $^3J(^{31}\text{P-}^1\text{H}) = 14.0$, [$^3J(^{119}\text{Sn-}^1\text{H})$: 45.2], [$^3J(^{117}\text{Sn-}^1\text{H})$: 43.2]). ^{31}P NMR (162 MHz, CD_2Cl_2): δ -26.60 (s), [$^1J(^{119}\text{Sn-}^{31}\text{P})$: 717.4], [$^1J(^{117}\text{Sn-}^{31}\text{P})$: 685.9]. ^{119}Sn NMR (186 MHz, CD_2Cl_2): δ -628 (t). Mass spectrum (APCI) $\{m/z$ [assignment] (%) $\}$: 655 $[\text{M}]^+$ (30), 586 $[\text{M} - 2\text{Cl}]^+$ (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 $\text{K}\alpha$ 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

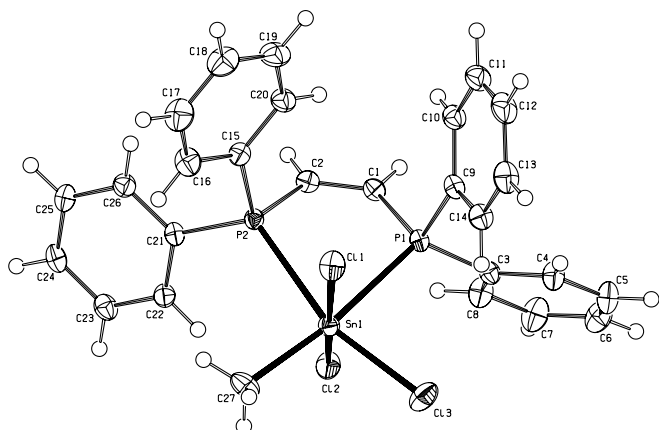


Fig. 1. Molecular structure of **1** with atom numbering scheme at 50% probability ellipsoids.

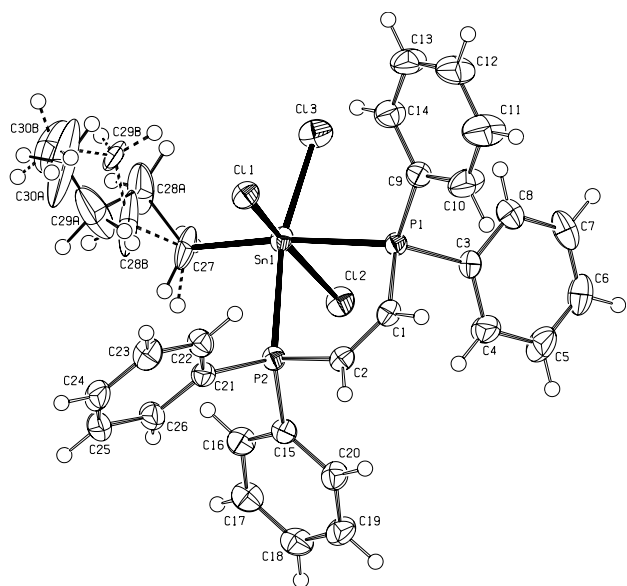


Fig. 2. Molecular structure of **2** with atom numbering scheme. The disordered ⁿBu group is shown with dashed bonds.

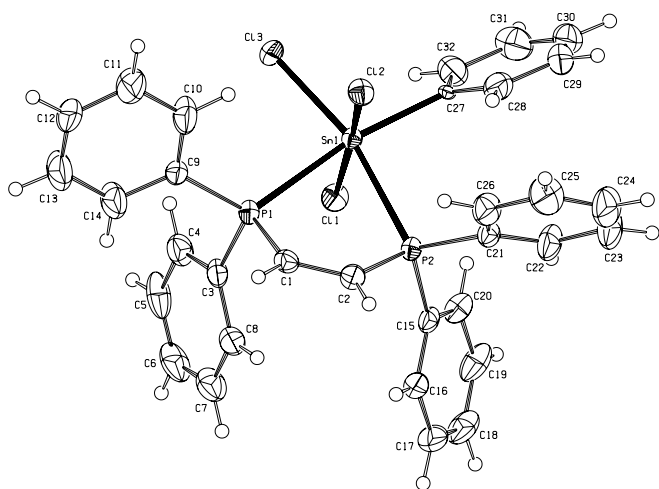


Fig. 3. Molecular structure of **3** with atom numbering scheme. The two CHCl₃ solvent molecules have been omitted for clarity.

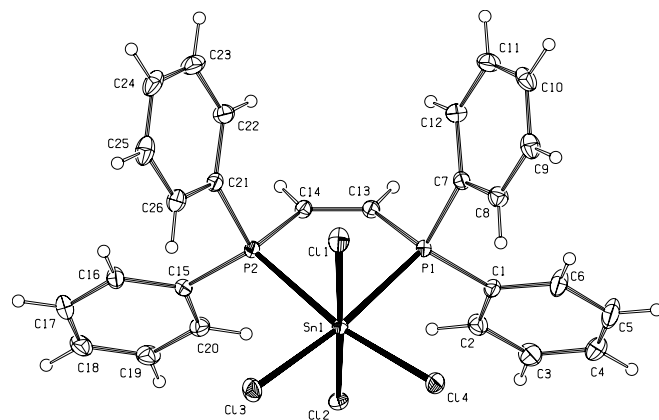


Fig. 4. Molecular structure of **4** with atom numbering scheme. The CH₂Cl₂ solvent molecule has been omitted for clarity.

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*-dppe with RSnCl₃ (R = Me, ⁿBu 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 dppe 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 $\nu(\text{P}=\text{O})$ [12], indicates that the ligand in the products remain unoxidised. The ¹H 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 ¹¹⁹Sn [²*J*(¹¹⁹Sn–¹H): 114.6 Hz] and ¹¹⁷Sn [²*J*(¹¹⁷Sn–¹H): 109.8 Hz]. The ¹H NMR spectrum of **2** exhibits a broad

resonance centered at 2.19 ppm for the CH₂ 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 ³¹P NMR of all the complexes at 300 K in CD₂Cl₂ 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 ³¹P NMR spectra represent the AB part while the ¹¹⁹Sn NMR spectra form the X part. The ³¹P NMR chemical shifts occur upfield to that of the free ligand (δ –21.95, CD₂Cl₂), 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 ³¹P 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 ¹¹⁹Sn 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) ³¹P NMR spectra are consistent with form **I**. The absence of tin satellites for the major peak at ambient temperature ³¹P 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 ³¹P and ¹¹⁹Sn NMR spectral data^a (δ in ppm and *J* in Hz) (for A, B and X notations see figure below)

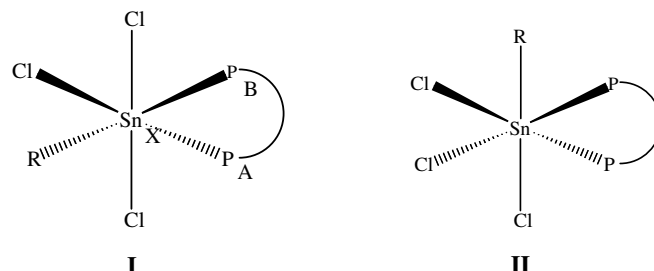
	δ _A (³¹ P)	δ _B (³¹ P)	δ _X (¹¹⁹ Sn)	<i>J</i> _{A-B}	<i>J</i> _{A-X}	<i>J</i> _{B-X}
1 ^b	–24.09	–31.32	–462.5	307	2419	1283
2 ^b	–23.07	–30.24	–456.3	292	2344	1530
3 ^c	–25.02	–32.51	–510.1	306	2327	1156

^a ABX system solved according to reference [25].

^b In CD₂Cl₂, 202.45 MHz (³¹P NMR), 186.40 MHz (¹¹⁹Sn NMR) at 200 K.

^c In CDCl₃, 202.45 MHz (³¹P NMR), 186.40 MHz (¹¹⁹Sn 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 ³¹P NMR spectra. In order to confirm the ligand dissociation, the ³¹P 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 CD₂Cl₂ at 300 K), indicating that the dissociation is complete at higher temperatures.

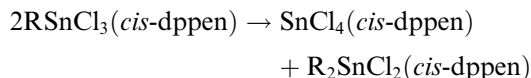


The minor signal in the ³¹P NMR spectra is observed upfield (–26.6 ppm) to that of the free ligand. Tin satellites could be observed for this peak in the spectrum of **3**, while for **1** and **2** the signal intensity is too low to observe

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 ₃ P ₂ Sn	C ₃₀ H ₃₁ Cl ₃ P ₂ Sn	C ₃₂ H ₂₇ Cl ₃ P ₂ Sn, 2(CHCl ₃)	C ₂₆ H ₂₂ Cl ₄ P ₂ Sn, CH ₂ Cl ₂
Formula weight	636.45	678.53	937.25	741.79
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Cc</i>	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/c</i>
<i>a</i> (Å)	17.6425(13)	11.1115(8)	15.6807(7)	13.0900(9)
<i>b</i> (Å)	9.5408(5)	13.0577(8)	21.9531(10)	11.0710(7)
<i>c</i> (Å)	15.9723(11)	20.5792(14)	22.7673(9)	21.2812(13)
β (°)	98.768(6)	101.109(9)	90	104.283(5)
<i>V</i> (Å ³)	2657.1(3)	2929.9(3)	7837.4(6)	2988.7(3)
<i>Z</i>	4	4	8	4
Absorption coefficient (mm ^{–1})	1.399	1.274	1.372	1.515
Collected reflections	16536	22631	45870	27530
Independent reflections	6918	5679	6968	8070
<i>R</i> _(int)	0.0211	0.0388	0.0823	0.0416
<i>R</i> ₁ (Observed data)	0.0166	0.0261	0.0550	0.0293
<i>wR</i> 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 $J(\text{P}-\text{Sn})$ coupling constants and the sharp feature, the signal has been attributed to the presence of $[\text{SnCl}_4(\text{cis-dppen})]$ due to a redistribution reaction in solution.



In order to support the above formulation $[\text{SnCl}_4(\text{cis-dppen})]$ 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 $[\text{SnCl}_4(\text{cis-dppen})]$ 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 $[\text{M}^*-\text{Cl}]^+$, where $\text{M}^* = [(\text{SnCl}_4)_2(\text{cis-dppen})]$ (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 $[\text{SnCl}_4(\text{Bu}_3\text{P})]$ has been observed previously for the reaction of PhSnCl_3 with Bu_3P [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 $[\text{R}_2\text{SnCl}_2(\text{cis-dppen})]$ complexes, their presence are indicated as low intensity signals in ^1H , ^{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 , $^n\text{BuSnCl}_3$ 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 $\text{P}(1)-\text{Sn}(1)-\text{P}(2)$ bite angle is the smallest amongst the cis angles, being equal to $75.46(1)^\circ$, $77.09(2)^\circ$ and $74.80(4)^\circ$ for **1**, **2** and **3**, respectively. In all

three complexes, the $\text{C}=\text{C}$ 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 $\text{Sn}-\text{C}$ 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 $\text{Sn}(1)-\text{P}(1)$ distances for complexes **1–3** [respectively, $2.667(1)$, $2.694(1)$ and $2.704(1)$ Å] are shorter than the $\text{Sn}(1)-\text{P}(2)$ distances [respectively, $2.758(1)$, $2.753(1)$ and $2.723(1)$ Å]. The disparity in the $\text{Sn}-\text{P}$ 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 $\text{Sn}(1)-\text{P}(1)$ distance being the bond *trans* to the carbon

Table 3
Selected interatomic distances (Å) and angles ($^\circ$) in **1–3**

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

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

<i>Bond lengths</i>			
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)		
<i>Bond angles</i>			
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 monoorganotin(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.

Acknowledgements

M.M.E. would like to thank the Swiss Federal Commission for a scholarship to study at the University of Neuchâtel. We express our sincere thanks to Dr. Klaus J. Kulicke, University of Basel for low temperature ¹¹⁹Sn and ³¹P NMR measurements.

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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