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Synthesis and characterisation of phosphinothiolate tin(IV) complexes. Crystal structure of $[Sn^tBu_2(OPPh_2C_6H_4S)(OH_2)]ClO_4\cdot H_2O$

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Abstract

$[SnR_2Cl_2]$ (R = Me, ^tBu) react with $OPPh_2C_6H_4SH$ in the presence of NaOEt affording mononuclear derivatives $[SnR_2(OPPh_2C_6H_4S)_2]$ (**1**, **2**) with two units of the oxide of the thiophenylphosphine. The loss of one of such units is achieved by the reaction of **1** and **2** with HCF_3SO_3 or $HClO_4$ giving rise to complexes with the formula $[SnR_2(OPPh_2C_6H_4S)]A$ (A = CF_3SO_3, ClO_4) (**3a**–**b**, **4a**–**b**). The crystal structure of $[Sn^tBu_2(OPPh_2C_6H_4S)]ClO_4$ (**4b**) has been determined by X-ray diffraction. © 2001 Published by Elsevier Science Ltd.

Keywords: Phosphinothiolate derivatives; Tin complexes; Phosphine oxide

1. Introduction

Metal thiolato complexes have been extensively studied because of their ability to adopt various nuclearities and their relevance in biology, since they form the inorganic part of the biologically active centres of some metalloproteins and enzymes [1–3]. Recently, attention has been paid to the coordination chemistry of polydentate ligands that incorporate both thiolato and tertiary phosphine donor sites, because they give potential access to new compounds with unusual structures and reactivities [4]. In this regard, the most studied systems are the proligands $PR_2C_6H_4SH$ and $PR_2CH_2CH_2SH$ [5–14] and some examples with the oxide of such phosphines, in particular the arene ones, have been reported [15–20].

As a result of our continuing interest in the coordination of main group metals with arenephosphinothiolate ligands [13,14], here we describe the synthesis and characterisation of some tin(IV) complexes with the oxide of the diphenylphosphinothiol: $OPPh_2(C_6H_4SH)$ and their reactivity in the presence of a non-coordinative acid. The crystal structure of $[Sn^tBu_2(OPPh_2C_6H_4S)]ClO_4$ is also reported.

2. Results and discussion

The reaction of $OPPh_2(C_6H_4SH)$ with tin(IV) complexes $[SnR_2Cl_2]$ (R = Me, ^tBu) in the presence of sodium ethoxide in a 1:2 ratio, affords complexes **1** and **2** with a similar formulation to that previously described [13] with the phosphine $PPh_2(C_6H_4SH)$ (Scheme 1, process i).

Their IR spectra do not show the band associated with ν(S–H), which appears at 2495 cm^{-1} in the free ligand. These spectra also show a band due to the ν(P=O) at about 1140 cm^{-1}, displaced 40 cm^{-1} down from the value of the starting phosphine. In the ^1H-NMR spectra the signal due to the S–H group, centred at 6.2 ppm in the free ligand, has disappeared, which confirms the presence of the anionic form of the ligand. In addition, the spectra show in both cases a singlet due

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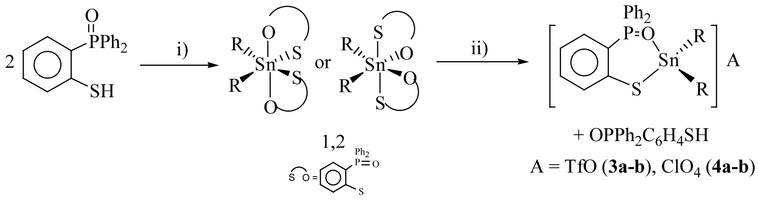

i) NaOEt, $[SnR_2Cl_2]$; ii) HA/acetone

Scheme 1.

to the methyl and ^{t}Bu radicals bonded to the tin centre flanked by tin satellites. The ^{31}P-NMR spectra display a singlet centred at about 33 ppm, again flanked by tin satellites and downfield displaced from the value of the free ligand, due to the coordination of the tin centre. The ^{119}Sn-NMR spectra show a doublet at -90 (**1**) and -97 (**2**) ppm as a consequence of the Sn–P coupling, with coupling constants of about 60 Hz. The presence of such Sn–P coupling in addition to the big displacement of the ν(P=O) in the IR spectra, suggests a coordination of the oxygen atom of the phosphine to the tin centre. This fact is also observed in complexes **3** and **4**, described below, and confirmed by X-ray diffraction in one of them. With this idea we can propose an hexacoordinated structure for the tin(IV) (Scheme 1), where the two oxides of the phosphinethiolate are mutually in *cis*. With such a disposition, two different isomers can be described, with both oxygen mutually *trans* or *cis*. We were not able to distinguish between them without any crystallographic data, but in solution only one of the isomers is present.

The LSIMS + (nba as matrix) mass spectra of these compounds show a small intensity molecular peak. The base peaks in both cases correspond to the loss of one of the phosphine ligands.

Since these species seem to be the most stable in the fragmentation process of **1** and **2**, we tried to isolate them by the reaction of complexes **1** and **2** with a non-coordinative acid. Thus, the reaction of complexes $[SnR_2(OPPh_2C_6H_4S)_2]$ (R = Me, ^{t}Bu) with HA (HCF_3SO_3 or $HClO_4$) gave complexes $[SnR_2(OPPh_2C_6H_4S)]A$ (R = Me, A = TfO **3a**, ClO_4 **3b**; R = ^{t}Bu, A = TfO **4a**, ClO_4 **3b**) as air-stable solids. The process can be described as the protonation of one of the phosphine ligands, giving rise to free $OPPh_2(C_6H_4SH)$ and the new complexes. (Scheme 1, process ii).

The IR spectra of complexes **3a**–**b** and **4a**–**b** show the vibration ν(P=O) displaced a few cm^{-1} compared with the starting derivatives **1** and **2**. Additionally the characteristic bands of the anionic triflate [21] and perchlorate [22] appear respectively.

Independent of the anion $CF_3SO_3^-$ or ClO_4^- the complexes show the same spectroscopic data. So the ^{1}H-NMR spectra show, apart from the multiplets in the phenyl region, a singlet due to the methyl or ^{t}Bu groups bonded to the metal showing the tin satellites. In the case of ^{31}P-NMR the singlets are down field displaced from the values of the starting derivatives. The ^{119}Sn-NMR spectra also show a doublet in all cases, due to the Sn–P coupling. The mass spectra (LSISM +, nba as matrix) show the parent peaks corresponding with the cation formulation $[M-X]^+$ as the base peaks in all cases. In addition, these complexes behave as 1:1 electrolytes in acetone solutions [23].

The crystallisation of one of these complexes (**4b**) afforded suitable crystals for X-ray studies that analysed as $[Sn^tBu_2(OPPh_2C_6H_4S)(OH_2)]ClO_4$, where an extra OH_2 molecule has been incorporated to the tin coordination sphere, probably from the crystallisation solvent. The molecular structure of its H_2O solvate has been determined and is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The cation consists of a pentacoordinated discrete molecular unit in which one molecule of water (O(6)), is coordinated to tin along with the oxidated phosphine (O(5)). The coordination environment around the tin atom is a distorted trigonal bipyramid, as in $[SnCl_5]^-$ [24], with both *tert*-butyl groups and the thiolate occupying the

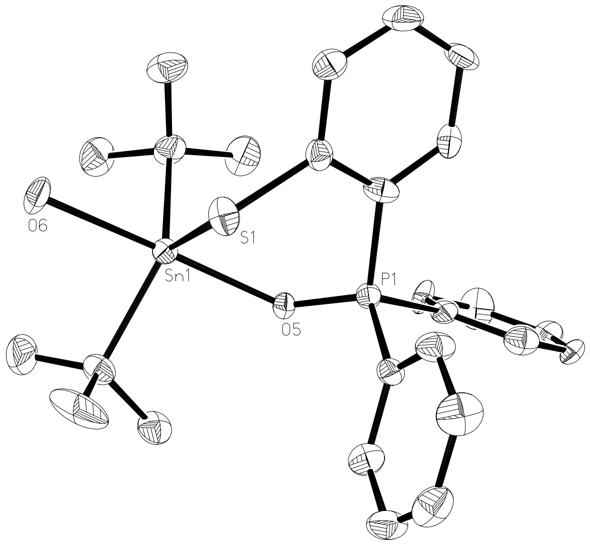

Fig. 1. Molecular structure of **4b** showing the cation. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 1
Bond lengths [Å] and angles [°] for **4b**

Bond lengths			
Sn(1)–C(2)	2.171(9)	Sn(1)–O(6)	2.332(5)
Sn(1)–O(5)	2.176(5)	Sn(1)–S(1)	2.451(2)
Sn(1)–C(1)	2.184(10)		
Bond angles			
C(2)–Sn(1)–O(5)	99.5(3)	O(6)–Sn(1)–S(1)	82.7(2)
C(2)–Sn(1)–C(1)	130.6(4)	C(11)–C(1)–Sn(1)	109.7(7)
O(5)–Sn(1)–C(1)	93.6(3)	C(12)–C(1)–Sn(1)	107.5(7)
C(2)–Sn(1)–O(6)	89.1(3)	C(13)–C(1)–Sn(1)	109.4(6)
O(5)–Sn(1)–O(6)	168.4(2)	C(21)–C(2)–Sn(1)	110.2(7)
C(1)–Sn(1)–O(6)	86.5(3)	C(23)–C(2)–Sn(1)	111.0(6)
C(2)–Sn(1)–S(1)	113.0(3)	C(22)–C(2)–Sn(1)	107.4(6)
O(5)–Sn(1)–S(1)	86.8(2)	C(101)–S(1)–Sn(1)	100.5(3)
C(1)–Sn(1)–S(1)	115.2(3)	P(1)–O(5)–Sn(1)	127.6(3)

equatorial sites and the oxygen atoms of the water and the oxidised phosphine ligand occupying the apical positions, the O(5)–Sn–O(6) angle being 168.4(2)°. The Sn–O bond lengths are Sn–O(6) 2.332(5) Å, typical of other tin complexes with water molecules in their structure [25], and Sn–O(5) 2.176(5) Å. In the bipyramidal equatorial plane, are two Sn–C and one Sn–S bonds, with angles: C(2)–Sn–C(1) 130.6(4), C(2)–Sn–S(1) 113.0(4) and C(1)–Sn–S(1) 115.2(3)°. The Sn–C bond lengths are Sn–C(1) 2.184(10) and Sn–C(2) 2.171(9) Å, that are in the range of other di-*tert*-butyl–tin complexes [26]. The Sn–S distance is 2.451(2) Å, similar to those found in the complex [Au$_2$Sn(^{t}Bu)$_2$(C$_6$F$_5$)$_2$-(SC$_6$H$_4$PPh$_2$)$_2$] namely 2.444(3) and 2.434(3) Å [13].

3. Experimental

3.1. General procedures

Infrared spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets, ^{1}H and ^{31}P-NMR spectra were recorded on a Bruker 300 or Varian UNITY 300 in CDCl$_3$ solutions; chemical shifts are quoted relative to SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (external ^{31}P). The C, H and S analyses were performed in a Perkin–Elmer 2400 microanalyser. Conductivities were measured in acetone with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS +) using nitrobenzylalcohol as matrix.

3.2. Starting materials

OPPh$_2$C$_6$H$_4$SH [27] was obtained according to the literature procedures, the rest of the reagents were used as supplied.

3.3. Preparation of [SnR$_2$(OPPh$_2$C$_6$H$_4$S)$_2$] R = Me (**1**), ^{t}Bu (**2**)

To a suspension of OPPh$_2$C$_6$H$_4$SH in ethanol (0.310 g, 1 mmol) under argon was added, over a period of 10 min, a 0.1 M solution of NaOEt (1.2 mmol, 12 ml) and either SnCl$_2$Me$_2$ or SnCl$_2{}^t$Bu$_2$ (0.5 mmol). After 4 h of stirring, the solution was evaporated to dryness, the addition of dichloromethane gave a white solid corresponding to NaCl which was filtered through celite. The resulting solution was concentrated to give white solids (**1**, **2**) which were filtered off and dried in vacuo. Yields: **1**, 82%; **2**, 79%. IR(film): ν(P=O) = 1144 cm^{-1} (**1**); 1151 cm^{-1} (**2**). ^{1}H-NMR (CDCl$_3$): **1**, δ = 7.6 (m, 2H), 7.57–7.31 (m, 20H), 7.26 (m, 2H), 6.9 (m, 2H), 7.01 (m, 2H), 0.61 (s, $J119_{\text{Sn–H}}$ = 87 Hz and $J117_{\text{Sn–H}}$ = 83.4 Hz, 6H, CH$_3$); **2**, δ = 7.68–7.26 (m, 28H), 1.05 (s, $J_{\text{Sn–H}}$ = 106 Hz, 18H, ^{t}Bu). ^{31}P-NMR (CDCl$_3$) **1**, δ = 33.9 ppm (s); **2**, δ = 33.1 ppm (s). ^{119}Sn-NMR (CDCl$_3$): **1**, δ = − 90.8 (d, $J_{\text{Sn–P}}$ = 55 Hz), **2** δ = − 97.4 (d, $J_{\text{Sn–P}}$ = 20 Hz). **1** C$_{38}$H$_{34}$O$_2$P$_2$S$_2$Sn (767.44): Calc. C, 59.45; H, 4.45; S, 8.35; Found: C, 60.1; H, 4.5; S, 8.0%; **2** C$_{44}$H$_{46}$O$_2$P$_2$S$_2$Sn (851.63): Calc. C, 62.05; H, 5.45; S, 7.5; Found: C, 61.6; H, 5.3; S, 7.05%. MS(LSISM +) (*m*/*z*) (%) = 766 (5) (**1**), 849 (6) (**2**). Λ_M (ohm^{-1} cm^2 mol^{-1}) = 2 (**1**), 1 (**2**).

3.4. Preparation of [SnR$_2$(OPPh$_2$C$_6$H$_4$S)]TfO R = Me (**3a**), ^{t}Bu (**4a**)

To a solution of [SnMe$_2$(OPPh$_2$C$_6$H$_4$S)$_2$] (0.076 g, 0.1 mmol) or [Sn^{t}Bu$_2$(OPPh$_2$C$_6$H$_4$S)$_2$] (0.085 g, 0.1 mmol) in acetone (30 ml) was added HTfO (0.1 mmol, 9 μl). After 4 h of stirring, the solution was concentrated, the addition of diethyl ether gave white solids (**3a**, **4a**) which were filtered off and dried in vacuo. Yields: **3a**, 90%, **4a**, 85%. IR(film): ν(P=O) = 1143 cm^{-1} (**3a**), 1145 cm^{-1} (**4a**). ^{1}H-NMR (CDCl$_3$): **3a**, δ = 7.81 (m, 1H), 7.61–7.39 (m, 11H), 7.15 (m, 1H), 6.78 (m, 1H), 0.92 (s, $J_{\text{Sn–H}}$ = 87 Hz, 6H, CH$_3$); **4a**, δ = 8 (m, 1H), 7.66–7.48 (m, 11H), 7.2 (m, 1H), 6.81 (m, 1H), 1.28 (s, $J_{\text{Sn–H}}$ = 114.4 Hz, 18H, ^{t}Bu). ^{31}P-NMR (CDCl$_3$) **3a**, δ = 39.7 ppm (s), **4a**, δ = 45.4 ppm (s). ^{119}Sn-NMR (CDCl$_3$): **3a**, δ = − 90.3 (d, $J_{\text{Sn–P}}$ = 50 Hz); **4a**, δ = − 169.2 (d, $J_{\text{Sn–P}}$ = 78 Hz). **3a** C$_{21}$H$_{20}$O$_4$PS$_2$F$_3$Sn (606.74): Calc. C, 41.55; H, 3.3; S, 10.55; Found: C, 41.1; H, 2.95; S, 9.9; **4a** C$_{27}$H$_{32}$O$_4$PS$_2$F$_3$Sn (691.35): Calc. C, 46.9; H, 4.65; S, 9.3; Found: C, 47.1; H, 4.9; S, 9.7. MS(LSISM +) (*m*/*z*) (%) = 459 (100) (**3a**), 543 (100) (**4a**). Λ_M (ohm^{-1} cm^2 mol^{-1}) = 78 (**3a**), 95 (**4a**).

3.5. Preparation of [SnR$_2$(OPPh$_2$C$_6$H$_4$S)]ClO$_4$ R = Me (**3b**), ^{t}Bu (**4b**)

To a solution of [SnMe$_2$(OPPh$_2$C$_6$H$_4$S)$_2$] (0.076 g, 0.1 mmol) or [Sn^{t}Bu$_2$(OPPh$_2$C$_6$H$_4$S)$_2$] (0.088 g, 0.1 mmol) in acetone (30 ml) was added a solution of $HClO_4$ 0.1 M (0.1 mmol, 1 ml). After 1 h of stirring at reflux temperature Na_2SO_4 was added and filtered through Celite. The resulting solution was concentrated and the addition of diethyl ether (20 ml) gave white solids (**3b**, **4b**) which were filtered off and dried in vacuo. Yields: **3b**, 86%, **4b**, 75%. IR(film): $\nu(P{=}O) = 1143\ cm^{-1}$ (**3b**), $1145\ cm^{-1}$ (**4b**). ^1H-NMR ($CDCl_3$): **3b**, $\delta = 7.84$ (m, 1H), 7.79 (m, 1H), 7.62–7.13 (m, 11H), 7.1 (m, 1H), 0.97 (s, $J_{Sn-H} = 87$ Hz, 6H, CH_3), **4b** $\delta = 8$ (m, 1H), 7.6–7.44 (m, 11H), 7.3 (m, 1H), 6.8 (m, 1H), 1.28 (s, $J_{Sn-H} = 114$ Hz, 18H, ^{t}Bu). ^{31}P-NMR ($CDCl_3$) **3a**, $\delta =$ 39.5 ppm (s) ($J_{Sn-P} = 49$ Hz), **4a**, $\delta = 45.6$ ppm (s) ($J_{Sn-P} = 79$ Hz). **3b** $C_{20}H_{20}O_5PSClSn$ (557.57): Calc. C, 43.05; H, 3.6; S, 5.75; Found: C, 43.5; H, 3.2; S, 5.2; **4b** $C_{26}H_{32}O_5PSClSn$ (605.86): Calc. C, 51.5; H, 5.3; S, 5.2; Found: C, 51.9; H, 5.2; S, 5.6. Λ_M ($ohm^{-1}\ cm^2\ mol^{-1}$) = 82 (**3b**), 90 (**4b**).

3.6. Crystallography

Single crystals were grown by diffusing diethyl ether into an acetone solution of complex $[Sn^tBu_2(OPPh_2C_6H_4S)]ClO_4$ (**4b**) at low temperature, and mounted in inert oil.

3.7. Crystal data and data collection parameters

$C_{26}H_{32}ClO_7PSSn$, $M = 673.69$, monoclinic, $a = 10.385(2)$, $b = 13.0960(10)$, $c = 10.8890(10)$ Å, $\beta = 97.060(12)°$, $U = 1469.7(3)$ Å^3, $T = 293$K, space group $P2_1$, graphite monochromated Mo Kα radiation $\lambda = 0.71069$Å, $Z = 2$, $D_{calc} = 1.522$ Mg m^{-3}, $F(000) = 684$, colourless prism with dimensions $0.20 \times 0.20 \times 0.18$ mm, $\mu = 1.126$ mm^{-1}; Delf Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator, following procedures described elsewhere [28], θ range for data collection 1.88 to 24.95°, $-11 \le h \le 11$, $-14 \le k \le 11$, $-10 \le l \le 12$; 5342 reflections collected, 3936 independent ($R_{int} = 0.074$).

3.8. Structure solution and refinement

The data processing solution was done using the direct methods of SHELXS 86 [29], the structure was refined by full-matrix least squares on F_o^2, using the program SHELXL 93 [30]. All data used were corrected for Lorentz-polarisation factors, and subsequently for absorption using the program DIFABS [31]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms from the water molecules have not been found the other hydrogen were included in idealised positions. Refinement proceeds to $R = 0.0429$, $\omega R = 0.1169$ and goodness of fit on F^2 1.112 for 340 parameters and 1 restraint, and $R = 0.0450$, $\omega R = 0.1174$ for all data. In the final Fourier synthesis the electron density fluctuates in the range 1.077 to -0.957 e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 163479 for compound **4b** (excluding structure factors). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

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