Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Polyhedron 25 (2006) 930–936

POLYHEDRON
www.elsevier.com/locate/poly

Synthesis and characterisation of tin(IV) fluoride complexes of phosphine and arsine oxide ligands

Martin F. Davis, William Levason *, Gillian Reid, Michael Webster

School of Chemistry, University of Southampton, Highfield, Southampton, Hampshire SO17 1BJ, UK

Received 18 July 2005; accepted 22 October 2005
Available online 6 December 2005

Dedicated to Professor Mike Hursthouse on the occasion of his retirement.

Abstract

The pseudooctahedral complexes $[SnF_4L_2]$ (L = Ph_3PO, Ph_3AsO, Me_3PO, Me_3AsO) and $[SnF_4(L\text{–}L)]$ (L–L = $Ph_2P(O)CH_2P(O)Ph_2$, $o\text{-}C_6H_4(P(O)Me_2)_2$, $o\text{-}C_6H_4(P(O)Ph_2)_2$) have been prepared from $[SnF_4(MeCN)_2]$ and the appropriate ligand in dichloromethane solution. The complexes have been characterised by analysis, IR, ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and ^{119}Sn NMR spectroscopy as appropriate; the NMR studies showing that the complexes of the monodentate ligands exist as mixtures of *trans* and *cis* isomers in solution. The crystal structures of *trans*-$[SnF_4(OPMe_3)_2]$, $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]\cdot CH_2Cl_2\cdot H_2O$ and $[o\text{-}C_6H_4(P(O)Ph_2)_2]\cdot CH_2Cl_2$ have been determined. Comparison of the structural and NMR spectroscopic data of the tetrafluorotin complexes with those of related $[SnX_4L_2]$ (X = Cl, Br or I) shows that SnF_4 is the strongest Lewis acid in the series towards hard Lewis bases.

Keywords: Tin(IV) fluoride; Phosphine oxide; Arsine oxide

---

1. Introduction

Although standard texts state (usually without quoting supporting evidence) that Lewis acidity of the four tin(IV) halides is greatest for SnF_4, remarkably few complexes of the latter are known [1–6] and only one example with a neutral ligand, $[SnF_4(2,2'\text{-bipy})]$, has been structurally characterised [1]. Tin(IV) chloride and bromide are strong Lewis acids forming adducts with a wide variety of neutral donor ligands, whereas tin(IV) iodide is only a weak Lewis acid forming similar, although much less stable, complexes which are often extensively dissociated in solution [7–9]. We have reported previously the syntheses, structural and spectroscopic characterisation (especially by multinuclear NMR techniques) of several series of SnX_4 (X = Cl, Br or I) adducts with soft donors, including dithioethers [10], diselenoethers [11], ditelluroethers [12], diphosphines and diarsines [13] and thiamacrocycles [14]. This work is now being extended to the investigation of the SnF_4 adducts and we report here of some examples with phosphine and arsine oxides.

2. Results and discussion

2.1. $[SnF_4L_2]$, L = Ph_3PO, Ph_3AsO, Me_3PO, Me_3AsO, L_2 = $Ph_2P(O)CH_2P(O)Ph_2$, $o\text{-}C_6H_4(P(O)Ph_2)_2$, $o\text{-}C_6H_4(P(O)Me_2)_2$

Unlike the other three tin(IV) halides which are tetrahedral molecules, anhydrous SnF_4 has a polymeric sheet structure based upon vertex sharing SnF_6 groups [15], and as a result, although moisture sensitive, it is otherwise rather unreactive towards neutral ligands. A convenient entry into the chemistry is provided by $[SnF_4(MeCN)_2]$ made from SnF_2, I_2 and MeCN as described by Tudela [16,17]. The reaction of $[SnF_4(MeCN)_2]$ with 2.1 mol equivalents of Ph_3PO, Ph_3AsO, Me_3PO or Me_3AsO in anhydrous CH_2Cl_2

---

* Corresponding author. Tel.: +2380593792; fax: +2380593781.
E-mail address: wxl@soton.ac.uk (W. Levason).

0277-5387/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2005.10.024

resulted in the formation of white [SnF_4L_2] complexes in high yield. The solids are moisture sensitive, tenaciously retain organic solvents – clearly evident in the ^1H NMR spectra, and are only modestly soluble in chlorocarbons. Solubility is not significantly better in acetone or nitromethane and stronger donor solvents were generally avoided for spectroscopic studies since they can lead to some displacement of the neutral ligands. The complexes could be recrystallised from a large volume of anhydrous CH_2Cl_2. The complexes with Ph_3PO, Ph_3AsO and Me_3PO were briefly reported in larger compilations of their metal complexes many years ago [4–6] but characterisation was limited to microanalysis and partial IR spectra. Our IR spectra (Table 1) are generally in good agreement with those reported; where differences occur they are probably attributable to various amounts of *cis* and *trans* isomers present in the samples resulting from differences in the isolation procedures and/or solvents used [18]. Three diphosphine dioxide complexes, [$SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}$], [$SnF_4\{o\text{-}C_6H_4(P(O)Me_2)_2\}$] and [$SnF_4\{Ph_2P(O)\text{-}CH_2P(O)Ph_2\}$] were made similarly.

The multinuclear NMR data (Tables 1 and 2) show the presence of both *cis* and *trans* isomers in CH_2Cl_2 solution for the R_3PO and R_3AsO complexes, the approximate isomer ratios being determined from the $^{19}F\{^1H\}$ NMR spectra. For [$SnF_4(Ph_3PO)_2$] the two isomers have similar abundance but for the other three the *trans* isomer predominates. Although resonances were observed at ambient temperatures in the ^1H, ^{31}P and ^{19}F spectra, the ^{119}Sn spectra showed broad and poorly resolved features and the samples were cooled to 273 K to improve resolution. The $^{31}P\{^1H\}$ NMR spectra show singlet resonances for each isomer with very similar chemical shifts, and no resolved coupling to ^{19}F, but with weak $^{119/117}Sn$ satellites. The $^2J(^{119/117}Sn–^{31}P)$ which lie in the range 20–65 Hz, appeared as single lines rather than as separate features for the two tin isotopes – no doubt the differences were lost in the line width, since from the magnetogyric ratios $\gamma^{119}Sn/\gamma^{117}Sn$ (1.046) the values are expected to differ by <2 Hz. The $^{19}F\{^1H\}$ spectra show singlet resonances for the *trans* isomers and two triplets for the *cis* (Table 2), with $\delta(^{19}F)$ in the range −135 to −170, and with $^1J(^{119}Sn–^{19}F)$ 1700–1950 Hz, similar to the values in substituted fluorostannates(IV) [3]. In these cases, the $^1J(^{117}Sn–^{19}F)$ satellites were also clearly resolved and although not quoted in Table 2, the magnitudes were consistent with expectation based upon $\gamma^{119}Sn/\gamma^{117}Sn$. Obtaining good quality ^{119}Sn NMR spectra proved difficult due to the modest receptivity of the tin ($D_c = 25$), poor solubilities, the presence of both isomers and also the complexity of the coupling patterns. For example, for [$SnF_4(Me_3PO)_2$] the symmetrical quintet of triplets of the *trans* isomer was clearly evident centred at δ −781.8 Underlying this resonance is another weaker and more complex pattern centred at δ −769.0 attributed to the *cis* isomer. Based upon the various coupling constants obtained from the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$spectra the major lines of the expected 27 line multiplet (t,t,t) were identified. The solubility of [$SnF_4(Ph_3PO)_2$] is lower, but again two multiplets can be discerned consistent with approximately equal amounts of the two geometric isomers, although in this case the spectral quality was poor. For the [$SnF_4(R_3AsO)_2$] complexes, the quintet due to the *trans* isomer was clearly identified in each case, but the resonance (t,t) of the less abundant *cis* form appeared near coincident and hence the chemical shift assignment less clear, although the more intense lines of the multiplets were found.

The diphosphine dioxide complexes [SnF_4(L–L)] (L–L = $Ph_2P(O)CH_2P(O)Ph_2$, $o\text{-}C_6H_4(P(O)Ph_2)_2$) are, as expected, *cis* isomers showing (Table 2) two triplets in the $^{19}F\{H\}$ NMR spectra and singlets in the $^{31}P\{^1H\}$ spectra. At temperatures a little above ambient the resonances in the $^{19}F\{H\}$ NMR spectra broaden, presumably due to some dynamic process, probably chelate ring opening. On cooling the solutions the complexes precipitate which prevented low temperature studies. The [$SnF_4\{o\text{-}C_6H_4(P(O)Me_2)_2\}$] was insoluble in chlorinated solvents, but dissolved with some decomposition (diphosphine dioxide displacement) in anhydrous *N*,*N*-dimethylformamide The $^{19}F\{H\}$ and $^{31}P\{^1H\}$ NMR spectra of the complex are given in Table 2, but the poor solubility and partial decomposition prevented a ^{119}Sn spectrum from being obtained.

Table 1
IR[a] and ^1H NMR[b] spectroscopic data

Compound	ν(P(As)O) (cm^{-1})	ν(Sn–X) (cm^{-1})	$\delta(^1H)$
[$SnF_4(Ph_3PO)_2$]	1137, 1082	580, 549, 537	7.36–7.88(m)
[$SnF_4(Me_3PO)_2$]	1085(br)	576, 559	1.855(d), $^2J_{PH} = 13.5$ Hz 1.860(d), $^2J_{PH} = 13.5$ Hz
[$SnF_4(Ph_3AsO)_2$]	877(br), 850(sh)	559(br)	7.40–7.87(m)
[$SnF_4(Me_3AsO)_2$]	865, 812(br)	550(br)	2.04(s), 2.05(s)
[$SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}$]	1145, 1087(br)	585, 569, 548	7.31–7.71(m)
[$SnF_4\{Ph_2P(O)CH_2P(O)Ph_2\}$]	1145, 1092	596, 577	4.00(t), $^2J_{PH} = 13$ Hz 7.36–7.75(m)[d]
[$SnF_4\{o\text{-}C_6H_4(P(O)Me_2)_2\}$]	1147, 1093	573(br)	1.81(m) 7.49–7.85(m)[c]

---

[a] Nujol mull.

[b] In $CDCl_3$ at 300 MHz.

[c] In d^6-dmso.

[d] In CD_2Cl_2.

Table 2
$^{31}P\{^1H\}$, ^{119}Sn and $^{19}F\{^1H\}$ NMR spectroscopic data[a]

Compound	$\delta^{31}P\{^1H\}$[b]	$\delta^{119}Sn$[c]	$\delta^{19}F\{^1H\}$[d]	$^1J(^{19}F–^{119}Sn)$	$^2J(^{19}F–^{19}F)$	$^2J(^{31}P–^{119}Sn)$	Isomer ratio
$[SnF_4\{Me_3PO)_2]$ *trans*	65.9(s)	−781.8(q,t)	−149.2(s)	1725		50	3
cis	65.4(s)	−769.0(t,t,t)	−147.2(t)	1772	51	50	1
			−158.0(t)	1850			
$[SnF_4(Ph_3PO)_2]$ *trans*	42.5(s)	−770.0(q,t)	−149.8(s)	1704		20	1
cis	42.3(s)	−775.1(t,t,t)	−146.2(t)	1730	53	22	1
			−159.8(t)	1850			
$[SnF_4\{Me_3AsO)_2]$ *trans*		−747.7(q)	−141.6(s)	1804			3
cis		−748.4(t,t)	−140.9(t)	1827	49		1
			−148.2(t)	1818			
$[SnF_4(Ph_3AsO)_2]$ *trans*		−757.5(q)	−141.3(s)	1788			2
cis		−758.6(t,t)	−137.8(t)	1800	51		1
			−151.9(t)	1860			
$[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$	45.5(s)	−790.0(t,t,t)	−142.9(br)	1730	53	63	
			−167.2(t)	1923			
$[SnF_4\{Ph_2P(O)CH_2P(O)Ph_2\}]$	44.1(s)	−792.4(t,t,t)	−143.0(t)	1753	50	57	
			−167.8(t)	1930			
$[SnF_4\{o\text{-}C_6H_4(P(O)Me_2)_2\}]$[e]	62.1(s)		−143.5(t)	1740	50	57	
			−165.4(t)	1930			

[a] To obtain good resolution of the complex couplings, spectra were typically recorded at 273 K.
[b] Relative to external 85% H_3PO_4.
[c] Relative to external neat $SnMe_4$.
[d] Relative to external $CFCl_3$.
[e] *N*,*N*-Dimethylformamide solution.

2.2. Structures of trans-$[SnF_4(Me_3PO)_2]$, $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ and $[o\text{-}C_6H_4(P(O)Ph_2)_2]$

Colourless crystals of $[SnF_4(Me_3PO)_2]$ were grown from a sample containing both isomers by vapour phase diffusion of hexane into a CH_2Cl_2 solution. These proved on structure solution to be the *trans* isomer (Table 3 and Fig. 1). The molecule is centrosymmetric with Sn–F = 1.937(2), 1.954(2) Å, not significantly different from the values in *cis*-$[SnF_4(2,2'\text{-bipy})]$ 1.924(3)–1.948(3) Å [1]. Comparison of *d*(P–O) in the complex (1.532(3) Å) with that in Me_3PO (1.489(6) Å) [19] shows the bond is significantly lengthened upon coordination.

The crystal structures of (*cis*) $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ (Table 4, Fig. 2) and of the parent ligand, $o\text{-}C_6H_4(P(O)Ph_2)_2$ (Table 5, Fig. 3) have also been determined and the key bond lengths may be compared similarly. The *d*(Sn–F) are very similar to those in $[SnF_4(Me_3PO)_2]$, and essentially independent of the nature of the *trans* ligand. The *d*(Sn–O) at 2.088(5) and 2.071(5) Å are rather longer than in the Me_3PO complex which probably reflects the effect of the seven-membered chelate ring. As found for

Table 3
Selected bond lengths (Å) and angles (°) for *trans*-$[SnF_4(Me_3PO)_2]$[a]

Sn1–F1	1.937(2)	Sn1–F2	1.954(2)
Sn1–O1	2.045(3)	P1–O1	1.532(3)
P1–C	1.774(4)–1.782(4)		
F1–Sn1–F2	89.85(10)	F1–Sn1–O1	91.13(11)
F2–Sn1–O1	89.48(10)	P1–O1–Sn1	131.50(17)
O1–P1–C	108.4(2)–111.7(2)	C–P1–C	107.2(2)–110.2(2)

[a] The tin atom is on a centre of symmetry.

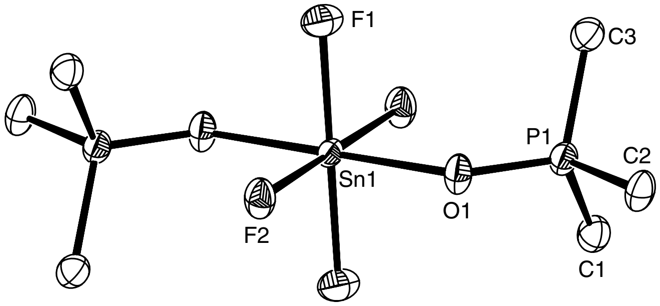

Fig. 1. Structure of *trans*-$[SnF_4(Me_3PO)_2]$ showing the atom numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. There is a centre of symmetry at the Sn1 atom.

Table 4
Selected bond lengths (Å) and angles (°) for $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}] \cdot CH_2Cl_2 \cdot H_2O$

Sn1–F1	1.951(4)	Sn1–F3	1.930(4)
Sn1–F2	1.941(4)	Sn1–F4	1.940(4)
Sn1–O1	2.088(5)	Sn1–O2	2.071(5)
P1–O1	1.512(5)	P2–O2	1.525(5)
P–C	1.786(7)–1.819(7)		
F1–Sn1–F2	174.39(18)	F2–Sn1–F3	91.50(18)
F1–Sn1–F3	93.20(18)	F2–Sn1–F4	91.57(17)
F1–Sn1–F4	91.00(18)	F3–Sn1–F4	95.65(19)
F1–Sn1–O1	89.18(18)	F1–Sn1–O2	87.81(18)
F2–Sn1–O1	87.67(17)	F2–Sn1–O2	87.26(18)
F3–Sn1–O1	91.13(18)	F3–Sn1–O2	175.41(19)
F4–Sn1–O1	173.19(18)	F4–Sn1–O2	88.80(19)
O1–Sn1–O2	84.40(18)		
P1–O1–Sn1	140.5(3)	P2–O2–Sn1	133.8(3)
O–P–C	106.5(3)–112.9(3)	C–P–C	106.9(3)–109.6(3)

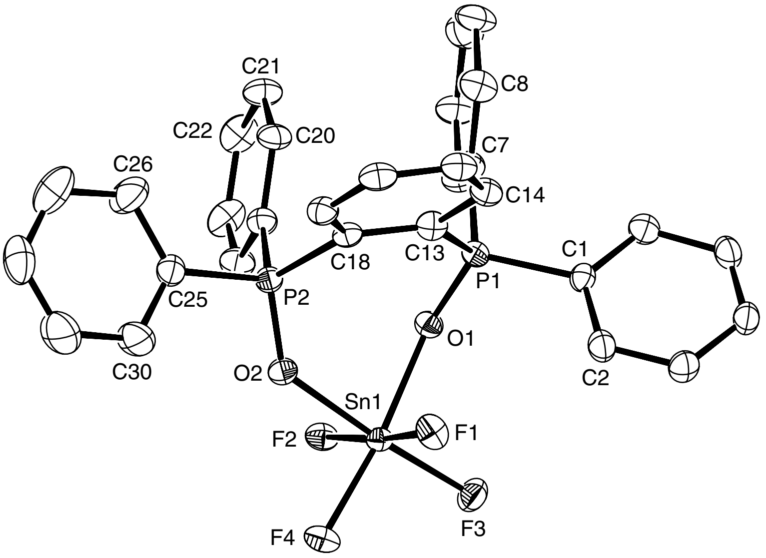

Fig. 2. Structure of the tin residue in $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}] \cdot CH_2Cl_2 \cdot H_2O$ showing the atom numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

Table 5
Selected bond lengths (Å) and angles (°) for $[o\text{-}C_6H_4(P(O)Ph_2)_2] \cdot CH_2Cl_2$

P1–O1	1.484(2)	P2–O2	1.485(2)
P1–C1	1.809(3)	P2–C18	1.838(3)
P1–C7	1.810(3)	P2–C19	1.800(3)
P1–C13	1.824(3)	P2–C25	1.815(3)
O1–P1–C1	115.74(13)	O2–P2–C18	114.46(12)
O1–P1–C7	110.22(12)	O2–P2–C19	116.22(13)
O1–P1–C13	112.88(13)	O2–P2–C25	109.84(12)
C1–P1–C7	105.49(13)	C18–P2–C19	105.81(13)
C1–P1–C13	105.77(13)	C18–P2–C25	104.88(13)
C7–P1–C13	106.02(13)	C19–P2–C25	104.60(13)

the Me_3PO case, coordination of the diphosphine dioxide to the SnF_4 results in a significant lengthening of the P–O bond, from 1.484(2), 1.485(2) in the "free" ligand to 1.512(5), 1.525(5) Å in the complex. A few poor quality crystals were also obtained from a solution of $[SnF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CH_2Cl_2 after several weeks. X-ray examination of these established them as the compound $[SnClF_3\{o\text{-}C_6H_4(P(O)Me_2)_2\}]$ containing a chelating diphosphine dioxide. The origin of the chlorine atom is presumably from reaction with the solvent and the oxygen in the phosphine oxide from aerial oxidation.[1]

Most interesting is the comparison with data on other tin(IV) phosphine oxides. Tudela [18] noted that in *cis*- and *trans*-$[SnBr_4(Ph_3PO)_2]$ the Sn–O (2.080(8), 2.101(9) Å) and P–O (1.515(8), 1.516(9)(av) Å) distances were the same within the usual criteria showing that the geometric isomer present has no effect, as might be expected for hard donor–acceptor interactions on a p-block metal. However, when one compares the key distances along the series $[SnX_4(R_3PO)_2]$ (Table 6) one finds that Sn–O increases with X F < Cl < Br < I. The substantially shorter Sn–O distance in the tin(IV) fluoride is clearly consistent with stronger binding of the ligand indicative of stronger Lewis acidity of the SnF_4. Moreover, studies of phosphine oxide complexes of hard early transition metals such as Y(III) or Sc(III) have shown that the metal–oxygen distances are independent of the R group (Me or Ph), although they do vary with the metal coordination number [20,21]. From Table 6 it is also notable that the P–O distance in the fluoride complex is markedly longer than in the other examples, (albeit some of the comparator data are not of high precision) which also supports stronger donation from O → Sn. The trends are replicated in $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ where the data in Table 4 can be compared with the structural data on $[SnI_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ [13] (Table 6). In the iodo-complex the *d*(Sn–O) are much longer, consistent with the relative Lewis acidity of the tin centres.

2.3. $[SnX_4L_2]$ X = Cl, Br or I; L = Ph_3PO, Ph_3AsO or Me_3PO – some comparisons

These complexes have been studied on several occasions and structures have been reported for *cis*-$[SnX_4(Ph_3PO)_2]$ (X = Cl or Br) [18,23,25] and *trans*-$[SnBr_4(Ph_3PO)_2]$ [22,24]. The IR spectra have been discussed in detail [5,6,26] and our data are generally in agreement with the literature and hence not discussed further. Curiously, little NMR data have been reported previously and complete data are presented in Table 7. As can be seen, whilst both isomers are present in CH_2Cl_2 solutions of the chloro-complexes, only one isomer was present for the iodo-complexes, and only small amounts or essentially none of the second form

---

[1] Crystal data for $[SnClF_3\{o\text{-}C_6H_4(P(O)Me_2)_2\}] \cdot 1/2CH_2Cl_2$: $M_w = 483.77$; orthorhombic, space group *Pbcn* (no. 60), $Z = 8$, $T = 120$ K, $a = 15.290(5)°$, $b = 17.266(6)°$, $c = 13.380(3)$ Å, $V = 3532.3(19)$ Å^3; 3772 unique data gave $R_1 = 0.095$, $wR_2 = 0.173(I > 2\sigma(I))$ based on 186 independent parameters with $S = 0.95$.

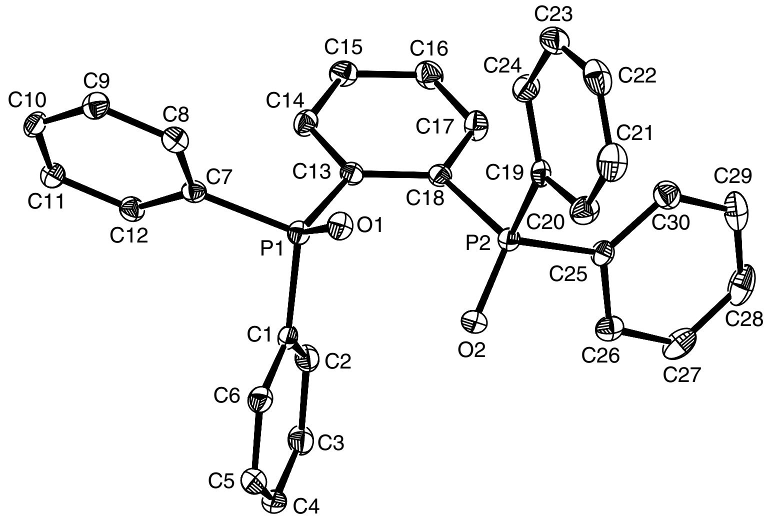

Fig. 3. Structure of $[o\text{-}C_6H_4(P(O)Ph_2)_2] \cdot CH_2Cl_2$ showing the atom numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

Table 6
Selected structural data on tin(IV) phosphine oxides

Compound	d(Sn–O) (Å)	d(P–O) (Å)	Ref.
trans-$[SnF_4(Me_3PO)_2]$[a]	2.045(3)	1.532(3)	this work
cis-$[SnCl_4(Ph_3PO)_2]$[b]	2.083(2)	1.510(2)	[22]
cis-$[SnCl_4(Ph_3PO)_2]$[c]	2.086(2)	1.505(2)	[23]
trans-$[SnBr_4(Ph_3PO)_2]$[b]	2.102(9), 2.100(8)	1.504(9), 1.527(9)	[24]
cis-$[SnBr_4(Ph_3PO)_2]$[b]	2.080(8)	1.515(8)	[18]
cis-$[SnI_4(Ph_3PO)_2]$[b]	2.11(2), 2.15(2)	1.47(2), 1.50(2)	[25]
$[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$[a]	2.071(5), 2.088(5)	1.512(5), 1.525(5)	this work
$[SnI_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$[d]	2.120(5), 2.138(5)	1.509(6), 1.513(5)	[13]

[a] 120 K.
[b] 295 K.
[c] 90 K.
[d] 150 K.

in the bromo-complexes. The complexes are labile in solution and cooling the samples is necessary to observe sharp resonances and resolve couplings; the temperatures at which the presented data were obtained are given in Table 7. The trends in the spectroscopic data were also examined to see if support for the greater Lewis acidity of the SnF_4 was forthcoming. The IR data, specifically the ν(PO), are not useful due to the broadness of the bands and the presence of overlapping bands of the geometric isomers, but even if this were not the case, coupling with other vibrations would complicate any comparisons. The $^{31}P\{^1H\}$ NMR data are more useful (Tables 2 and 7). The chemical shift differences between the geometric isomers are small and therefore one can compare directly the changes in chemical shift simply as a function of the halide present. This shows a small but clear shift to high frequency along the series F > Cl > Br > I consistent with decreased acceptor power along this series and in agreement with the conclusions from the X-ray data above. The ^{119}Sn NMR data are not useful in this respect since the chemical shifts reflect a number of competing factors including electronegativity of the substituents, mutual ligand interactions and ligand polarisabilities [7,29]. The shift to low frequency $[SnCl_4(R_3EO)_2] > [SnF_4(R_3EO)_2] > [SnBr_4(R_3EO)_2]$ parallels that in the hexahalostannates(IV) [27–29]. Tin-119 resonances are rarely observed for iodotin species mainly due to exchange reactions in solution resulting from the weak Lewis acidity of SnI_4. The data show that SnF_4 is the strongest Lewis acid in the series SnX_4 (X = F, Cl, Br, I) towards hard bases.

3. Experimental

All compounds were made under a dinitrogen atmosphere using dry solvents and standard Schlenk and glove box techniques. SnF_2, $SnCl_4$, $SnBr_4$ and SnI_4 were obtained from Aldrich and used as received. $[SnF_4(MeCN)_2]$ and $[SnF_4(THF)_2]$ were made as described [17]. Ligands were obtained from Aldrich (Me_3PO, Ph_3PO, Ph_3AsO) and were dried by heating in vacuo before use. Other ligands were made by literature methods: $o\text{-}C_6H_4(P(O)Ph_2)_2$, $o\text{-}C_6H_4(P(O)Me_2)_2$, Me_3AsO, $Ph_2P(O)CH_2P(O)Ph_2$ [13,30,31]. IR spectra were recorded as Nujol mulls on a Perkin Elmer PE 983G spectrometer, ^1H NMR spectra in $CDCl_3$ solutions on a Bruker AV300, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and ^{119}Sn NMR spectra on a Bruker DPX400 and referenced to 85% H_3PO_4, $CFCl_3$ and neat $SnMe_4$, respectively. Microanalytical measurements were performed by the microanalytical service, Strathclyde University.

3.1. $[SnF_4(Ph_3PO)_2]$

$[SnF_4(MeCN)_2]$ (0.277 g, 1.0 mmol) was suspended in CH_2Cl_2 (20 mL) and Ph_3PO (0.612 g, 2.2 mmol) added

Table 7
Selected NMR data on comparator complexes

Compound	δ^{31}P{^{1}H}[a]	$^{2}J(^{31}P–^{119}Sn)$ (Hz)[b]	δ ^{119}Sn	Ratio of isomers
$[SnCl_4(Me_3PO)_2]$	+63.4 (273 K)[c]	140	−695(t) (243 K)	4
	+62.5	106	−686(t)	1
$[SnBr_4(Me_3PO)_2]$	+61.0 (223 K)	140	−1439(t)	
$[SnI_4(Me_3PO)_2]$	+58.3 (193 K)	n.o.	n.o.[d]	
$[SnCl_4(Ph_3PO)_2]$	+40.8 (233 K)	198	−710(t) (233 K)	1
	+40.35	162	−698(t)	5
$[SnBr_4(Ph_3PO)_2]$	+38.9 (223 K)	214	−1480(t) (223 K)	
$[SnI_4(Ph_3PO)_2]$	+36.5 (183 K)	n.o.	n.o.	
$[SnCl_4(Ph_3AsO)_2]$			−639(s) (243 K)	1
			−637(s)	2
$[SnBr_4(Ph_3AsO)_2]$			−1364(s) (233 K)	
$[SnI_4(Ph_3AsO)_2]$			n.o.	
[SnCl$_4${o-C$_6$H$_4$(P(O)Ph$_2$)$_2$}][e]	+42.4 (295 K)			
[SnBr$_4${o-C$_6$H$_4$(P(O)Ph$_2$)$_2$}][e]	+41.6 (295 K)			
[SnI$_4${o-C$_6$H$_4$(P(O)Ph$_2$)$_2$}][e]	+39.8 (295 K)			

[a] In CH_2Cl_2–10% $CDCl_3$.

[b] Separate resonances for ^{119}Sn and ^{117}Sn couplings not resolved in ^{31}P NMR spectra, couplings are from ^{119}Sn spectra.

[c] Ligand chemical shifts are: Me_3PO + 38, Ph_3PO + 28, *o*-C$_6$H$_4$(P(O)Ph$_2$)$_2$ + 31.

[d] n.o., Not observed in temperature range 295–180 K.

[e] Data from [13].

and the mixture stirred at room temperature for 2 h. The white solid was filtered off, recrystallised from hot CH_2Cl_2 and dried in vacuo. Yield: 0.66 g, 88%. *Anal.* Calc. for $C_{36}H_{30}F_4O_2P_2Sn \cdot 3CH_2Cl_2$: C, 46.6; H, 3.6. Found: C, 47.1; H, 3.7%.

3.2. *[SnF$_4$(Ph$_3$AsO)$_2$]*

Prepared similarly from $[SnF_4(MeCN)_2]$ (0.156 g, 0.56 mmol) and Ph_3AsO (0.40 g, 1.24 mmol). Yield: 0.30 g, 64%. *Anal.* Calc. for $C_{36}H_{30}As_2F_4O_2Sn \cdot 2CH_2Cl_2$: C, 45.2; H, 3.4. Found: C, 45.3; H, 3.2%.

3.3. *[SnF$_4$(Me$_3$PO)$_2$]*

Prepared similarly from $[SnF_4(MeCN)_2]$ (0.28 g, 1.0 mmol) and Me_3PO (0.19 g, 2.05 mmol) and stirred for 8 h. Yield: 0.30 g, 79%. *Anal.* Calc. for $C_6H_{18}F_4O_2P_2Sn$: C, 19.0; H, 4.8. Found: C, 18.2; H, 4.7%.

3.4. *[SnF$_4$(Me$_3$AsO)$_2$]*

Prepared similarly from $[SnF_4(MeCN)_2]$ (0.32 g, 1.15 mmol) and Me_3AsO (0.34 g, 2.5 mmol). Yield: 0.495 g, 92%.

3.5. *[SnF$_4${o-C$_6$H$_4$(P(O)Ph$_2$)$_2$}]*

$[SnF_4(MeCN)_2]$ (0.138 g, 0.50 mmol) and *o*-C$_6$H$_4$(P(O)Ph$_2$)$_2$ (0.239 g, 0.50 mmol) were stirred together for 0.5 h in CH_2Cl_2 (20 mL). The white precipitate was filtered off and dried in vacuo. Yield: 0.23 g, 68%. *Anal.* Calc. for $C_{30}H_{24}F_4O_2P_2Sn \cdot 0.5CH_2Cl_2$: C, 51.2; H, 3.5. Found: C, 51.2; H, 3.3%.

3.6. *[SnF$_4${Ph$_2$P(O)CH$_2$P(O)Ph$_2$}]*

Powdered $Ph_2P(O)CH_2P(O)Ph_2$ (0.22 g, 0.53 mmol) and $[SnF_4(MeCN)_2]$ (0.133 g, 0.48 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature overnight. The white precipitate was then filtered off and dried in vacuo. Yield: 0.27 g, 92%. *Anal.* Calc. for $C_{25}H_{22}F_4O_2P_2Sn \cdot 0.5CH_2Cl_2$: C, 46.9; H, 3.6. Found: C, 46.5; H, 3.7%.

3.7. *[SnF$_4${o-C$_6$H$_4$(P(O)Me$_2$)$_2$}]*

$[SnF_4(THF)_2]$ (0.30 g, 0.88 mmol) was dissolved in CH_2Cl_2 (5 mL), *o*-C$_6$H$_4$(P(O)Me$_2$)$_2$ (0.20 g, 0.87 mmol) dissolved in CH_2Cl_2 (5 mL) was added and the mixture stirred at room temperature for 2 h. The white solid was filtered off and dried in vacuo. Yield: 0.257 g, 68%.

3.8. *[SnX$_4$L$_2$] (X = Cl, Br or I; L = Ph$_3$PO, Ph$_3$AsO or Me$_3$PO)*

These were made by reaction of the anhydrous tin(IV) halide with the ligand in anhydrous CH_2Cl_2 using literature methods [6,26].

3.9. *X-ray experimental*

Crystals of [SnF$_4${*o*-C$_6$H$_4$(P(O)Ph$_2$)$_2$}] · CH$_2$Cl$_2$ · H$_2$O were obtained from CH_2Cl_2 solution layered with hexane and *o*-C$_6$H$_4$(P(O)Ph$_2$)$_2$ from CH_2Cl_2 solution. Brief details of the data collection and refinement are presented in Table 8. Data collection used a Bruker–Nonius Kappa CCD diffractometer with the crystal held at 120 K in a cold nitrogen stream. Structure solution [32] and refinement [33]

Table 8
Crystallographic data[a]

Compound	$[SnF_4(Me_3PO)_2]$	$[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}] \cdot CH_2Cl_2 \cdot H_2O$	$[o\text{-}C_6H_4(P(O)Ph_2)_2] \cdot CH_2Cl_2$
Formula	$C_6H_{18}F_4O_2P_2Sn$	$C_{31}H_{28}Cl_2F_4O_3P_2Sn$	$C_{31}H_{26}Cl_2O_2P_2$
Formula weight	378.83	776.06	563.36
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	6.190(2)	17.579(3)	10.840(2)
b (Å)	11.089(4)	10.1696(15)	14.734(3)
c (Å)	9.504(3)	18.178(4)	17.576(2)
β (°)	94.32(3)	99.160(8)	104.467(12)
U (Å^3)	650.5(4)	3208.2(10)	2718.3(8)
Z	2	4	4
μ(Mo Kα) (mm^{-1})	2.24	1.12	0.38
Total no. of observations	6333	35141	28169
No. of unique observations (R_{int})	1486 (0.056)	7058 (0.055)	4775 (0.101)
No. of parameters, restraints	71, 0	395, 5	335, 0
R_1, wR_2 ($I > 2\sigma(I)$)[b]	0.034, 0.073	0.070, 0.183	0.046, 0.095
R_1, wR_2 (all data)	0.049, 0.079	0.082, 0.188	0.088, 0.112

[a] Other items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; $\theta_{max} = 27.5°$.

[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

were routine. In $[SnF_4\{o\text{-}C_6H_4(P(O)Ph_2)_2\}] \cdot CH_2Cl_2 \cdot H_2O$ the $CH_2Cl_2$was disordered with one of the chlorine atoms occupying three sites. The two remaining peaks in the difference map were interpreted as half occupancy water molecules with the O···O distance appropriate for an H-bond. No H atoms were included for these solvate molecules. Several attempts were made to grow X-ray quality crystals of $[SnF_4(Me_3AsO)_2]$ by vapour diffusion from EtOH and Et_2O. The data from the crystals obtained did not lead to a structure possibly due to twinning.

4. Supplementary data

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 278050–278052. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

Acknowledgements

We thank EPSRC for support (MFD), and M.J. Darmody for the preparation of some of the tin(IV) complexes in Section 3.8.

References

[1] A.D. Adley, P.H. Bird, A.R. Fraser, M. Onyszchuk, Inorg. Chem. 11 (1972) 1402.

[2] C.E. Michelson, D.S. Dyer, R.O. Ragsdale, J. Inorg. Nucl. Chem. 32 (1970) 833.

[3] P.A.W. Dean, D.F. Evans, J. Chem. Soc. A (1968) 1154.

[4] C.J. Wilkins, H.M. Haendler, J. Chem. Soc. (1965) 3174.

[5] J.P. Clark, V.M. Langford, C.J. Wilkins, J. Chem. Soc. A (1967) 792.

[6] S.H. Hunter, V.M. Langford, G.A. Rodley, C.J. Wilkins, J. Chem. Soc. A (1968) 305.

[7] P.G. Harrison, The Chemistry of Tin, Blackie & Son, London, 1989.

[8] S.J. Ruzicka, A.E. Merbach, Inorg. Chim. Acta 20 (1976) 221.

[9] S.J. Ruzicka, A.E. Merbach, Inorg. Chim. Acta 22 (1977) 191.

[10] S.E. Dann, A.R.J. Genge, W. Levason, G. Reid, J. Chem. Soc., Dalton Trans. (1996) 4471.

[11] S.E. Dann, A.R.J. Genge, W. Levason, G. Reid, J. Chem. Soc., Dalton Trans. (1997) 2207.

[12] A.R.J. Genge, W. Levason, G. Reid, J. Chem. Soc., Dalton Trans. (1997) 4549.

[13] A.R.J. Genge, W. Levason, G. Reid, Inorg. Chim. Acta 288 (1999) 142.

[14] W. Levason, M.L. Matthews, R. Patel, G. Reid, M. Webster, New J. Chem. 27 (2003) 1784.

[15] M. Bork, R. Hoppe, Z. Anorg. Allgem. Chem. 622 (1996) 1557.

[16] D. Tudela, F. Rey, Z. Anorg. Allgem. Chem. 575 (1989) 202.

[17] D. Tudela, J.A. Patron, Inorg. Synth. 31 (1997) 92.

[18] D. Tudela, J.D. Tornero, A. Monge, A.J. Sánchez-Herencia, Inorg. Chem. 32 (1993) 3928.

[19] L.M. Engelhardt, C.L. Raston, C.R. Whitaker, A.H. White, Aust. J. Chem. 39 (1986) 2151.

[20] L. Deakin, W. Levason, M.C. Popham, G. Reid, M. Webster, J. Chem. Soc., Dalton Trans. (2000) 2439.

[21] N.J. Hill, W. Levason, M.C. Popham, G. Reid, M. Webster, Polyhedron 21 (2002) 445.

[22] A.I. Tursina, L.A. Aslanov, S.V. Medvedev, A.V. Yatsenko, Koord. Khim. 11 (1985) 417.

[23] T. Szymanska-Buzar, T. Glowiak, I. Czelusniak, Main Group Met. Chem. 24 (2001) 821.

[24] A.I. Tursina, A.V. Yatsenko, S.V. Medvedev, V.V. Chernyshev, L.A. Aslanov, Zh. Strukt. Khim. 27 (1986) 157.

[25] A.I. Tursina, L.A. Aslanov, V.V. Chernyshev, S.V. Medvedev, A.V. Yatsenko, Koord. Khim. 12 (1986) 420.

[26] P.G. Harrison, B.C. Lane, J.J. Zuckerman, Inorg. Chem. 11 (1972) 1537.

[27] K.B. Dillon, A. Marshall, J. Chem. Soc., Dalton Trans. (1984) 1245.

[28] R. Colton, D. Dakternieks, Inorg. Chim. Acta 71 (1983) 101.

[29] J. Mason, Multinuclear NMR, Plenum, New York, 1987.

[30] A. Merijanian, R.A. Zingaro, Inorg. Chem. 5 (1966) 187.

[31] W. Levason, R. Patel, G. Reid, J. Organomet. Chem. 688 (2003) 280.

[32] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Göttingen, 1997.

[33] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.