DOI: 10.1002/ejic.200600202

Tin(IV) Fluoride Complexes with Tertiary Phosphane Ligands – A Comparison of Hard and Soft Donor Ligands

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Keywords: Tin / Fluoride / Phosphane / Multinuclear NMR / Crystal structures

The first phosphane complexes of the hard Lewis acid SnF_4 have been synthesised including *trans*-$[SnF_4(PR_3)_2]$ (R = Me or Cy) and *cis*-$[SnF_4$(diphosphane)] [diphosphane = $R_2P(CH_2)_2PR_2$, R = Me, Et, Ph or Cy; *o*-$C_6H_4(PR_2)_2$, R = Me or Ph] and characterised by IR and multinuclear NMR (^1H, ^{19}F, ^{31}P, ^{119}Sn) spectroscopy. The crystal structures of *trans*-$[SnF_4(PCy_3)_2]$ and *cis*-$[SnF_4\{Et_2P(CH_2)_2PEt_2\}]$ are reported. Tin(IV) fluoride complexes of 2,2′-bipyridyl, 1,10-phenanthroline, $MeO(CH_2)_2OMe$, $Me_2N(CH_2)_2NMe_2$, pyridine and THF have been characterised by multinuclear NMR spectroscopy, the structures of *cis*-$[SnF_4$(L–L)] (L–L = 1,10-phenanthroline and $MeO(CH_2)_2OMe$) determined, and the properties were compared with those of the phosphane complexes. Complexes of *o*-$C_6H_4(PMe_2)_2$, $Et_2P(CH_2)_2PEt_2$, and $MeC(CH_2AsMe_2)_3$ with $SnCl_4$ and $SnBr_4$ are also reported and the structures of *cis*-$[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$ and *cis*-$[SnBr_4\{\kappa^2\text{-}MeC(CH_2AsMe_2)_3\}]$ described. Attempts to prepare tertiary arsane complexes of SnF_4 have been unsuccessful.

Introduction

Tin(IV) chloride is widely used in synthesis both as a source of tin(IV) and as a strong Lewis acid.[1,2] A very wide range of adducts of $SnCl_4$ with neutral ligands (L) are known, mostly six-coordinate $[SnCl_4L_2]$, and similar complexes are formed by $SnBr_4$ and SnI_4, although Lewis acidity decreases $SnCl_4 > SnBr_4 >> SnI_4$. The majority of these ligands have hard O or N donor atoms, but examples with softer P, As, S, Se or Te donors have also been characterised.[3–10] In marked contrast little is known about adducts of SnF_4 with neutral ligands. Some examples were reported in the period 1950–1975, often as part of larger surveys including the heavier tin(IV) halides, but little data were provided and only a single complex, $[SnF_4$(2,2′-bipy)], was structurally characterised.[11–16] There appear to be no reports of SnF_4 complexes with softer donor ligands. This neglect in part is similar to that of other p-block fluorides, whose Lewis acidity, except towards F^- or in superacid media (for MF_5, M = As or Sb), is little explored, but also reflects the more difficult synthetic entry into the complexes. The SnX_4 (X = Cl, Br or I) are tetrahedral molecules readily soluble in weak or non-coordinating solvents such as chlorocarbons, hydrocarbons or arenes, and synthesis of $[SnX_4(L)_2]$ usually involves simply mixing the constituents in a solvent with precautions to avoid hydrolysis. In contrast, SnF_4 has a polymeric structure based upon vertex sharing SnF_6 octahedra,[17] and although readily hydrolysed, is otherwise rather unreactive and insoluble in weak donor solvents. Tudela and co-workers have reported[18] the preparation of $[SnF_4(MeCN)_2]$ from SnF_2 and I_2 in MeCN. We have found that this provides a convenient entry into the chemistry of SnF_4, and recently reported the synthesis and detailed spectroscopic and structural studies of a series of tin(IV) fluoride complexes of phosphane- or arsane oxides, including $[SnF_4(R_3EO)_2]$ (R_3EO = Ph_3PO, Ph_3AsO, Me_3PO or Me_3AsO) and $[SnF_4$(L–L)] {L–L = *o*-$C_6H_4[P(O)Ph_2]_2$, *o*-$C_6H_4[P(O)Me_2]_2$ or $Ph_2P(O)CH_2P(O)Ph_2$}.[19] These studies showed that toward pnictogen oxide ligands, SnF_4 was the strongest Lewis acid of the four tin(IV) halides, evidenced by shorter Sn–O and longer P–O bonds and larger ^{31}P NMR coordination shifts in the fluorides, compared to corresponding data in complexes with the heavier halides. Here we report the first investigations of the synthesis, structures and spectroscopy of tin(IV) fluoride adducts with tertiary phosphanes and arsanes. Comparisons of these complexes with SnF_4 species containing N- or O donor ligands and with the heavier Sn^{IV} halides are described.

Results and Discussion

Phosphane Complexes: The reactions of $[SnF_4(MeCN)_2]$ with PMe_3 or PCy_3 (L), in anhydrous dichloromethane under a dinitrogen atmosphere yielded $[SnF_4L_2]$ complexes in moderate to good yields. However we were unable to obtain a pure sample of $[SnF_4(PPh_3)_2]$ by this route. Since neither the $[SnF_4(MeCN)_2]$ nor the resulting complexes are easily soluble in this solvent, some care is needed to obtain pure

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products. The complexes are both moisture and dioxygen sensitive in solution, although the dry solids only slowly decomposed in air (see below). They are much less soluble in chlorocarbons than corresponding complexes of the heavier tin halides, and prone to retain lattice solvent as evidenced in their ^{1}H NMR spectra and in some of the X-ray structures.[19] [SnF$_4$(THF)$_2$][18] was also explored as a synthon, but appeared to have no advantages over the acetonitrile complex. We also reacted [SnF$_4$(MeCN)$_2$] with molten PPh$_3$, but the ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra showed a complex mixture of products, and it appears that some fluorination of the phosphane occurs under these conditions. The [SnF$_4$L$_2$] complexes were identified as *trans* isomers from their ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra which are respectively triplets and quintets [in each case with weak satellites due to ^{119}Sn and ^{117}Sn (^{117}Sn: I = 1/2, 7.7%, Ξ = 35.63 MHz; ^{119}Sn: I = 1/2, 8.6%, Ξ = 37.27 MHz)] (Table 1). The ^{119}Sn NMR spectra are 15-line patterns (triplet of quintets) with the coupling constants shown in Table 1. The structure of [SnF$_4$(PCy$_3$)$_2$] was determined and shows (Table 2, Figure 1) a centrosymmetric molecule with Sn–P = 2.654(1) Å and Sn–F = 1.959(2), 1.980(2) Å. The Sn–P is longer than that in *trans*-[SnCl$_4$(PEt$_3$)$_2$] [2.615(5) Å],[20] and marginally longer than in *trans*-[SnCl$_4${κ^1-Ph$_2$PCH$_2$PPh$_2$}$_2$] [2.649(1) Å],[21] but shorter than found in *trans*-[SnI$_4$(P*i*Pr$_3$)$_2$] [2.69(1) Å],[22] although the differing steric requirements of the three phosphanes preclude a more detailed discussion.

Table 2. Selected bond lengths [Å] and angles [°] for *trans*-[SnF$_4$(PCy$_3$)$_2$].[a]

Sn1–F1	1.959(2)	Sn1–F2	1.980(2)
Sn1–P1	2.6538(11)	P1–C1	1.860(4)
P1–C7	1.845(4)	P1–C13	1.851(4)
F1–Sn1–F2	91.21(10)	F1–Sn1–F2a	88.79(10)
F1–Sn1–P1	89.86(7)	F2–Sn1–P1	88.24(7)
C1–P1–C7	108.09(17)	C7–P1–C13	104.81(16)
C1–P1–C13	107.96(17)	Sn1–P1–C1	112.95(12)
Sn1–P1–C7	113.77(12)	Sn1–P1–C13	108.81(12)
F1–Sn1–P1–C1	–60.0(2)	F1–Sn1–P1–C7	63.7(2)
F1–Sn1–P1–C13	–179.9(2)		

[a] Symmetry operation, a: –*x*, –*y*, 2–*z*.

The corresponding reactions of [SnF$_4$(MeCN)$_2$] with the diphosphanes Me$_2$P(CH$_2$)$_2$PMe$_2$, Et$_2$P(CH$_2$)$_2$PEt$_2$, Cy$_2$P(CH$_2$)$_2$PCy$_2$, *o*-C$_6$H$_4$(PPh$_2$)$_2$, Ph$_2$P(CH$_2$)$_2$PPh$_2$ and *o*-C$_6$H$_4$(PMe$_2$)$_2$ (L–L) gave [SnF$_4$(L–L)]. The [SnF$_4${Me$_2$P(CH$_2$)$_2$PMe$_2$}] was essentially insoluble in chlorocarbons or nitromethane and decomposed by DMSO, and although it appeared to be similar to the other examples, we were unable to obtain any solution spectroscopic data and it will not be discussed further. The other examples are as expected *cis* isomers showing doublet of doublets of triplets in their ^{31}P{^{1}H} NMR spectra and two ^{19}F{^{1}H} resonances, a triplet of triplets for the F$_{trans\text{-F}}$ and a doublet of doublet of triplets for the F$_{trans\text{-P}}$, with the coupling constants shown in Table 1 (again all resonances have tin satellites). The ^{119}Sn NMR resonances of the diphosphane com-

Table 1. Selected NMR spectroscopic data for SnF$_4$ complexes.[a]

Compound	δ(^{31}P{^{1}H})[b]	ΔP[c]	δ(^{119}Sn)[d]	δ(^{19}F{^{1}H})	^1J(^{19}F-^{119}Sn)	^nJ(^{31}P-^{19}F)	^2J(^{19}F-^{19}F)	^nJ(^{31}P-^{119}Sn)
[SnF$_4${*o*-C$_6$H$_4$(PMe$_2$)$_2$}]	–37.8 (t,d,d)	17	–657.6 (t,t,t)	–131.7 (t,t)	2470	117, 98, 54	42	1520
				–161.1 (d,d,t)	2160			
[SnF$_4${*o*-C$_6$H$_4$(PPh$_2$)$_2$}]	–18.9 (t,d,d)	–6	–665.9 (t,t,t)	–123.8 (t,t)	2627	93, 73, 48	52	1512
				–155.5 (d,d,t)	2207			
trans-[SnF$_4$(Me$_3$P)$_2$]	–19.1 (q)	43	–628.0 (t,q)	–132.8 (t)	2745	155		2975
trans-[SnF$_4$(Cy$_3$P)$_2$]	+22.2 (q)	11	–628.5 (t,q)	–98.9 (t)	2993	124		2530
[SnF$_4${Et$_2$P(CH$_2$)$_2$PEt$_2$}]	–11.6 (t,d,d)	6	–649.4 (t,t,t)	–123.8 (t,t)	2552	110, 95, 46	40	1628
				–150.2 (d,d,t)	2183			
[SnF$_4${Cy$_2$P(CH$_2$)$_2$PCy$_2$}]	–9.9 (t,d,d)	–12	–639.1 (t,t,t)	–113.7 (t,t)	2644	98, 88, 46	46	1528
				–139.5 (d,d,t)	2205			
[SnF$_4${Ph$_2$P(CH$_2$)$_2$PPh$_2$}]	–17.8 (t,d,d)	–4	–668.1 (t,t,t)	–112.4 (t,t)	2650	118, 87, 44	46	1630
				–147.1 (d,d,t)	2212			
[SnF$_4$(2,2′-bipyridyl)]			–708.2 (t,t)	–149.8 (t)	1964		48	
				–179.8 (t)	1978			
[SnF$_4$(1,10-phen)]			–715.1 (t,t)	–149.5 (t)	1987		50	
				–180.8 (t)	1982			
[SnF$_4$(THF)$_2$] (220 K)								
trans isomer			–775.4 (q)	–166.7 (s)	1910			
cis isomer			–775.3 (t,t)	–166.2 (t)	1918		54	
				–178.8 (t)	2074			
trans-[SnF$_4$(pyridine)$_2$]			–670.8 (q)	–163.8 (s)	1983			
[SnF$_4${Me$_2$N(CH$_2$)$_2$NMe$_2$}]			[e]	–167.8 (t)	2266		50	
				–184.4 (t)	2096			
[SnF$_4$(MeCN)$_2$]			n.o.[f]	–181.0 (s)	n.o.			
[SnF$_4${MeO(CH$_2$)$_2$OMe}]			–753.8 (t,t)	–167.1	2233		61	
(190 K)				–183.3	2189			

[a] In CH$_2$Cl$_2$/10% CDCl$_3$. [b] Ligand chemical shifts are: *o*-C$_6$H$_4$(PMe$_2$)$_2$ –55 ppm; *o*-C$_6$H$_4$(PPh$_2$)$_2$ –13 ppm; Ph$_2$P(CH$_2$)$_2$PPh$_2$ –13 ppm; Et$_2$P(CH$_2$)$_2$PEt$_2$ –18 ppm; Me$_2$P(CH$_2$)$_2$PMe$_2$ –48 ppm; Cy$_2$P(CH$_2$)$_2$PCy$_2$ +2 ppm; PMe$_3$ –62 ppm; PCy$_3$ +11.5 ppm. [c] Coordination shift ($\delta_{\text{complex}}-\delta_{\text{ligand}}$). [d] ^{119}Sn NMR spectra were typically recorded at 250 K. [e] Insufficently soluble to record spectrum. [f] n.o. = not observed in temperature range 295–180 K.

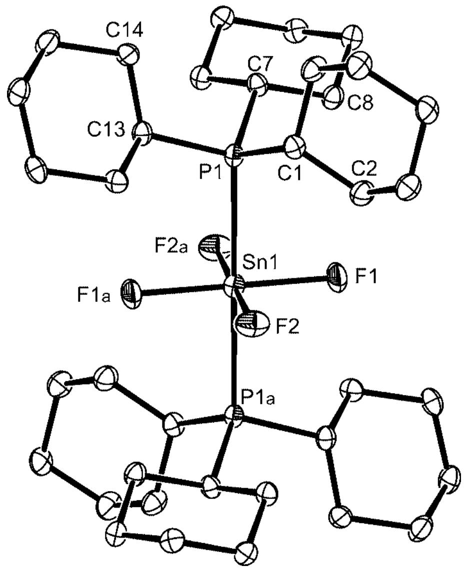

Figure 1. Structure of *trans*-$[SnF_4(PCy_3)_2]$ showing a partial atom numbering scheme. Cyclohexyl groups are numbered cyclically starting at the P-bonded C atom. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Sn1 is positioned on a centre of symmetry. Symmetry operation, a: $-x$, $-y$, $2-z$.

plexes are 27-line patterns (triplet of triplets of triplets), the spectra typically being recorded at 250 K to reduce any line broadening due to the onset of reversible ligand dissociation. The modest solubility necessitated long accumulations, and in some cases the weakest outer lines of the multiplets were rather unclear, although the various couplings were readily extracted (Table 1). The trends in the various NMR parameters will be discussed in a later section in comparison with those of related complexes (see below). The structure of $[SnF_4\{Et_2P(CH_2)_2PEt_2\}]$ was determined and confirms the *cis* geometry deduced from the NMR studies (Table 3, Figure 2). The Sn–P distance is 2.606(1) Å, shorter than in the *trans*-$[SnF_4(PCy_3)_2]$ [2.654(1) Å], and also shorter than the value in *cis*-$[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$ [2.648(2) Å] described below. The Sn–$F_{trans\text{-}F}$ 1.986(2) Å is significantly longer than Sn–$F_{trans\text{-}P}$ 1.953(2) Å, a pattern which is found in most adducts of SnX_4 (X = Cl, Br or I) with soft donor ligands.[6–10]

Table 3. Selected bond lengths [Å] and angles [°] for $[SnF_4\{Et_2P(CH_2)_2PEt_2\}]$.[a]

Sn1–F1	1.9863(17)	P1–C1	1.821(3)
Sn1–F2	1.9532(16)	P1–C2	1.815(3)
Sn1–P1	2.6058(9)	P1–C4	1.814(3)
P1···P1a	3.409(2)		
F1–Sn1–F2	92.60(7)	P1–Sn1–F1	84.66(5)
F1–Sn1–F2a	91.36(7)	P1–Sn1–F2	93.14(6)
F1–Sn1–F1a	174.29(10)	P1–Sn1–F1a	91.02(5)
F2–Sn1–F2a	92.29(10)	P1–Sn1–F2a	173.40(5)
P1–Sn1–P1a	81.70(4)	Sn1–P1–C1	102.52(9)
Sn1–P1–C2	114.54(10)	Sn1–P1–C4	116.34(10)

[a] Symmetry operation, a: $-x$, y, $½-z$.

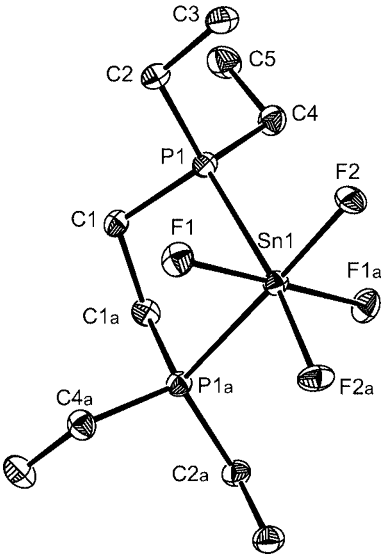

Figure 2. Structure of $[SnF_4\{Et_2P(CH_2)_2PEt_2\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. A twofold axis passes through Sn1 and the centre of the C1–C1a bond. Symmetry operation, a: $-x$, y, $1/2-z$.

Other SnF_4 Complexes: A small number of complexes of hard N- or O-donor ligands, previously obtained directly from SnF_4, were re-prepared in this study for comparison purposes from $[SnF_4(MeCN)_2]$, viz $[SnF_4(L–L)]$ (L–L = 2,2′-bipyridyl, 1,10-phenanthroline, *N*,*N*,*N′N′*-tetramethylethanediamine and 1,2-dimethoxyethane) and $[SnF_4(pyridine)_2]$. The complexes with N donor ligands are unaffected by exposure to air for several hours, although moisture-sensitive in solution. They are much less readily decomposed than the phosphane complexes. The solid $[SnF_4(L)_2]$ [L = THF or L_2 = $MeO(CH_2)_2OMe$] are very deliquescent. The $^{19}F\{^1H\}$ and ^{119}Sn NMR spectroscopic data are shown in Table 1. Although the ranges overlap, there is a general shift to lower frequency in the ^{119}Sn NMR shifts with donor, P → N → O. The complexes with L–L = 2,2′-bipyridyl, 1,10-phenanthroline, $Me_2N(CH_2)_2NMe_2$ have the expected *cis* geometry, whilst the $[SnF_4(pyridine)_2]$ is the *trans* isomer. In contrast to the N donor complexes, the ether adducts, $[SnF_4\{MeO(CH_2)_2OMe\}]$ and $[SnF_4(THF)_2]$, are undergoing rapid neutral ligand exchange in solution at ambient temperatures, and only at low temperatures was it possible to record $^{19}F\{^1H\}$ and ^{119}Sn NMR spectroscopic data. These revealed that in CH_2Cl_2 solution at 220 K the THF complex was a mixture of *cis* and *trans* isomers in approximately equal amounts. On the basis of IR and Mössbauer data Tudela[18] concluded that the $[SnF_4L'_2]$ (L′ = pyridine or THF) were *trans* isomers in the solid state. Crystals of $[SnF_4\{MeO(CH_2)_2OMe\}]$ and $[SnF_4(1,10\text{-phenanthroline})]$ were grown from CH_2Cl_2/*n*-hexane. The structure of the former shows (Table 4, Figure 3) the expected *cis* geometry with Sn–O = 2.156(2), 2.144(2) Å, which are shorter than those in *trans*-$[SnCl_4(THF)_2]$[23] but significantly longer than the Sn–O distances in phosphane oxide adducts of

SnF_4, which lie in the range of ca. 2.045(3)–2.088(5) Å.[18] The latter complexes show no dissociation in solution, which is indicative of stronger binding of the phosphane oxide ligands compared to the ethers. The differences in the distances Sn–$F_{trans\text{-}F}$ [1.926(2), 1.927(2) Å] and Sn–$F_{trans\text{-}O}$ [1.921(2), 1.923(2) Å] are much less than in the phosphane complex described previously. The structure of [SnF_4(1,10-phenanthroline)] [Sn–N = 2.157(7) Å] (Table 5, Figure 4) may be compared with that of [$SnCl_4$(1,10-phenanthroline)],[24] which possess Sn–N = 2.234(7)–2.251(8) Å. One can also compare the literature data on [SnX_4(2,2′-bipyridyl)] for which Sn–N are X = F [2.181(3), 2.183(3) Å], X = Cl [2.247(4), 2.226(4) Å], X = Br [2.23(1), 2.23(1) Å], X = I [2.28(2) Å].[16,25,26] The 2,2′-bipyridyl series shows the longest Sn–N bonds in the iodide and the shortest in the fluoride, with the chloride and bromide less clearly discriminated, support for the fluoride being the strongest Lewis acid of the four halides.

Table 4. Selected bond lengths [Å] and angles [°] for [SnF_4{$MeO(CH_2)_2OMe$}].

Sn1–F1	1.9263(17)	Sn1–F3	1.9274(17)
Sn1–F2	1.9210(18)	Sn1–F4	1.9234(18)
Sn1–O1	2.1559(19)	Sn1–O2	2.144(2)
O1–C1	1.463(3)	O2–C3	1.454(3)
O1–C2	1.456(3)	O2–C4	1.463(3)
C2–C3	1.502(4)	O1···O2	2.673(3)
F2–Sn1–F4	99.27(8)	F1–Sn1–F3	170.07(7)
F–Sn1–F (the rest)	92.09(8)–93.93(8)	O2–Sn1–O1	76.88(8)
F2–Sn1–O2	169.84(8)	F4–Sn1–O1	167.62(8)
F–Sn1–O (the rest)	84.27(8)–93.07(8)		
Sn1–O1–C1	117.34(18)	Sn1–O2–C3	112.38(17)
Sn1–O1–C2	111.60(15)	Sn1–O2–C4	121.09(17)
O1–C2–C3	107.0(2)	O2–C3–C2	106.5(2)

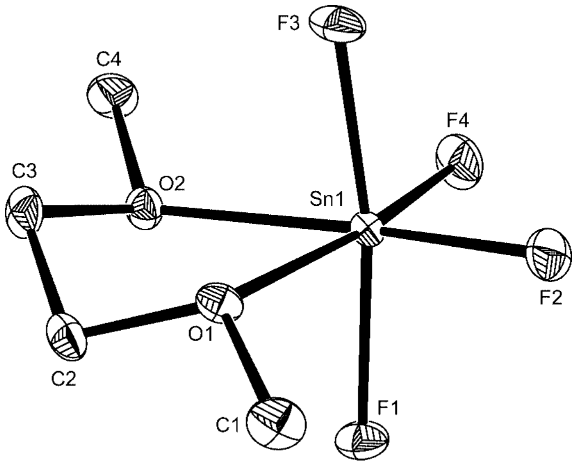

Figure 3. Structure of [SnF_4{$MeO(CH_2)_2OMe$}] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

Table 5. Selected bond lengths [Å] and angles [°] for [SnF_4(1,10-phenanthroline)]·MeOH.[a]

Sn1–F1	1.887(5)	Sn1–N1	2.157(7)
Sn1–F2	1.860(6)	N1–C1	1.339(11)
N1···N1a	2.670(13)	N1–C6	1.349(10)
F1–Sn1–F2	93.3(3)	F1–Sn1–F2a	91.9(3)
F2–Sn1–F2a	99.2(4)	F1–Sn1–F1a	172.0(3)
F1–Sn1–N1	88.0(3)	F2–Sn1–N1	168.4(3)
N1–Sn1–N1a	76.5(3)		
Sn1–N1–C1	126.4(5)	Sn1–N1–C6	115.1(5)

[a] Symmetry operation, a: 1–*x*, 1/2–*y*, *z*.

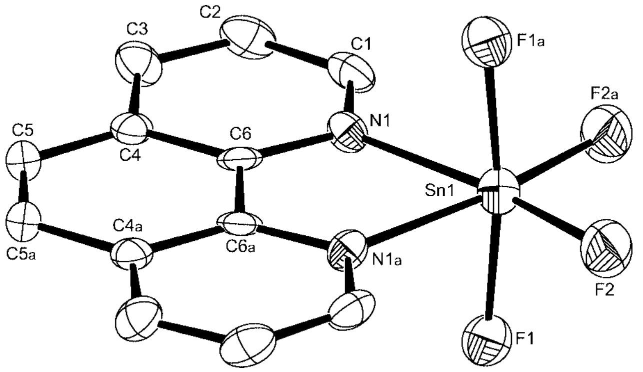

Figure 4. Structure of [SnF_4(1,10-phenanthroline)]·MeOH showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. The tin atom is on a twofold axis. Symmetry operation, a: 1–*x*, 1/2–*y*, *z*.

Other Tin(IV) Halide Adducts: For comparison several new complexes of SnX_4 (X = Cl, Br or I) with phosphane or arsane ligands were also prepared, in these cases by direct reaction of SnX_4 with the appropriate ligand in anhydrous

Table 6. Selected NMR spectroscopic data for SnX_4 (X = Cl, Br or I) complexes.[a]

Compound	$\delta(^{31}P\{^1H\})$[b]	ΔP[c]	$\delta(^{119}Sn)$[d]	$^1J(^{31}P\text{-}^{119}Sn)$	Ref.
[$SnCl_4${*o*-$C_6H_4(PMe_2)_2$}]	–28.1	27	–616 (t)	945	this work
[$SnBr_4${*o*-$C_6H_4(PMe_2)_2$}]	–31.9	23	–1188 (t)	581	this work
[SnI_4{*o*-$C_6H_4(PMe_2)_2$}]	–59.5 (243 K)	–5	n.o.[e]	240	this work
[$SnCl_4${$Et_2P(CH_2)_2PEt_2$}]	–4.9	13	–615 (t)	1049	this work
[$SnCl_4${$Me_2P(CH_2)_2PMe_2$}]	–20.9	27	–617 (t)	1005	[9]
[$SnCl_4${$Ph_2P(CH_2)_2PPh_2$}]	–18.8	–5.5	–626 (t)	890	[9]
[$SnCl_4${*o*-$C_6H_4(PPh_2)_2$}]	–13.9	–1	–607.5 (t)	890	[9]
[$SnCl_4${*o*-$C_6H_4(AsMe_2)_2$}]	–	–	–675 (s)	–	[9]
[$SnBr_4${*o*-$C_6H_4(AsMe_2)_2$}]	–	–	–1354 (s)	–	[9]
[$SnCl_4${$MeC(CH_2AsMe_2)_3$}]	–	–	–696 (s)	–	this work
[$SnBr_4${$MeC(CH_2AsMe_2)_3$}]	–	–	–1290 (s)	–	this work

[a] In CH_2Cl_2/10% $CDCl_3$. [b] Ligand chemical shifts are: *o*-$C_6H_4(PMe_2)_2$ –55 ppm; *o*-$C_6H_4(PPh_2)_2$ –13 ppm; $Ph_2P(CH_2)_2PPh_2$ –13 ppm; $Et_2P(CH_2)_2PEt_2$ –18 ppm; $Me_2P(CH_2)_2PMe_2$ –48 ppm; $Cy_2P(CH_2)_2PCy_2$ +2 ppm; PMe_3 –62 ppm; PCy_3 +11.5 ppm. [c] Coordination shift ($\delta_{complex}-\delta_{ligand}$). [d] ^{119}Sn NMR spectra were typically recorded at 250 K. [e] n.o. = not observed in temperature range 295–180 K.

dichloromethane, and the NMR spectra were recorded (Table 6). Like other complexes of this type, they are very moisture sensitive and also dioxygen sensitive to varying degrees in solution,[9,27] but also much more soluble in chlorocarbons than their tin(IV) fluoride analogues. The ^{119}Sn chemical shifts are surprisingly similar for corresponding complexes of SnF_4 and $SnCl_4$, but those of $SnBr_4$ and SnI_4 show much more deshielded resonances (Table 6). The $^1J(^{119}Sn\text{-}^{31}P)$ coupling constants fall with halogen F > Cl > Br > I. The structure of *cis*-$[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$ was determined (Table 7, Figure 5) and provides a direct comparison with the fluoride structure discussed above. Again there is a marked difference between $Sn\text{–}Cl_{trans\text{-}Cl}$ [2.453(1) Å] and $Sn\text{–}Cl_{trans\text{-}P}$ [2.408(1) Å] with Sn–P = 2.648(2) Å. Other structurally characterised phosphane complexes of $SnCl_4$ are *trans*-$[SnCl_4(PEt_3)_2]$ [Sn–P = 2.615(5) Å],[20] *trans*-$[SnCl_4(\kappa^1\text{-}Ph_2PCH_2PPh_2)_2]$ [Sn–P = 2.649(1) Å],[21] and *cis*-$[SnCl_4\{Ph_2P(CH_2)_2PPh_2\}]$ [Sn–P = 2.679(2), 2.653(2) Å, Sn–Cl = 2.402(2), 2.406(2), 2.408(2), 2.447(2) Å].[28]

Table 7. Selected bond lengths [Å] and angles [°] for $[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$.[a]

Sn1–Cl1	2.4529(14)	Sn1–P1	2.6481(17)
Sn1–Cl2	2.4084(14)	P1–C2	1.821(6)
P1–C4	1.824(6)	P1–C5	1.825(5)
P1···P1a	3.422(3)		
Cl1–Sn1–Cl2	90.16(5)	Cl1–Sn1–Cl2a	93.97(5)
Cl1–Sn1–Cl1a	174.00(7)	Cl2–Sn1–Cl2a	92.99(7)
Cl1–Sn1–P1	84.19(5)	Cl2–Sn1–P1	171.65(5)
P1–Sn1–P1a	80.49(7)	Sn1–P1–C2	117.0(2)
Sn1–P1–C4	114.0(2)	Sn1–P1–C5	102.09(18)
P1–C5–C5a–P1a	67.7(6)		

[a] Symmetry operation, a: 1–*x*, *y*, 1/2–*z*.

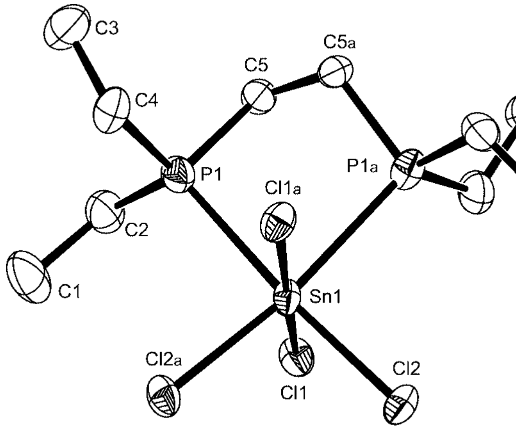

Figure 5. Structure of $[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. The tin atom is on a twofold axis. Symmetry operation, a: 1–*x*, *y*, 1/2–*z*.

Reactions with Dioxygen: We have reported elsewhere[9] that mixtures of phosphanes or diphosphanes and SnX_4 (X = Cl, Br or I) in chlorocarbon solution air-oxidise readily to the corresponding phosphane oxides. Catalytic amounts of SnI_4 can be used to cleanly generate phosphane oxides from the corresponding phosphanes using dry air or dioxygen, and whilst the mechanism remains obscure, the use of $^{18}O_2$ in these reactions showed that the source of the oxygen is O_2, not water as in a halogenation/hydrolysis mechanism.[27] The phosphane complexes of tin(IV) fluoride made in the present study also show varying degrees of oxygen sensitivity, especially in solution. The $[SnF_4(PCy_3)_2]$ is particularly sensitive and even brief exposure to air of a CH_2Cl_2 solution produced substantial oxidation. The $[SnF_4(PMe_3)_2]$ and the diphosphane complexes are less rapidly air-oxidised, but modest amounts of phosphane oxides can be detected by ^{31}P NMR in solutions exposed to air for some hours. In these systems the phosphane oxide binds strongly to the SnF_4 (cf. ref.[19]), and thus in contrast to the extensively dissociated SnI_4 systems[27] the formation of phosphane oxide is stoichiometric, because the phosphane oxides remove the SnF_4 by complexation preventing further reaction. Crystals of $[SnF_4(OPPh_3)_2]$ were obtained over several days from a CH_2Cl_2 solution of the products of melting $[SnF_4(MeCN)_2]$ with excess PPh_3. The structure (Figure 6, Table 8) shows it to be the *trans* isomer, and the bond lengths are entirely in keeping with our previous conclusions[19] that SnF_4 is the strongest Lewis acid of the four tin(IV) halides towards O donor phosphane oxide ligands.

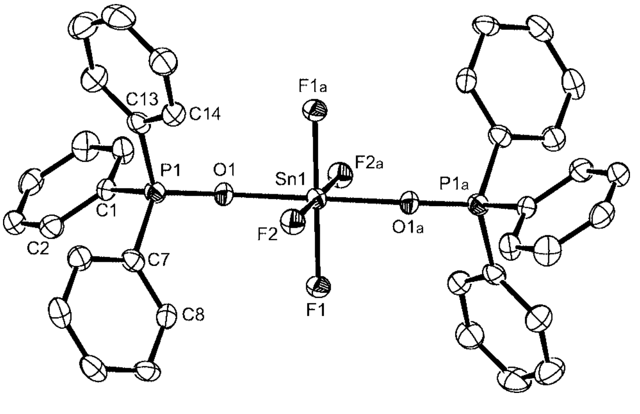

Figure 6. Structure of *trans*-$[SnF_4(Ph_3PO)_2]$ showing a partial atom numbering scheme. Phenyl groups are numbered cyclically starting at the *ipso* C atom. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Sn1 is positioned on a centre of symmetry. Symmetry operation, a: –*x*, 1–*y*, 1–*z*.

Table 8. Selected bond lengths [Å] and angles [°] for *trans*-$[SnF_4(Ph_3PO)_2]\cdot 2CH_2Cl_2$.

Sn1–F1	1.928(3)	Sn1–O1	2.050(3)
Sn1–F2	1.934(3)	O1–P1	1.523(3)
P1–C1	1.792(5)	P1–C7	1.795(5)
P1–C13	1.797(6)		
F1–Sn1–F2	90.56(12)	F1–Sn1–O1	89.06(13)
F2–Sn1–O1	91.79(13)	Sn1–O1–P1	146.3(2)
O1–P1–C1	108.0(2)	O1–P1–C7	112.5(2)
O1–P1–C13	111.4(2)		

Attempted Preparation of Tertiary Arsane Complexes: In contrast to the results with phosphane ligands, repeated attempts to isolate complexes of SnF_4 with tertiary arsanes including $AsMe_3$, *o*-$C_6H_4(AsMe_2)_2$ and $MeC(CH_2AsMe_2)_3$ were unsuccessful. The reaction of $[SnF_4(MeCN)_2]$ or $[SnF_4(THF)_2]$ in CH_2Cl_2 or toluene with *o*-$C_6H_4(AsMe_2)_2$,

Table 9. Selected bond lengths [Å] and angles [°] for $[SnBr_4\{MeC(CH_2AsMe_2)_3\}]$.

Sn1–Br1	2.5708(6)	Sn1–Br3	2.6340(5)
Sn1–Br2	2.5479(5)	Sn1–Br4	2.5807(5)
Sn1–As1	2.6932(5)	Sn1–As2	2.7095(6)
As1–C6	1.930(4)	As2–C8	1.935(3)
As1–C7	1.932(3)	As2–C9	1.928(3)
As3–C10	1.966(3)	As3–C11	1.972(3)
As1–C3	1.953(4)	As2–C4	1.954(3)
As3–C5	1.987(3)	As1···As2	3.712(1)
Br–Sn1–Br (ca. 90°)	91.979(17)–94.850(17)	Br3–Sn1–Br4	170.563(15)
Br–Sn1–As (ca. 90°)	82.905(16)–90.337(16)	Br1–Sn1–As2	173.739(14)
Br2–Sn1–As1	174.623(16)	As1–Sn1–As2	86.791(16)
C–As1–C	101.08(16)–108.21(15)	C–As2–C	99.62(13)–107.75(14)
C–As3–C	93.50(15)–98.69(16)		

which is a very strongly coordinating ligand towards many d-block metals,[29] resulted in white solids of variable composition which appeared to be mixtures of the starting complex, possibly $[SnF_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ and SnF_4. The IR spectra showed the presence of the diarsane, a broad υ(SnF) at ca. 570 cm^{-1}, and usually some MeCN or THF. The ^1H NMR spectra of these products in CD_2Cl_2 solution showed only MeCN or THF and "free" $o\text{-}C_6H_4(AsMe_2)_2$ [as $o\text{-}C_6H_4(AsMe_2)_2$ is a liquid, this is evidence for coordination of the diarsane to tin in the solids]. The $^{19}F\{^1H\}$ NMR spectra showed no resonances at room temperature, but below ca. 210 K, two new broad resonances at $\delta = -138$ and -152 were observed, which seem reasonable for $[SnF_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$, but no F–F coupling was resolved even at 190 K. The data suggest that $[SnF_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ forms in the reaction, but that it is extensively dissociated in solution and even use of a substantial excess of diarsane does not produce a pure product. In the cases of $AsMe_3$ or $MeC(CH_2AsMe_2)_3$ there was little evidence for coordination to SnF_4. In contrast, arsane complexes of SnX_4 (X = Cl, Br or I) form readily,[9] and indeed $[SnI_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ is one of the very small number of structurally characterised neutral ligand adducts of SnI_4. The explanation of this marked difference to phosphanes probably arises from the fact the SnF_4 is a very hard Lewis acid with contracted tin acceptor orbitals, and correspondingly has less ability to bind the large soft arsenic centre. For many transition-metal systems the differences between binding corresponding phosphanes and arsanes is small, but becomes very significant with high oxidation state and/or harder metal centres of the 3d series such as Fe^{IV}, Ni^{IV} or Mn^{II}, where the phosphanes result in significantly more stable complexes.[29] Our results suggest similar discrimination by SnF_4.

In the course of this work the $[SnX_4\{MeC(CH_2AsMe_2)_3\}]$ (X = Cl or Br) were prepared from the appropriate SnX_4 and triarsane in CH_2Cl_2 and their ^1H NMR spectra show the triarsane bound as a bidentate to a six-coordinate tin centre. The ^{119}Sn NMR chemical shifts of $\delta = -696$ and -1290 ppm (Table 6) are typical of SnX_4As_2 donor sets.[9] The structures were confirmed by a X-ray study of $[SnBr_4\{MeC(CH_2AsMe_2)_3\}]$ (Table 9, Figure 7), which showed a distorted octahedral tin centre with $Sn\text{–}Br_{trans\text{-}Br}$ [2.5807(5), 2.6340(5) Å] longer than $Sn\text{–}Br_{trans\text{-}As}$ [2.5708(6), 2.5479(5) Å], and with the axial Br–Sn–Br unit bent towards the neutral ligand (Br3–Sn1–Br4 = 170.6°), as found in tin(IV) halide structures with a variety of soft donors.[6–9] The Sn–As [2.6932(5), 2.7095(6) Å] are slightly shorter than those in the only other structurally characterised tin–arsane complexes $[SnI_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ [2.716(2), 2.752(2) Å],[9] and *trans*-$[SnCl_4(AsPh_3)_2]$ [2.762(1) Å].[30] The wide As–Sn–As angle [86.79(2)°] in the present complex reflects the six-membered chelate ring present and compares with 78.43(7)° in $[SnI_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ which contains a five-membered ring.

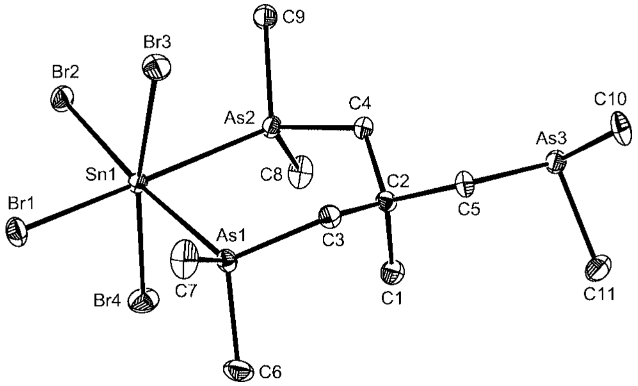

Figure 7. Structure of $[SnBr_4\{MeC(CH_2AsMe_2)_3\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

Comparisons and Conclusions

This work has provided the first examples of SnF_4 adducts with soft phosphane ligands and also a considerable amount of spectroscopic and structural data on comparable complexes with hard N- or O-donor ligands and with the heavier tin(IV) halides. The structural data discussed in preceding sections clearly show that for a fixed hard neutral ligand the Sn–ligand bond lengths are shortest in the fluoride complexes, consistent with SnF_4 being the strongest Lewis acid. The corresponding data for *cis*-$[SnX_4\{Et_2P(CH_2)_2PEt_2\}]$ (X = F or Cl), which are exact analogues (isostructural), also show the shortest Sn–P bond in the fluoride, indicating that similar trends hold with the soft (but strong σ-donor) phosphorus. The longer Sn–P bond in *trans*-[$SnF_4(PCy_3)_2$] is almost certainly due to steric effects caused by the bulky cyclohexyl substituents (PCy_3 has a cone angle of ca. 170°). However, the instability of SnF_4 adducts of arsanes suggests that towards even softer ligands, $SnCl_4$ will be more strongly coordinated.

These studies have also produced a wealth of NMR spectroscopic data (Table 1 and Table 6), but although several empirical trends in the chemical shifts and coupling constants with change in halide or neutral ligand can be discerned, the patterns are complicated, indicating several competing factors are present. Thus, the ^{119}Sn chemical shifts show consistent low frequency shifts with X: Cl → F → Br → I, the same as observed in halostannates(IV),[31,32] evidence that electronegativity is not the dominant factor.[33] Low frequency shifts also occur with neutral donor atoms P → N → O. The ^{31}P chemical shifts and the coordination shifts ($\delta_{\text{complex}}-\delta_{\text{ligand}}$) for the phosphane complexes are not systematic with changes in halide co-ligand. Although phosphanes mostly show high frequency coordination shifts when bound to transition metals, both high and low frequency shifts have been observed in p-block element complexes, and the reasons remain obscure.[33,34] The $^1J(^{31}\text{P-}^{119}\text{Sn})$ coupling constants are largest for the fluorides and much larger for *trans*-P–Sn–P than for *cis*-P–Sn–P arrangements (Table 1), whilst the $^1J(^{19}\text{F-}^{119}\text{Sn})$ couplings are larger in the phosphane complexes than in the N- or O-donor ligand cases. The $^1J(^{19}\text{F-}^{119}\text{Sn})_{\text{F}-trans\text{-F}}$ are markedly larger than $^1J(^{19}\text{F-}^{119}\text{Sn})_{\text{F}-cis\text{-F}}$ in the phosphane complexes, but this difference is small or absent in the complexes with harder donor co-ligands. A more detailed understanding of the factors responsible for these trends must await further work on related systems.

Given that stable complexes of soft phosphane donor ligands have now been prepared for the hard Lewis acid SnF_4, similar complexes should be obtainable for other main-group fluorides. Studies to explore this are underway.

Experimental Section

All compounds were made under dinitrogen 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. [$SnF_4(MeCN)_2$] was made as described.[18] Ligands were obtained from Aldrich: PMe_3, PPh_3, PCy_3, $AsMe_3$, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$, $Cy_2P(CH_2)_2PCy_2$, or were made by literature methods: *o*-$C_6H_4(PPh_2)_2$, $Ph_2P(CH_2)_2PPh_2$, *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, $MeC(CH_2AsMe_2)_3$.[35–38] 2,2′-Bipyridyl and 1,10-phenanthroline were dried by heating in vacuo, 1,2-dimethoxyethane was dried with sodium and freshly distilled. Pyridine and $Me_2N(CH_2)_2NMe_2$ were dried by distillation from BaO, tetrahydrofuran was dried by distillation from Na-benzophenone ketyl, MeCN and CH_2Cl_2 from CaH_2. IR spectra were recorded as Nujol mulls on a Perkin–Elmer PE 983G spectrometer, ^{1}H NMR spectra in $CDCl_3$, CD_2Cl_2 or CD_3NO_2 solutions on a Bruker AV300, ^{31}P{^{1}H}, ^{19}F{^{1}H} and ^{119}Sn NMR spectra on a Bruker DPX400 and referenced to 85% H_3PO_4, $CFCl_3$ and neat $SnMe_4$ respectively. The ^{119}Sn NMR spectra were recorded from solutions containing [$Cr(acac)_3$] as a relaxation agent and without proton decoupling to avoid NOE diminution of the signal due to the negative magnetogyric ratio of the isotope. Microanalytical measurements on new complexes were performed by the microanalytical service at Strathclyde University.

[SnF_4{*o*-$C_6H_4(PMe_2)_2$}]: [$SnF_4(MeCN)_2$] (0.276 g, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and *o*-$C_6H_4(PMe_2)_2$ (0.198 g, 1.0 mmol) added and the mixture stirred overnight at ambient temperatures. The white precipitate was filtered off and dried in vacuo. Yield 0.205 g, 52%. $C_{10}H_{16}F_4P_2Sn{\cdot}CH_2Cl_2$ (477.8): calcd. C 27.6, H 3.8; found C 26.9, H 3.8. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.87 (t, $^2J+{}^5J_{\text{P–H}}$ = 4 Hz, 12 H, Me), 5.4 (CH_2Cl_2), 7.75–7.81 (m, 4 H, C_6H_4) ppm. IR (Nujol): $\tilde{\nu}$ = 564 (s), 534 (s) υ(SnF) cm^{-1}.

[$SnCl_4${*o*-$C_6H_4(PMe_2)_2$}]: A solution of $SnCl_4$ (0.12 mL, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to *o*-$C_6H_4(PMe_2)_2$ (0.198 g, 1.0 mmol) in CH_2Cl_2 (20 mL) producing an immediate white precipitate. After 30 min the solid was filtered off and dried in vacuo. Yield 0.427 g, 93%. $C_{10}H_{16}Cl_4P_2Sn$ (458.7): calcd. C 26.2, H 3.5; found C 25.9, H 3.2. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.97 (t, $^2J+{}^5J_{\text{P–H}}$ = 4.4 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C_6H_4) ppm. IR (Nujol): $\tilde{\nu}$ = 307 (s), 296 (s) υ(SnCl) cm^{-1}.

[$SnBr_4${*o*-$C_6H_4(PMe_2)_2$}]: Prepared similarly to the chloride as a yellow solid. Yield 93%. $C_{10}H_{16}Br_4P_2Sn$ (636.5): calcd. C 18.9, H 2.5; found C 18.7, H 2.4. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.95 (t, $^2J+{}^5J_{\text{P–H}}$ = 4.5 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C_6H_4) ppm. IR (Nujol): $\tilde{\nu}$ = 205 (sh), 202 (s), 199 (sh), 196 (s) υ(SnBr) cm^{-1}.

[SnI_4{*o*-$C_6H_4(PMe_2)_2$}]: Prepared similarly to the chloride as a brown powder. Yield 80%. $C_{10}H_{16}I_4P_2Sn$ (824.5): calcd. C 14.6, H 2.0; found C 14.6, H 1.9. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.83 (t, $^2J+{}^5J_{\text{P–H}}$ = 4.8 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C_6H_4) ppm.

[SnF_4{*o*-$C_6H_4(PPh_2)_2$}]: [$SnF_4(MeCN)_2$] (0.276 g, 1.00 mmol) was suspended in CH_2Cl_2 (20 mL) and a solution of *o*-$C_6H_4(PPh_2)_2$ (0.446 g, 1.00 mmol) in CH_2Cl_2 (5 mL) added and the mixture stirred for 8 h at ambient temperatures. The white precipitate was filtered off and dried in vacuo. Yield 0.17 g, 27%. $C_{30}H_{24}F_4P_2Sn$ (641.2): calcd. C 56.2, H 3.8; found C 56.9, H 4.1. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30–7.68 (m, Ph) ppm. IR (Nujol): $\tilde{\nu}$ = 574 (s), 557 (s), 526 (s) υ(SnF) cm^{-1}.

[$SnF_4(PMe_3)_2$]: [$SnF_4(MeCN)_2$] (0.277 g, 1.00 mmol) was suspended in CH_2Cl_2 (10 mL), trimethylphosphane (0.167 g, 2.20 mmol) was added and stirred at room temperature for 1 h. Some of the CH_2Cl_2 was removed in vacuo and then dry hexane (20 mL) was added. A white solid precipitated out which was filtered off under nitrogen and dried in vacuo. Yield 0.250 g, 68%. $C_6H_{18}F_4P_2Sn{\cdot}2CH_2Cl_2$ (516.7): calcd. C 18.6, H 4.3; found C 18.3, H 4.5. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.68 (m, Me), 5.4 (CH_2Cl_2) ppm. IR (Nujol): $\tilde{\nu}$ = 546 (br) υ(SnF) cm^{-1}.

[$SnF_4(PCy_3)_2$]: [$SnF_4(MeCN)_2$] (0.277 g, 1.00 mmol) was suspended in CH_2Cl_2 (10 mL), tricyclohexylphosphane (0.588 g, 2.10 mmol) was added and stirred at room temperature for 3 h. No precipitation had occurred so the solution was reduced to ca. 5 mL in vacuo and then dry hexane (5 mL) was added. A white solid precipitated out which was filtered off under nitrogen and dried in vacuo. Yield 0.45 g, 60%. $C_{32}H_{66}F_4P_2Sn{\cdot}1/2CH_2Cl_2$ (750.0): calcd. C 54.9, H 8.5; found C 54.4, H 8.8. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.29–2.34 (m, Cy), 5.4 (CH_2Cl_2) ppm. IR (Nujol): $\tilde{\nu}$ = 557 (s), 535 (s) υ(SnF) cm^{-1}.

[SnF_4{$Et_2P(CH_2)_2PEt_2$}]: [$SnF_4(MeCN)_2$] (0.278 g, 1.00 mmol) was suspended in CH_2Cl_2 (20 mL), 1,2-bis(diethylphosphanyl)ethane (0.28 mL, 1.20 mmol) was added dropwise and stirred for 1.5 h.

Table 10. Crystal data and structure refinement details.[a]

Compound	$[SnF_4(Ph_3PO)_2]\cdot 2CH_2Cl_2$	$[SnF_4\{Et_2P(CH_2)_2PEt_2\}]$	$[SnF_4\{MeO(CH_2)_2OMe\}]$
Formula	$C_{38}H_{34}Cl_4F_4O_2P_2Sn$	$C_{10}H_{24}F_4P_2Sn$	$C_4H_{10}F_4O_2Sn$
M	921.08	400.92	284.81
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a [Å]	8.8697(16)	8.8994(12)	6.2957(15)
b [Å]	14.771(4)	11.663(3)	20.987(6)
c [Å]	14.446(4)	14.774(4)	6.693(2)
α [°]	90	90	90
β [°]	95.236(16)	104.257(12)	111.941(15)
γ [°]	90	90	90
U [Å^3]	1884.7(8)	1486.2(5)	820.2(4)
Z	2	4	4
μ [mm^{-1}]	1.101	1.956	3.137
$F(000)$	924	800	544
Total no. of observations (R_{int})	21329 (0.138)	9486 (0.053)	6388 (0.037)
Unique observations	4312	1708	1867
Min., max. transmission	0.681, 1.000	0.726, 1.000	0.651, 1.000
No. of parameters, restraints	232, 0	78, 0	100, 0
Goodness-of-fit on F^2	0.98	1.07	1.14
Resid. electron density [e·Å^{-3}]	–0.83 to +0.74	–0.64 to +0.69	–0.76 to +0.48
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.058, 0.106	0.030, 0.053	0.023, 0.054
R_1, wR_2 (all data)	0.135, 0.131	0.042, 0.056	0.027, 0.056

Compound	$[SnF_4(1,10\text{-phenanthroline})]\cdot MeOH$	$[SnF_4(PCy_3)_2]$	$[SnCl_4\{Et_2P(CH_2)_2PEt_2\}]$
Formula	$C_{13}H_{12}F_4N_2OSn$	$C_{36}H_{66}F_4P_2Sn$	$C_{10}H_{24}Cl_4P_2Sn$
M	406.94	755.52	466.72
Crystal system	tetragonal	triclinic	monoclinic
Space group	$I4_1/a$ (no. 88)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a [Å]	9.471(3)	8.251(2)	9.708(3)
b [Å]	9.471(3)	9.868(3)	12.177(2)
c [Å]	29.964(8)	11.832(4)	16.301(5)
α [°]	90	77.192(15)	90
β [°]	90	85.601(10)	107.108(12)
γ [°]	90	69.240(15)	90
U [Å^3]	2687.8(15)	878.3(4)	1841.7(9)
Z	8	1	4
μ [mm^{-1}]	1.948	0.864	2.122
$F(000)$	1584	398	928
Total no. of observations (R_{int})	9075 (0.097)	18769 (0.088)	8628 (0.049)
Unique observations	1539	4030	2100
Min., max. transmission	0.569, 1.000	0.778, 1.000	0.722, 1.000
No. of parameters, restraints	96, 1	196, 0	80, 0
Goodness-of-fit on F^2	1.04	1.05	1.05
Resid electron density [e·Å^{-3}]	–1.12 to +1.17	–0.69 to +0.97	–0.88 to +1.65
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.072, 0.180	0.051, 0.101	0.054, 0.112
R_1, wR_2 (all data)	0.128, 0.207	0.070, 0.108	0.092, 0.126

Compound	$[SnBr_4\{MeC(CH_2AsMe_2)_3\}]$
Formula	$C_{11}H_{27}As_3Br_4Sn$
M	822.42
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a [Å]	11.371(2)
b [Å]	12.839(2)
c [Å]	15.227(2)
α [°]	90
β [°]	91.731(10)
γ [°]	90
U [Å^3]	2221.9(6)
Z	4
μ [mm^{-1}]	12.766
$F(000)$	1528
Total no. of observations (R_{int})	22702 (0.064)
Unique observations	5084
Min., max. transmission	0.767, 1.000
No. of parameters, restraints	179, 0
Goodness-of-fit on F^2	1.03
Resid electron density [e·Å^{-3}]	–0.91 to +0.84
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.026, 0.050
R_1, wR_2 (all data)	0.045, 0.053

[a] Common items: temperature = 120 K; wavelength (Mo-K_α) = 0.71073 Å; $\theta_{max.}$ = 27.5°. [b] $R_1 = \Sigma|| F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$.

The white precipitate was filtered off and dried in vacuo. Yield 0.32 g, 80%. $C_{10}H_{24}F_4P_2Sn$ (400.95): calcd. C 29.9, H 6.0; found C 29.0, H 6.0. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.13–2.07 (m, 2 H, CH_2), 1.37–1.26 (m, 6 H, Me) ppm. IR (Nujol): $\tilde{\nu}$ = 553 (m), 526 (s) υ(SnF) cm^{-1}.

[$SnF_4\{Cy_2P(CH_2)_2PCy_2\}$]: [$SnF_4(MeCN)_2$] (0.278 g, 1.00 mmol) was suspended in CH_2Cl_2 (10 mL), 1,2-bis(dicyclohexylphosphanyl)ethane (0.444 g, 1.05 mmol) in CH_2Cl_2 (5 mL) was added. This was stirred under nitrogen for 3 h. No precipitation had occurred so the solution was reduced to ca. 5 mL in vacuo and then dry hexane (5 mL) was added. Again no significant precipitate was observed so the solvent was removed in vacuo to give a white solid. Yield 0.51 g, 83%. $C_{26}H_{48}F_4P_2Sn\cdot 1/2CH_2Cl_2$ (826.1): calcd. C 48.2, H 7.5; found C 49.2, H 8.3. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.21–1.255 (m, CH_2, Cy), 5.4 (CH_2Cl_2) ppm. IR (Nujol): $\tilde{\nu}$ = 560 (s), 530 (s) υ(SnF) cm^{-1}.

[$SnF_4\{Ph_2P(CH_2)_2PPh_2\}$]: [$SnF_4(MeCN)_2$] (0.28 g, 1.0 mmol) was suspended in CH_2Cl_2 (15 mL), 1,2-bis(diphenylphosphanyl)ethane (0.42 g, 1.05 mmol) in CH_2Cl_2 (10 mL) was added and the mixture stirred for 3 h. Most of the solvent was removed in vacuo and the white precipitate was filtered off and dried in vacuo. Yield 0.46 g, 78%. $C_{26}H_{24}F_4P_2Sn\cdot 1/2CH_2Cl_2$ (635.6): calcd. C 50.0, H 4.0; found C 49.6, H 3.7. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.89–7.45 (m, 5 H, Ph), 5.4 (CH_2Cl_2). 2.81 (br, 1 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 566 (br) υ(SnF) cm^{-1}.

[$SnCl_4\{Et_2P(CH_2)_2PEt_2\}$]: $SnCl_4$ (0.260 g, 1.00 mmol) was dissolved in CH_2Cl_2 (15 mL), 1,2-bis(diethylphosphanyl)ethane (0.245 mL, 1.05 mmol) was added and stirred for 2 h. Immediate precipitation occurred, and the solid was filtered off and dried in vacuo to give a white crystalline solid. Yield 0.45 g, 96%. $C_{10}H_{24}Cl_4P_2Sn\cdot CH_2Cl_2$ (551.7): calcd. C 23.95, H 4.8; found C 23.5, H 5.0. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.12–2.11 (m, 6 H, CH_2), 1.39–1.21 (m, 6 H, Me), 5.4 (CH_2Cl_2) ppm. IR (Nujol): $\tilde{\nu}$ = 318 (sh), 307 (sh), 282 (br) υ(SnCl) cm^{-1}.

[SnF_4(2,2′-bipyridyl)]: [$SnF_4(MeCN)_2$] (0.276 g, 1.00 mmol) was suspended in CH_2Cl_2 (10 mL) and a solution of 2,2′-bipy (0.156 g, 1.00 mmol) in CH_2Cl_2 (5 mL) added and the mixture refluxed for 2 h. The white precipitate was filtered off and dried in vacuo. Yield 0.365 g, 97%. ^1H NMR (300 MHz, CD_3NO_2, 25 °C): δ = 9.41 (s, 1 H), 9.15 (s, 1 H), 8.99 (s, 1 H), 8.49 (s, 1 H) ppm. IR (Nujol): $\tilde{\nu}$ = 580 (s), 560, 520 (sh) υ(SnF) cm^{-1}.

[SnF_4(1,10-phenanthroline)]: Prepared similarly to the above. Yield 60%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.35 (m, 2 H), 9.16 (m, 2 H), 8.45 (m, 4 H) ppm. IR (Nujol): $\tilde{\nu}$ = 587 (s), 566 (s) υ(SnF) cm^{-1}.

[$SnF_4\{MeO(CH_2)_2OMe\}$]: 1,2-Dimethoxyethane (0.1 mL, 1.0 mmol) was added to a solution of [$SnF_4(MeCN)_2$] (0.276 g, 1.0 mmol) in CH_2Cl_2 (10 mL), and the mixture stirred at reflux for 2 h. The white precipitate was filtered off and dried in vacuo. Yield 77%. ^1H NMR (300 MHz, $CDCl_3$, 200 K): δ = 3.98 (s, 3 H, Me), 4.25 (s, 2 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 609 (s), 584 (s), 540 (m) υ(SnF) cm^{-1}.

[$SnF_4(pyridine)_2$]: Pyridine (0.16 g, 2.0 mmol) was added to a solution of [$SnF_4(MeCN)_2$] (0.186 g, 0.67 mmol) in CH_2Cl_2 (10 mL). This was stirred at reflux under nitrogen for 2 h. The white precipitate was filtered off and dried in vacuo. Yield 80%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.00 (m, 2 H), 8.2 (m, 1 H), 7.7 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 568 (s) υ(SnF) cm^{-1}.

[$SnF_4\{Me_2N(CH_2)_2NMe_2\}$]: [$SnF_4(MeCN)_2$] (0.276 g, 1.0 mmol) was suspended in CH_2Cl_2 (10 mL), *N*,*N*,*N′N′*-tetramethylethylenediamine (0.15 g, 1.00 mmol) was added and the mixture stirred for 12 h. The white precipitate was filtered off and dried in vacuo. Yield 0.14 g, 54%. $C_6H_{16}F_4N_2Sn\cdot 1/2CH_2Cl_2$ (277.4): calcd. C 22.1, H 4.9, N 7.9; found C 22.3, H 5.1, N 8.1. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.89 (s, 12 H, Me), 3.02 (s, 4 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 570 (s), 547 (s) υ(SnF) cm^{-1}.

[$SnF_4(THF)_2$]: Was made as described.[18] ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.1 (br., 2 H, CH_2), 4.4(br., 2 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 600 (vbr) υ(SnF), 1013 (br), 845 (m) υ(COC) cm^{-1}.

[$SnCl_4\{MeC(CH_2AsMe_2)_3\}$]: $MeC(CH_2AsMe_2)_3$ (0.384 g, 1.0 mmol) was dissolved in CH_2Cl_2 (10 mL) under nitrogen. To this solution $SnCl_4$ (0.26 g, 1.0 mmol) was added and an immediate white precipitate formed. This was filtered off and dried in vacuo to give a white powder. Yield 0.21 g, 33%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.03 (s, 6 H, AsMe), 1.35 (s, 3 H, CMe), 1.73 (s, 12 H, AsMe), 1.77 (s, 2 H, CH_2), 2.39 (d, ^2J = 12 Hz, 2 H, CH_2) 2.54 (d, ^2J = 12 Hz, 2 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 310 (sh), 302 (s), 280 (sh) υ(SnCl) cm^{-1}.

[$SnBr_4\{MeC(CH_2AsMe_2)_3\}$]: $MeC(CH_2AsMe_2)_3$ (0.384 g, 1.0 mmol) was dissolved in CH_2Cl_2 (10 mL) under nitrogen. To this solution $SnBr_4$ (0.438 g, 1.0 mmol) was added and an immediate yellow precipitate formed in a yellow solution. This was filtered and the filtrate was left to stand to give yellow crystals. Yield 0.18 g, 22%. $C_{11}H_{27}As_3Br_4Sn$ (822.4): calcd. C 16.1, H 3.3; found C 15.3, H 3.1. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.04 (s, 6 H, AsMe), 1.37 (s, 3 H, CMe), 1.70 (br., 12 H, AsMe), 1.78 (br., 2 H, CH_2), 2.32 (br., 2 H, CH_2) 2.55 (br., 2 H, CH_2) ppm. IR (Nujol): $\tilde{\nu}$ = 215 (sh), 207 (s), 199 (s) υ(SnBr) cm^{-1}.

X-ray Experimental: Crystals were grown from anhydrous CH_2Cl_2 solutions of the complexes by vapour diffusion of *n*-hexane under dinitrogen. Brief details of the crystal data and refinement are given in Table 10. Data collections were carried out with a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were routine[39–41] except as discussed below, with in all cases H atoms added in calculated positions. The [SnF_4(1,10-phenanthroline)]·MeOH complex showed, after identifying the tin residue, two peaks in the difference electron-density map associated with a solvent molecule. The larger of the peaks positioned on a twofold axis (proposed as an O atom) with the second peak and its symmetry related peak being a disordered C atom of an adventitious MeOH solvate molecule. No attempt was made to position H atoms on this residue.

CCDC-299706 [for F/O(P)], -299707 [for F/P(Et_2)], -299708 [for F/O(Me)], -299709 (for F/N), -299710 [for F/P(R_3)], -299711 (for Cl/P), -299712 (for Br/As) contain the supplementary crystallographic data for this paper (the atoms in parentheses indicate the atoms bonded to Sn). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank EPSRC for support (GR/T09613/01).

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Received: March 6, 2006