

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

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The first phosphane complexes of the hard Lewis acid SnF_4 have been synthesised including *trans*- $[\text{SnF}_4(\text{PR}_3)_2]$ ($\text{R} = \text{Me}$ or Cy) and *cis*- $[\text{SnF}_4(\text{diphosphane})]$ [diphosphane = $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$, $\text{R} = \text{Me}$, Et , Ph or Cy ; $o\text{-C}_6\text{H}_4(\text{PR}_2)_2$, $\text{R} = \text{Me}$ or Ph] and characterised by IR and multinuclear NMR (^1H , ^{19}F , ^{31}P , ^{119}Sn) spectroscopy. The crystal structures of *trans*- $[\text{SnF}_4(\text{PCy}_3)_2]$ and *cis*- $[\text{SnF}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$ are reported. Tin(IV) fluoride complexes of 2,2'-bipyridyl, 1,10-phenanthroline, $\text{MeO}(\text{CH}_2)_2\text{OMe}$, $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$, pyridine and THF have been characterised by multinuclear NMR spectroscopy, the structures of *cis*- $[\text{SnF}_4(\text{L-L})]$ ($\text{L-L} = 1,10\text{-phen-}$

anthroline and $\text{MeO}(\text{CH}_2)_2\text{OMe}$) determined, and the properties were compared with those of the phosphane complexes. Complexes of $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$, $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$, and $\text{MeC}(\text{CH}_2\text{AsMe}_2)_3$ with SnCl_4 and SnBr_4 are also reported and the structures of *cis*- $[\text{SnCl}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$ and *cis*- $[\text{SnBr}_4\{\kappa^2\text{-MeC}(\text{CH}_2\text{AsMe}_2)_3\}]$ described. Attempts to prepare tertiary arsane complexes of SnF_4 have been unsuccessful.

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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 $[\text{SnCl}_4\text{L}_2]$, and similar complexes are formed by SnBr_4 and SnI_4 , although Lewis acidity decreases $\text{SnCl}_4 > \text{SnBr}_4 >> \text{SnI}_4$. 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, $[\text{SnF}_4(2,2'\text{-bipy})]$, 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 , $\text{M} = \text{As}$ or Sb), is little explored, but also reflects the more difficult synthetic entry into the complexes. The SnX_4 ($\text{X} = \text{Cl}$, Br or I) are tetrahedral molecules readily soluble in weak or non-coordinating solvents such as chlorocarbons, hydrocarbons or arenes, and synthesis of $[\text{SnX}_4(\text{L})_2]$ 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 hydro-

lysed, is otherwise rather unreactive and insoluble in weak donor solvents. Tudela and co-workers have reported^[18] the preparation of $[\text{SnF}_4(\text{MeCN})_2]$ 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 $[\text{SnF}_4(\text{R}_3\text{EO})_2]$ ($\text{R}_3\text{EO} = \text{Ph}_3\text{PO}$, Ph_3AsO , Me_3PO or Me_3AsO) and $[\text{SnF}_4(\text{L-L})]$ [$\text{L-L} = o\text{-C}_6\text{H}_4\text{-}[\text{P}(\text{O})\text{Ph}_2]_2$, $o\text{-C}_6\text{H}_4[\text{P}(\text{O})\text{Me}_2]_2$ or $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$].^[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 $[\text{SnF}_4(\text{MeCN})_2]$ with PMe_3 or PCy_3 (L), in anhydrous dichloromethane under a dinitrogen atmosphere yielded $[\text{SnF}_4\text{L}_2]$ complexes in moderate to good yields. However we were unable to obtain a pure sample of $[\text{SnF}_4(\text{PPh}_3)_2]$ by this route. Since neither the $[\text{SnF}_4(\text{MeCN})_2]$ 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 ^1H NMR spectra and in some of the X-ray structures.^[19] $[\text{SnF}_4(\text{THF})_2]$ ^[18] was also explored as a synthon, but appeared to have no advantages over the acetonitrile complex. We also reacted $[\text{SnF}_4(\text{MeCN})_2]$ with molten PPh_3 , but the $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra showed a complex mixture of products, and it appears that some fluorination of the phosphane occurs under these conditions. The $[\text{SnF}_4\text{L}_2]$ complexes were identified as *trans* isomers from their $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ 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%, $\mathcal{E} = 35.63$ MHz; ^{119}Sn : $I = 1/2$, 8.6%, $\mathcal{E} = 37.27$ 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 $[\text{SnF}_4(\text{PCy}_3)_2]$ was determined and shows (Table 2, Figure 1) a centrosymmetric molecule with $\text{Sn}-\text{P} = 2.654(1)$ Å and $\text{Sn}-\text{F} = 1.959(2)$, 1.980(2) Å. The $\text{Sn}-\text{P}$ is longer than that in *trans*- $[\text{SnCl}_4(\text{PET}_3)_2]$ [2.615(5) Å],^[20] and marginally longer than in *trans*- $[\text{SnCl}_4\{\kappa^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2\}_2]$ [2.649(1) Å],^[21] but shorter than found in *trans*- $[\text{SnI}_4(\text{P}i\text{Pr}_3)_2]$ [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*- $[\text{SnF}_4(\text{PCy}_3)_2]$.^[a]

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

[a] Symmetry operation, a: $-x, -y, 2-z$.

The corresponding reactions of $[\text{SnF}_4(\text{MeCN})_2]$ with the diphosphanes $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$, $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$, $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$, *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ (L-L) gave $[\text{SnF}_4(\text{L-L})]$. The $[\text{SnF}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and two $^{19}\text{F}\{^1\text{H}\}$ resonances, a triplet of triplets for the $F_{\text{trans-F}}$ and a doublet of doublets of triplets for the $F_{\text{trans-P}}$ 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	$\delta(^{31}\text{P}\{^1\text{H}\})$ [b]	ΔP [c]	$\delta(^{119}\text{Sn})$ [d]	$\delta(^{19}\text{F}\{^1\text{H}\})$	$^1J(^{19}\text{F}-^{119}\text{Sn})$	$^nJ(^{31}\text{P}-^{19}\text{F})$	$^2J(^{19}\text{F}-^{19}\text{F})$	$^nJ(^{31}\text{P}-^{119}\text{Sn})$
$[\text{SnF}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	-37.8 (t,d,d)	17	-657.6 (t,t,t)	-131.7 (t,t) -161.1 (d,d,t)	2470 2160	117, 98, 54	42	1520
$[\text{SnF}_4\{o\text{-C}_6\text{H}_4(\text{PPh}_2)_2\}]$	-18.9 (t,d,d)	-6	-665.9 (t,t,t)	-123.8 (t,t) -155.5 (d,d,t)	2627 2207	93, 73, 48	52	1512
<i>trans</i> - $[\text{SnF}_4(\text{Me}_3\text{P})_2]$	-19.1 (q)	43	-628.0 (t,q)	-132.8 (t)	2745	155		2975
<i>trans</i> - $[\text{SnF}_4(\text{Cy}_3\text{P})_2]$	+22.2 (q)	11	-628.5 (t,q)	-98.9 (t)	2993	124		2530
$[\text{SnF}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$	-11.6 (t,d,d)	6	-649.4 (t,t,t)	-123.8 (t,t) -150.2 (d,d,t)	2552 2183	110, 95, 46	40	1628
$[\text{SnF}_4\{\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2\}]$	-9.9 (t,d,d)	-12	-639.1 (t,t,t)	-113.7 (t,t) -139.5 (d,d,t)	2644 2205	98, 88, 46	46	1528
$[\text{SnF}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$	-17.8 (t,d,d)	-4	-668.1 (t,t,t)	-112.4 (t,t) -147.1 (d,d,t)	2650 2212	118, 87, 44	46	1630
$[\text{SnF}_4(2,2'\text{-bipyridyl})]$			-708.2 (t,t)	-149.8 (t) -179.8 (t)	1964 1978		48	
$[\text{SnF}_4(1,10\text{-phen})]$			-715.1 (t,t)	-149.5 (t) -180.8 (t)	1987 1982		50	
$[\text{SnF}_4(\text{THF})_2]$ (220 K)								
<i>trans</i> isomer			-775.4 (q)	-166.7 (s)	1910			
<i>cis</i> isomer			-775.3 (t,t)	-166.2 (t) -178.8 (t)	1918 2074		54	
<i>trans</i> - $[\text{SnF}_4(\text{pyridine})_2]$			-670.8 (q)	-163.8 (s)	1983			
$[\text{SnF}_4\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2\}]$			^[e]	-167.8 (t) -184.4 (t)	2266 2096		50	
$[\text{SnF}_4(\text{MeCN})_2]$			n.o. ^[f]	-181.0 (s)	n.o.			
$[\text{SnF}_4\{\text{MeO}(\text{CH}_2)_2\text{OMe}\}]$ (190 K)			-753.8 (t,t)	-167.1 -183.3	2233 2189		61	

[a] In $\text{CH}_2\text{Cl}_2/10\%$ CDCl_3 . [b] Ligand chemical shifts are: *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ -55 ppm; *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ -13 ppm; $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ -13 ppm; $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2$ -18 ppm; $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ -48 ppm; $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$ +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] Insufficiently soluble to record spectrum. [f] n.o. = not observed in temperature range 295–180 K.

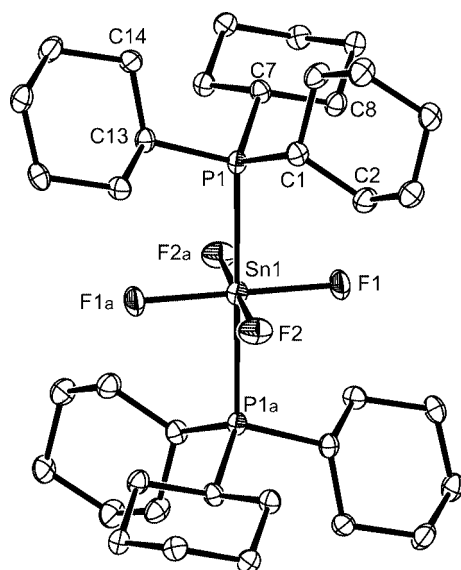


Figure 1. Structure of *trans*-[SnF₄(PCy₃)₂] showing a partial atom numbering scheme. Cyclohexyl groups are numbered cyclically starting at the P-bonded C atom. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Sn1 is positioned on a centre of symmetry. Symmetry operation, a: $-x, -y, 2-z$.

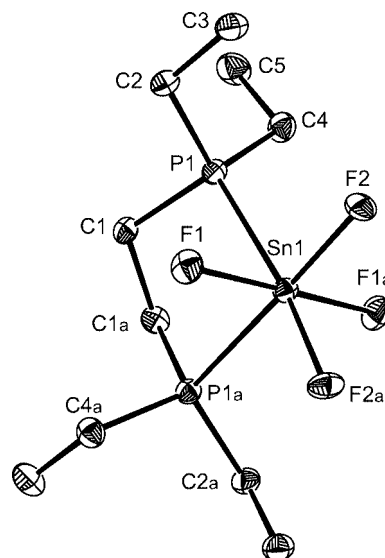


Figure 2. Structure of [SnF₄{Et₂P(CH₂)₂PEt₂}] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. A twofold axis passes through Sn1 and the centre of the C1–C1a bond. Symmetry operation, a: $-x, y, 1/2-z$.

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 [SnF₄{Et₂P(CH₂)₂PEt₂}] 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*-[SnF₄(PCy₃)₂] [2.654(1) Å], and also shorter than the value in *cis*-[SnCl₄{Et₂P(CH₂)₂PEt₂}] [2.648(2) Å] described below. The Sn–F_{*trans*-F} 1.986(2) Å is significantly longer than Sn–F_{*trans*-P} 1.953(2) Å, a pattern which is found in most adducts of SnX₄ (X = Cl, Br or I) with soft donor ligands.^[6–10]

Table 3. Selected bond lengths [Å] and angles [°] for [SnF₄{Et₂P(CH₂)₂PEt₂}].^[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: $-x, y, 1/2-z$.

Other SnF₄ Complexes: A small number of complexes of hard N- or O-donor ligands, previously obtained directly from SnF₄, were re-prepared in this study for comparison purposes from [SnF₄(MeCN)₂], viz [SnF₄(L–L)] (L–L = 2,2'-bipyridyl, 1,10-phenanthroline, *N,N,N',N'*-tetramethylethanediamine and 1,2-dimethoxyethane) and [SnF₄(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 [SnF₄(L)₂] [L = THF or L₂ = MeO(CH₂)₂OMe] are very deliquescent. The ¹⁹F{¹H} and ¹¹⁹Sn NMR spectroscopic data are shown in Table 1. Although the ranges overlap, there is a general shift to lower frequency in the ¹¹⁹Sn NMR shifts with donor, P → N → O. The complexes with L–L = 2,2'-bipyridyl, 1,10-phenanthroline, Me₂N(CH₂)₂NMe₂ have the expected *cis* geometry, whilst the [SnF₄(pyridine)₂] is the *trans* isomer. In contrast to the N donor complexes, the ether adducts, [SnF₄{MeO(CH₂)₂OMe}] and [SnF₄(THF)₂], are undergoing rapid neutral ligand exchange in solution at ambient temperatures, and only at low temperatures was it possible to record ¹⁹F{¹H} and ¹¹⁹Sn NMR spectroscopic data. These revealed that in CH₂Cl₂ 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 [SnF₄L'₂] (L' = pyridine or THF) were *trans* isomers in the solid state. Crystals of [SnF₄{MeO(CH₂)₂OMe}] and [SnF₄(1,10-phenanthroline)] were grown from CH₂Cl₂/*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*-[SnCl₄(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 $\text{Sn}-\text{F}_{\text{trans-F}}$ [1.926(2), 1.927(2) Å] and $\text{Sn}-\text{F}_{\text{trans-O}}$ [1.921(2), 1.923(2) Å] are much less than in the phosphane complex described previously. The structure of $[\text{SnF}_4(1,10\text{-phenanthroline})]$ [$\text{Sn}-\text{N} = 2.157(7)$ Å] (Table 5, Figure 4)

Table 4. Selected bond lengths [Å] and angles [°] for $[\text{SnF}_4\{\text{MeO}(\text{CH}_2)_2\text{OMe}\}]$.

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)

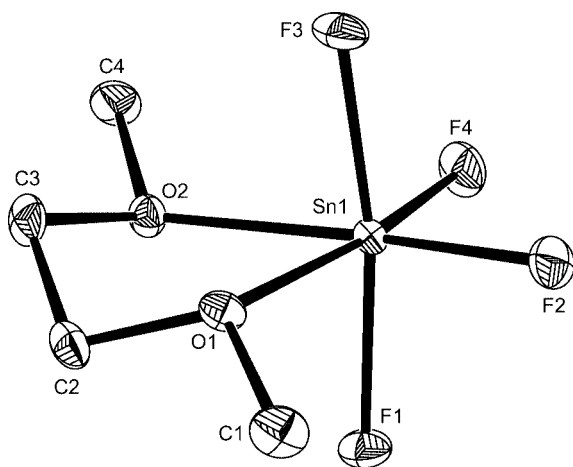


Figure 3. Structure of $[\text{SnF}_4\{\text{MeO}(\text{CH}_2)_2\text{OMe}\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

may be compared with that of $[\text{SnCl}_4(1,10\text{-phenanthroline})]$,^[24] which possess $\text{Sn}-\text{N} = 2.234(7)$ – $2.251(8)$ Å. One can also compare the literature data on $[\text{SnX}_4(2,2'\text{-bipyridyl})]$ for which $\text{Sn}-\text{N}$ are $\text{X} = \text{F}$ [2.181(3), 2.183(3) Å], $\text{X} = \text{Cl}$ [2.247(4), 2.226(4) Å], $\text{X} = \text{Br}$ [2.23(1), 2.23(1) Å], $\text{X} = \text{I}$ [2.28(2) Å].^[16,25,26] The 2,2'-bipyridyl series shows the longest $\text{Sn}-\text{N}$ 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 5. Selected bond lengths [Å] and angles [°] for $[\text{SnF}_4(1,10\text{-phenanthroline})]\cdot\text{MeOH}$.^[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: $1-x, 1/2-y, z$.

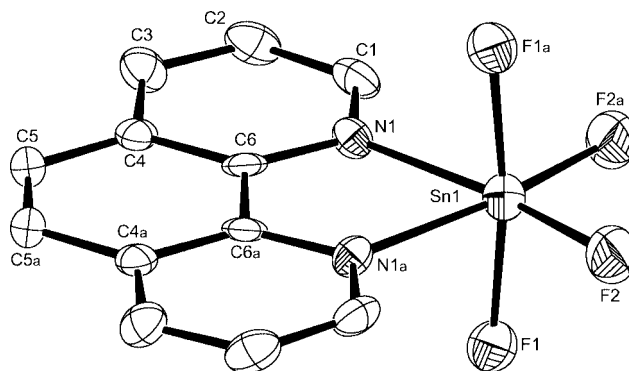


Figure 4. Structure of $[\text{SnF}_4(1,10\text{-phenanthroline})]\cdot\text{MeOH}$ showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. The tin atom is on a twofold axis. Symmetry operation, a: $1-x, 1/2-y, z$.

Other Tin(IV) Halide Adducts: For comparison several new complexes of SnX_4 ($\text{X} = \text{Cl}, \text{Br}$ 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 ($\text{X} = \text{Cl}, \text{Br}$ or I) complexes.^[a]

Compound	$\delta(^{31}\text{P}\{^1\text{H}\})$ ^[b]	$\Delta\rho$ ^[c]	$\delta(^{119}\text{Sn})$ ^[d]	$^1J(^{31}\text{P}-^{119}\text{Sn})$	Ref.
$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	–28.1	27	–616 (t)	945	this work
$[\text{SnBr}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	–31.9	23	–1188 (t)	581	this work
$[\text{SnI}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	–59.5 (243 K)	–5	n.o. ^[e]	240	this work
$[\text{SnCl}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PET}_2\}]$	–4.9	13	–615 (t)	1049	this work
$[\text{SnCl}_4\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$	–20.9	27	–617 (t)	1005	[9]
$[\text{SnCl}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$	–18.8	–5.5	–626 (t)	890	[9]
$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PPh}_2)_2\}]$	–13.9	–1	–607.5 (t)	890	[9]
$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$	–	–	–675 (s)	–	[9]
$[\text{SnBr}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$	–	–	–1354 (s)	–	[9]
$[\text{SnCl}_4\{\text{MeC}(\text{CH}_2\text{AsMe}_2)_3\}]$	–	–	–696 (s)	–	this work
$[\text{SnBr}_4\{\text{MeC}(\text{CH}_2\text{AsMe}_2)_3\}]$	–	–	–1290 (s)	–	this work

[a] In $\text{CH}_2\text{Cl}_2/10\%$ CDCl_3 . [b] Ligand chemical shifts are: $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ –55 ppm; $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ –13 ppm; $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ –13 ppm; $\text{Et}_2\text{P}(\text{CH}_2)_2\text{PET}_2$ –18 ppm; $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ –48 ppm; $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$ +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] 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 ¹¹⁹Sn chemical shifts are surprisingly similar for corresponding complexes of SnF₄ and SnCl₄, but those of SnBr₄ and SnI₄ show much more deshielded resonances (Table 6). The ¹J(¹¹⁹Sn–³¹P) coupling constants fall with halogen F > Cl > Br > I. The structure of *cis*-[SnCl₄{Et₂P(CH₂)₂PEt₂}] 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–Cl_{trans}-Cl [2.453(1) Å] and Sn–Cl_{trans}-P [2.408(1) Å] with Sn–P = 2.648(2) Å. Other structurally characterised phosphane complexes of SnCl₄ are *trans*-[SnCl₄(PEt₃)₂] [Sn–P = 2.615(5) Å],^[20] *trans*-[SnCl₄(κ¹-Ph₂PCH₂PPh₂)₂] [Sn–P = 2.649(1) Å],^[21] and *cis*-[SnCl₄{Ph₂P(CH₂)₂PPh₂}] [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 [SnCl₄{Et₂P(CH₂)₂PEt₂}].^[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.

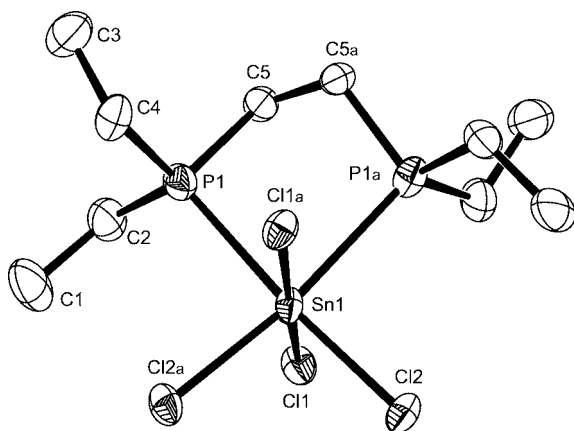


Figure 5. Structure of [SnCl₄{Et₂P(CH₂)₂PEt₂}] showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity. The tin atom is on a twofold axis. Symmetry operation, a: 1–x, y, 1/2–z.

Reactions with Dioxygen: We have reported elsewhere^[9] that mixtures of phosphanes or diphosphanes and SnX₄ (X = Cl, Br or I) in chlorocarbon solution air-oxidise readily to the corresponding phosphane oxides. Catalytic amounts of SnI₄ can be used to cleanly generate phosphane oxides from the corresponding phosphanes using dry air or di-

oxygen, and whilst the mechanism remains obscure, the use of ¹⁸O₂ in these reactions showed that the source of the oxygen is O₂, 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 [SnF₄(PCy₃)₂] is particularly sensitive and even brief exposure to air of a CH₂Cl₂ solution produced substantial oxidation. The [SnF₄(PMe₃)₂] and the diphosphane complexes are less rapidly air-oxidised, but modest amounts of phosphane oxides can be detected by ³¹P NMR in solutions exposed to air for some hours. In these systems the phosphane oxide binds strongly to the SnF₄ (cf. ref.^[19]), and thus in contrast to the extensively dissociated SnI₄ systems^[27] the formation of phosphane oxide is stoichiometric, because the phosphane oxides remove the SnF₄ by complexation preventing further reaction. Crystals of [SnF₄(OPPh₃)₂] were obtained over several days from a CH₂Cl₂ solution of the products of melting [SnF₄(MeCN)₂] with excess PPh₃. 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 SnF₄ is the strongest Lewis acid of the four tin(IV) halides towards O donor phosphane oxide ligands.

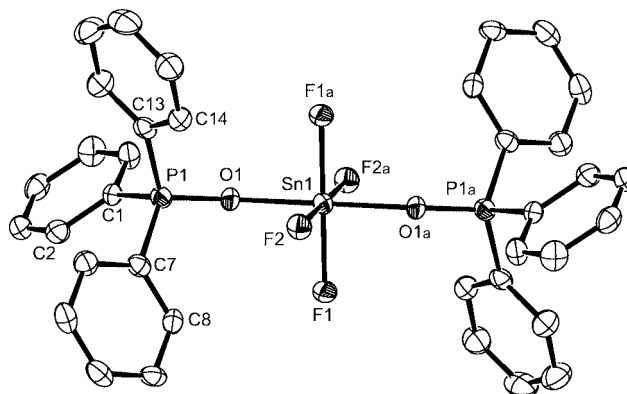


Figure 6. Structure of *trans*-[SnF₄(Ph₃PO)₂] showing a partial atom numbering scheme. Phenyl groups are numbered cyclically starting at the *ipso* C atom. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Sn1 is positioned on a centre of symmetry. Symmetry operation, a: –x, 1–y, 1–z.

Table 8. Selected bond lengths [Å] and angles [°] for *trans*-[SnF₄(Ph₃PO)₂].2CH₂Cl₂.

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 SnF₄ with tertiary arsanes including AsMe₃, *o*-C₆H₄(AsMe₂)₂ and MeC(CH₂AsMe₂)₃ were unsuccessful. The reaction of [SnF₄(MeCN)₂] or [SnF₄(THF)₂] in CH₂Cl₂ or toluene with *o*-C₆H₄(AsMe₂)₂,

Table 9. Selected bond lengths [Å] and angles [°] for [SnBr₄{MeC(CH₂AsMe₂)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 [SnF₄{*o*-C₆H₄(AsMe₂)₂}] and SnF₄. The IR spectra showed the presence of the diarsane, a broad ν(SnF) at ca. 570 cm⁻¹, and usually some MeCN or THF. The ¹H NMR spectra of these products in CD₂Cl₂ solution showed only MeCN or THF and “free” *o*-C₆H₄(AsMe₂)₂ [as *o*-C₆H₄(AsMe₂)₂ is a liquid, this is evidence for coordination of the diarsane to tin in the solids]. The ¹⁹F{¹H} NMR spectra showed no resonances at room temperature, but below ca. 210 K, two new broad resonances at δ = –138 and –152 were observed, which seem reasonable for [SnF₄{*o*-C₆H₄(AsMe₂)₂}], but no F–F coupling was resolved even at 190 K. The data suggest that [SnF₄{*o*-C₆H₄(AsMe₂)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 AsMe₃ or MeC(CH₂AsMe₂)₃ there was little evidence for coordination to SnF₄. In contrast, arsane complexes of SnX₄ (X = Cl, Br or I) form readily,^[9] and indeed [SnI₄{*o*-C₆H₄(AsMe₂)₂}] is one of the very small number of structurally characterised neutral ligand adducts of SnI₄. The explanation of this marked difference to phosphanes probably arises from the fact the SnF₄ 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 SnF₄.

In the course of this work the [SnX₄{MeC(CH₂AsMe₂)₃}] (X = Cl or Br) were prepared from the appropriate SnX₄ and triarsane in CH₂Cl₂ and their ¹H NMR spectra show the triarsane bound as a bidentate to a six-coordinate tin centre. The ¹¹⁹Sn NMR chemical shifts of δ = –696 and –1290 ppm (Table 6) are typical of SnX₄As₂ donor sets.^[9] The structures were confirmed by a X-ray study of [SnBr₄{MeC(CH₂AsMe₂)₃}] (Table 9, Figure 7), which showed a distorted octahedral tin centre with Sn–Br_{trans}–Br [2.5807(5), 2.6340(5) Å] longer than Sn–Br_{trans}–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 [SnI₄{*o*-C₆H₄(AsMe₂)₂}] [2.716(2), 2.752(2) Å],^[9] and *trans*-[SnCl₄(AsPh₃)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 [SnI₄{*o*-C₆H₄(AsMe₂)₂}] which contains a five-membered ring.

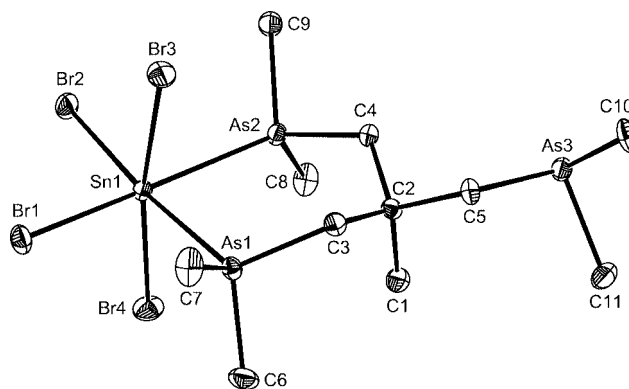


Figure 7. Structure of [SnBr₄{MeC(CH₂AsMe₂)₃}] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

Comparisons and Conclusions

This work has provided the first examples of SnF₄ 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 SnF₄ being the strongest Lewis acid. The corresponding data for *cis*-[SnX₄{Et₂P(CH₂)₂PEt₂}] (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*-[SnF₄(PCy₃)₂] is almost certainly due to steric effects caused by the bulky cyclohexyl substituents (PCy₃ has a cone angle of ca. 170°). However, the instability of SnF₄ adducts of arsanes suggests that towards even softer ligands, SnCl₄ 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 ¹¹⁹Sn 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 ³¹P 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(³¹P–¹¹⁹Sn) 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(¹⁹F–¹¹⁹Sn) couplings are larger in the phosphane complexes than in the N- or O-donor ligand cases. The ¹J(¹⁹F–¹¹⁹Sn)_{F–*trans*-F} are markedly larger than ¹J(¹⁹F–¹¹⁹Sn)_{F–*cis*-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 SnF₄, 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. SnF₂, SnCl₄, SnBr₄ and SnI₄ were obtained from Aldrich and used as received. [SnF₄(MeCN)₂] was made as described.^[18] Ligands were obtained from Aldrich: PMe₃, PPh₃, PCy₃, AsMe₃, Me₂P(CH₂)₂PMe₂, Et₂P(CH₂)₂PEt₂, Cy₂P(CH₂)₂PCy₂, or were made by literature methods: *o*-C₆H₄(PPh₂)₂, Ph₂P(CH₂)₂PPh₂, *o*-C₆H₄(PMe₂)₂, *o*-C₆H₄(AsMe₂)₂, MeC(CH₂AsMe₂)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 Me₂N(CH₂)₂NMe₂ were dried by distillation from BaO, tetrahydrofuran was dried by distillation from Na-benzophenone ketyl, MeCN and CH₂Cl₂ from CaH₂. IR spectra were recorded as Nujol mulls on a Perkin–Elmer PE 983G spectrometer, ¹H NMR spectra in CDCl₃, CD₂Cl₂ or CD₃NO₂ solutions on a Bruker AV300, ³¹P{¹H}, ¹⁹F{¹H} and ¹¹⁹Sn NMR spectra on a Bruker DPX400 and referenced to 85% H₃PO₄, CFCl₃ and neat SnMe₄ respectively. The ¹¹⁹Sn 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 magne-

togyric ratio of the isotope. Microanalytical measurements on new complexes were performed by the microanalytical service at Strathclyde University.

[SnF₄{*o*-C₆H₄(PMe₂)₂}]: [SnF₄(MeCN)₂] (0.276 g, 1.0 mmol) was dissolved in CH₂Cl₂ (20 mL) and *o*-C₆H₄(PMe₂)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%. C₁₀H₁₆F₄P₂Sn·CH₂Cl₂ (477.8): calcd. C 27.6, H 3.8; found C 26.9, H 3.8. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.87 (t, ²J + ⁵J_{P–H} = 4 Hz, 12 H, Me), 5.4 (CH₂Cl₂), 7.75–7.81 (m, 4 H, C₆H₄) ppm. IR (Nujol): $\tilde{\nu}$ = 564 (s), 534 (s) ν (SnF) cm^{–1}.

[SnCl₄{*o*-C₆H₄(PMe₂)₂}]: A solution of SnCl₄ (0.12 mL, 1.0 mmol) in CH₂Cl₂ (5 mL) was added to *o*-C₆H₄(PMe₂)₂ (0.198 g, 1.0 mmol) in CH₂Cl₂ (20 mL) producing an immediate white precipitate. After 30 min the solid was filtered off and dried in vacuo. Yield 0.427 g, 93%. C₁₀H₁₆Cl₄P₂Sn (458.7): calcd. C 26.2, H 3.5; found C 25.9, H 3.2. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.97 (t, ²J + ⁵J_{P–H} = 4.4 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C₆H₄) ppm. IR (Nujol): $\tilde{\nu}$ = 307 (s), 296 (s) ν (SnCl) cm^{–1}.

[SnBr₄{*o*-C₆H₄(PMe₂)₂}]: Prepared similarly to the chloride as a yellow solid. Yield 93%. C₁₀H₁₆Br₄P₂Sn (636.5): calcd. C 18.9, H 2.5; found C 18.7, H 2.4. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.95 (t, ²J + ⁵J_{P–H} = 4.5 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C₆H₄) ppm. IR (Nujol): $\tilde{\nu}$ = 205 (sh), 202 (s), 199 (sh), 196 (s) ν (SnBr) cm^{–1}.

[SnI₄{*o*-C₆H₄(PMe₂)₂}]: Prepared similarly to the chloride as a brown powder. Yield 80%. C₁₀H₁₆I₄P₂Sn (824.5): calcd. C 14.6, H 2.0; found C 14.6, H 1.9. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.83 (t, ²J + ⁵J_{P–H} = 4.8 Hz, 12 H, Me), 7.75–7.81 (m, 4 H, C₆H₄) ppm.

[SnF₄{*o*-C₆H₄(PPh₂)₂}]: [SnF₄(MeCN)₂] (0.276 g, 1.00 mmol) was suspended in CH₂Cl₂ (20 mL) and a solution of *o*-C₆H₄(PPh₂)₂ (0.446 g, 1.00 mmol) in CH₂Cl₂ (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%. C₃₀H₂₄F₄P₂Sn (641.2): calcd. C 56.2, H 3.8; found C 56.9, H 4.1. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.30–7.68 (m, Ph) ppm. IR (Nujol): $\tilde{\nu}$ = 574 (s), 557 (s), 526 (s) ν (SnF) cm^{–1}.

[SnF₄(PMe₃)₂]: [SnF₄(MeCN)₂] (0.277 g, 1.00 mmol) was suspended in CH₂Cl₂ (10 mL), trimethylphosphane (0.167 g, 2.20 mmol) was added and stirred at room temperature for 1 h. Some of the CH₂Cl₂ 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%. C₆H₁₈F₄P₂Sn·2CH₂Cl₂ (516.7): calcd. C 18.6, H 4.3; found C 18.3, H 4.5. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.68 (m, Me), 5.4 (CH₂Cl₂) ppm. IR (Nujol): $\tilde{\nu}$ = 546 (br) ν (SnF) cm^{–1}.

[SnF₄(PCy₃)₂]: [SnF₄(MeCN)₂] (0.277 g, 1.00 mmol) was suspended in CH₂Cl₂ (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%. C₃₂H₆₆F₄P₂Sn·1/2CH₂Cl₂ (750.0): calcd. C 54.9, H 8.5; found C 54.4, H 8.8. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.29–2.34 (m, Cy), 5.4 (CH₂Cl₂) ppm. IR (Nujol): $\tilde{\nu}$ = 557 (s), 535 (s) ν (SnF) cm^{–1}.

[SnF₄{Et₂P(CH₂)₂PEt₂}]: [SnF₄(MeCN)₂] (0.278 g, 1.00 mmol) was suspended in CH₂Cl₂ (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 ₃ PO) ₂]-2CH ₂ Cl ₂	[SnF ₄ {Et ₂ P(CH ₂) ₂ PEt ₂ }]	[SnF ₄ {MeO(CH ₂) ₂ OMe}]
Formula	C ₃₈ H ₃₄ Cl ₄ F ₄ O ₂ P ₂ Sn	C ₁₀ H ₂₄ F ₄ P ₂ Sn	C ₄ H ₁₀ F ₄ O ₂ Sn
<i>M</i>	921.08	400.92	284.81
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> [Å]	8.8697(16)	8.8994(12)	6.2957(15)
<i>b</i> [Å]	14.771(4)	11.663(3)	20.987(6)
<i>c</i> [Å]	14.446(4)	14.774(4)	6.693(2)
<i>a</i> [°]	90	90	90
<i>β</i> [°]	95.236(16)	104.257(12)	111.941(15)
<i>γ</i> [°]	90	90	90
<i>U</i> [Å ³]	1884.7(8)	1486.2(5)	820.2(4)
<i>Z</i>	2	4	4
<i>μ</i> [mm ⁻¹]	1.101	1.956	3.137
<i>F</i> (000)	924	800	544
Total no. of observations (<i>R</i> _{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 <i>F</i> 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
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.058, 0.106	0.030, 0.053	0.023, 0.054
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.135, 0.131	0.042, 0.056	0.027, 0.056
Compound	[SnF ₄ (1,10-phenanthroline)]·MeOH	[SnF ₄ (PCy ₃) ₂]	[SnCl ₄ {Et ₂ P(CH ₂) ₂ PEt ₂ }]
Formula	C ₁₃ H ₁₂ F ₄ N ₂ OSn	C ₃₆ H ₆₆ F ₄ P ₂ Sn	C ₁₀ H ₂₄ Cl ₄ P ₂ Sn
<i>M</i>	406.94	755.52	466.72
Crystal system	tetragonal	triclinic	monoclinic
Space group	<i>I</i> 4 ₁ / <i>a</i> (no. 88)	<i>P</i> 1̄ (no. 2)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> [Å]	9.471(3)	8.251(2)	9.708(3)
<i>b</i> [Å]	9.471(3)	9.868(3)	12.177(2)
<i>c</i> [Å]	29.964(8)	11.832(4)	16.301(5)
<i>a</i> [°]	90	77.192(15)	90
<i>β</i> [°]	90	85.601(10)	107.108(12)
<i>γ</i> [°]	90	69.240(15)	90
<i>U</i> [Å ³]	2687.8(15)	878.3(4)	1841.7(9)
<i>Z</i>	8	1	4
<i>μ</i> [mm ⁻¹]	1.948	0.864	2.122
<i>F</i> (000)	1584	398	928
Total no. of observations (<i>R</i> _{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 <i>F</i> 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
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.072, 0.180	0.051, 0.101	0.054, 0.112
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.128, 0.207	0.070, 0.108	0.092, 0.126
Compound	[SnBr ₄ {MeC(CH ₂ AsMe ₂) ₃ }]		
Formula	C ₁₁ H ₂₇ As ₃ Br ₄ Sn		
<i>M</i>	822.42		
Crystal system	monoclinic		
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)		
<i>a</i> [Å]	11.371(2)		
<i>b</i> [Å]	12.839(2)		
<i>c</i> [Å]	15.227(2)		
<i>a</i> [°]	90		
<i>β</i> [°]	91.731(10)		
<i>γ</i> [°]	90		
<i>U</i> [Å ³]	2221.9(6)		
<i>Z</i>	4		
<i>μ</i> [mm ⁻¹]	12.766		
<i>F</i> (000)	1528		
Total no. of observations (<i>R</i> _{int})	22702 (0.064)		
Unique observations	5084		
Min., max. transmission	0.767, 1.000		
No. of parameters, restraints	179, 0		
Goodness-of-fit on <i>F</i> ²	1.03		
Resid. electron density [e·Å ⁻³]	−0.91 to +0.84		
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.026, 0.050		
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.045, 0.053		

[a] Common items: temperature = 120 K; wavelength (Mo-*K*_α) = 0.71073 Å; *θ*_{max} = 27.5°. [b] *R*₁ = Σ|| *F*_o| − |*F*_c||/Σ|*F*_o|. *wR*₂ = [Σ(*w*(*F*_o − *F*_c)²)/Σ(*w**F*_o)⁴)^{1/2}.

The white precipitate was filtered off and dried in vacuo. Yield 0.32 g, 80%. C₁₀H₂₄F₄P₂Sn (400.95): calcd. C 29.9, H 6.0; found C 29.0, H 6.0. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.13–2.07 (m, 2 H, CH₂), 1.37–1.26 (m, 6 H, Me) ppm. IR (Nujol): ν̄ = 553 (m), 526 (s) ν(SnF) cm⁻¹.

[SnF₄{C₆H₅P(CH₂)₂PCy₂}]: [SnF₄(MeCN)₂] (0.278 g, 1.00 mmol) was suspended in CH₂Cl₂ (10 mL), 1,2-bis(dicyclohexylphosphanyl)ethane (0.444 g, 1.05 mmol) in CH₂Cl₂ (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%. C₂₆H₄₈F₄P₂Sn·1/2CH₂Cl₂ (826.1): calcd. C 48.2, H 7.5; found C 49.2, H 8.3. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.21–1.255 (m, CH₂, Cy), 5.4 (CH₂Cl₂) ppm. IR (Nujol): ν̄ = 560 (s), 530 (s) ν(SnF) cm⁻¹.

[SnF₄{Ph₂P(CH₂)₂PPh₂}]: [SnF₄(MeCN)₂] (0.28 g, 1.0 mmol) was suspended in CH₂Cl₂ (15 mL), 1,2-bis(diphenylphosphanyl)ethane (0.42 g, 1.05 mmol) in CH₂Cl₂ (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%. C₂₆H₂₄F₄P₂Sn·1/2CH₂Cl₂ (635.6): calcd. C 50.0, H 4.0; found C 49.6, H 3.7. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.89–7.45 (m, 5 H, Ph), 5.4 (CH₂Cl₂). 2.81 (br, 1 H, CH₂) ppm. IR (Nujol): ν̄ = 566 (br) ν(SnF) cm⁻¹.

[SnCl₄{Et₂P(CH₂)₂PEt₂}]: SnCl₄ (0.260 g, 1.00 mmol) was dissolved in CH₂Cl₂ (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%. C₁₀H₂₄Cl₄P₂Sn·CH₂Cl₂ (551.7): calcd. C 23.95, H 4.8; found C 23.5, H 5.0. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.12–2.11 (m, 6 H, CH₂), 1.39–1.21 (m, 6 H, Me), 5.4 (CH₂Cl₂) ppm. IR (Nujol): ν̄ = 318 (sh), 307 (sh), 282 (br) ν(SnCl) cm⁻¹.

[SnF₄(2,2'-bipyridyl)]: [SnF₄(MeCN)₂] (0.276 g, 1.00 mmol) was suspended in CH₂Cl₂ (10 mL) and a solution of 2,2'-bipy (0.156 g, 1.00 mmol) in CH₂Cl₂ (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, CD₃NO₂, 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): ν̄ = 580 (s), 560, 520 (sh) ν(SnF) cm⁻¹.

[SnF₄(1,10-phenanthroline)]: Prepared similarly to the above. Yield 60%. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.35 (m, 2 H), 9.16 (m, 2 H), 8.45 (m, 4 H) ppm. IR (Nujol): ν̄ = 587 (s), 566 (s) ν(SnF) cm⁻¹.

[SnF₄{MeO(CH₂)₂OMe}]: 1,2-Dimethoxyethane (0.1 mL, 1.0 mmol) was added to a solution of [SnF₄(MeCN)₂] (0.276 g, 1.0 mmol) in CH₂Cl₂ (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, CDCl₃, 200 K): δ = 3.98 (s, 3 H, Me), 4.25 (s, 2 H, CH₂) ppm. IR (Nujol): ν̄ = 609 (s), 584 (s), 540 (m) ν(SnF) cm⁻¹.

[SnF₄(pyridine)₂]: Pyridine (0.16 g, 2.0 mmol) was added to a solution of [SnF₄(MeCN)₂] (0.186 g, 0.67 mmol) in CH₂Cl₂ (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, CDCl₃, 25 °C): δ = 9.00 (m, 2 H), 8.2 (m, 1 H), 7.7 (m, 2 H) ppm. IR (Nujol): ν̄ = 568 (s) ν(SnF) cm⁻¹.

[SnF₄{Me₂N(CH₂)₂NMe₂}]: [SnF₄(MeCN)₂] (0.276 g, 1.0 mmol) was suspended in CH₂Cl₂ (10 mL), *N,N,N',N'*-tetramethylethyl-

enediamine (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%. C₆H₁₆F₄N₂Sn·1/2CH₂Cl₂ (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, CDCl₃, 25 °C): δ = 2.89 (s, 12 H, Me), 3.02 (s, 4 H, CH₂) ppm. IR (Nujol): ν̄ = 570 (s), 547 (s) ν(SnF) cm⁻¹.

[SnF₄(THF)₂]: Was made as described.^[18] ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.1 (br, 2 H, CH₂), 4.4 (br, 2 H, CH₂) ppm. IR (Nujol): ν̄ = 600 (vbr) ν(SnF), 1013 (br), 845 (m) ν(COC) cm⁻¹.

[SnCl₄{MeC(CH₂AsMe₂)₃}]: MeC(CH₂AsMe₂)₃ (0.384 g, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL) under nitrogen. To this solution SnCl₄ (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, CDCl₃, 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, CH₂), 2.39 (d, ²J = 12 Hz, 2 H, CH₂) 2.54 (d, ²J = 12 Hz, 2 H, CH₂) ppm. IR (Nujol): ν̄ = 310 (sh), 302 (s), 280 (sh) ν(SnCl) cm⁻¹.

[SnBr₄{MeC(CH₂AsMe₂)₃}]: MeC(CH₂AsMe₂)₃ (0.384 g, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL) under nitrogen. To this solution SnBr₄ (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%. C₁₁H₂₇As₃Br₄Sn (822.4): calcd. C 16.1, H 3.3; found C 15.3, H 3.1. ¹H NMR (300 MHz, CDCl₃, 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, CH₂), 2.32 (br, 2 H, CH₂) 2.55 (br, 2 H, CH₂) ppm. IR (Nujol): ν̄ = 215 (sh), 207 (s), 199 (s) ν(SnBr) cm⁻¹.

X-ray Experimental: Crystals were grown from anhydrous CH₂Cl₂ 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 [SnF₄(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(Et₂)], -299708 [for F/O(Me)], -299709 (for F/N), -299710 [for F/P(R₃)], -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.

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