

# Neutral and cationic phosphine and arsine complexes of tin(IV) halides: synthesis, properties, structures and anion influence

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## Abstract

The reaction of *trans*-[SnCl<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Me or Et) with trimethylsilyltriflate (TMSOTf) in CH<sub>2</sub>Cl<sub>2</sub> solution substitutes one chloride to form [SnCl<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(OTf)]; addition of excess TMSOTf does not substitute further chlorides. The complexes have been fully characterised by microanalysis, IR and multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, <sup>119</sup>Sn) spectroscopy. The crystal structure of [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>(OTf)] revealed *mer*-chlorines and *trans* phosphines. In contrast, *trans*-[SnBr<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>], [SnCl<sub>4</sub>{Et<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PEt<sub>2</sub>}], [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] and [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>}] did not react with TMSOTf in CH<sub>2</sub>Cl<sub>2</sub> solution even after 3 days.

The arsine complexes, [SnX<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (X = Cl, Br), were confirmed as *trans*-isomers by similar spectroscopic and structural studies, while attempts to isolate [SnI<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] were unsuccessful and reaction of SnX<sub>4</sub> with SbR<sub>3</sub> (R = Et, <sup>i</sup>Pr) resulted in reduction to SnX<sub>2</sub> and formation of R<sub>3</sub>SbX<sub>2</sub>. *Trans*-[SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] is converted by TMSOTf into [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>(OTf)], whose X-ray structure reveals the same geometry found in the phosphine analogues, with the triflate coordinated.

The salts, [SnCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>] and [SnCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> were made by treatment of [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] with one and two mol. equivalents, respectively, of AlCl<sub>3</sub> in anhydrous CH<sub>2</sub>Cl<sub>2</sub>, whereas reaction of [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] with AlCl<sub>3</sub> produced a mixture including Et<sub>3</sub>AsCl<sub>2</sub> and [Et<sub>3</sub>AsCl][Sn(AsEt<sub>3</sub>)Cl<sub>5</sub>] (the latter identified crystallographically). In contrast, using Na[BAR<sup>F</sup>] (BAR<sup>F</sup> = B{3,5-CF<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>}) produced [SnCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>][BAR<sup>F</sup>] and also allowed clean isolation of the arsine analogue, [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>][BAR<sup>F</sup>]. [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] also reacts with AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> to form [SnCl<sub>3</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}][AlCl<sub>4</sub>] and [SnCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}][AlCl<sub>4</sub>]<sub>2</sub>. Multinuclear NMR spectroscopy on the [AlCl<sub>4</sub>]<sup>-</sup> salts show that δ<sup>31</sup>P and δ<sup>119</sup>Sn move progressively to high frequency on conversion from the neutral complex to the mono- and the di-cations, whilst <sup>1</sup>J(<sup>119</sup>Sn-<sup>31</sup>P) follow the trend: [SnCl<sub>3</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}]<sup>+</sup> > [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] > [SnCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}]<sup>2+</sup>. DFT studies on selected complexes show only small changes in ligand geometries and bond lengths between the halide and triflate complexes, consistent with the X-ray crystallographic data reported and the HOMO and LUMO energies are relatively unperturbed upon the introduction of (coordinated) triflate, whereas the energies of both are *ca.* 4 eV lower in the cationic species and reveal significant hybridisation across the pnictine ligands.

## Introduction

Much of the coordination chemistry of the transition metal ions with neutral ligands is based around metal halide complexes.<sup>1</sup> In addition to neutral complexes  $[ML_aX_b]$  ( $M$  = transition metal,  $X$  = halide,  $L$  = neutral ligand), related cations  $[ML_cX_{b-1}]^+$  or  $[ML_dX_{b-2}]^{2+}$  ( $c, d \geq a$ ) are commonly known, formed either spontaneously in the presence of excess  $L$ , or upon the addition of large, weakly coordinating anions.<sup>1</sup> In some cases complexes of the type  $[ML_xX_y][MX_z]$  form spontaneously under appropriate conditions, a process sometimes labelled as ‘self-ionisation’. In contrast, complexes of p-block metal and metalloid halides are overwhelmingly neutral  $[M'L_aX_b]$  ( $M'$  = p-block metal) with much stronger  $M-X$  than  $M-L$  bonding.<sup>1</sup> In general, p-block Lewis acids coordinate the neutral ligands relatively weakly, and these are often partially dissociated in solution or undergoing rapid dissociative exchange. The neutral ligands fill ‘free’ coordination sites, but do not compete with the halide ligands for the metal centre. The tin(IV) halides,  $SnX_4$ , typify this pattern in that the majority of complexes are octahedral with neutral ligands filling two coordination sites.<sup>2</sup> Rare exceptions are provided by 1,4,7-trimethyl-1,4,7-triazacyclonane, 1,3,5-trimethyl-1,3,5-triazacyclohexane and 1,4,7-trithiacyclonane ( $L^3$ ), which generate the ‘self-ionisation’ complexes,  $[SnX_3(L^3)]_2[SnX_6]$  ( $X = Cl$  or  $Br$ ),<sup>3</sup> although more flexible acyclic polydentate ligands, such as  $MeC(CH_2AsMe_2)_3$ , behave as bidentate ligands, as in  $[SnX_4\{\kappa^2-MeC(CH_2AsMe_2)_3\}]$ .<sup>4</sup>

Complexes of the tin(IV) halides,  $SnX_4$  ( $X = Cl$  or  $Br$ ), with neutral phosphine and arsine ligands have been explored in considerable detail<sup>5</sup> and almost all are of the octahedral *trans*- $[SnX_4(ER_3)_2]$  or *cis*- $[SnX_4(\text{bidentate})]$  (bidentate = diphosphine or diarsine) types.  $SnI_4$  is a weaker Lewis acid and forms similar, but less stable adducts,<sup>5</sup> whilst complexes of  $SnF_4$  have been much less studied.<sup>4,5</sup> Reported examples of stibine complexes of p-block halides are extremely rare.<sup>5,6</sup>

The formation of cationic complexes would be expected to enhance the Lewis acidity of the tin centre, and examples of halo- or organo-tin cations with polydentate and pincer ligands have been described.<sup>7-12</sup> MacDonald *et al.*<sup>11</sup> obtained  $[SnCl_3(PMe_3)_2][AlCl_4]$  and  $[SnCl_2(PMe_3)_2][AlCl_4]_2$  by treatment of *trans*- $[SnCl_4(PMe_3)_2]$  with one or two mol. equivalents of  $AlCl_3$ , respectively. The former has a distorted trigonal bipyramidal geometry with *trans* axial  $PMe_3$  ligands. The dication has *trans*  $PMe_3$  groups, and two *cis* interactions from the  $[AlCl_4]^-$  anions completing a very distorted octahedron. The  $Sn-Cl$  distances decrease along the series  $[SnCl_4(PMe_3)_2] > [SnCl_3(PMe_3)_2]^+ > [SnCl_2(PMe_3)_2]^{2+}$ . In the present work we have explored the reaction of tin(IV) halides with a series of mono- and bi-dentate phosphine, arsine and stibine ligands and the abstraction/replacement of some of the halides from the resulting complexes by other weakly coordinating anions, including triflate ( $[CF_3SO_3]^-$ ) via treatment with trimethylsilyltriflate,  $[AlX_4]^-$  via addition of aluminium trihalides and using the large diffuse  $[BAR^F]^-$  anion, via addition of its  $Na^+$  salt ( $BAR^F = B\{3,5-CF_3(C_6H_3)_4\}$ ).

## Experimental

All complex syntheses were carried out using standard Schlenk and vacuum line techniques. Samples were handled and stored in a glove box under a dry dinitrogen atmosphere to exclude moisture. Tin(IV) halides, TMSOTf, and aluminium halides were obtained from Sigma-Aldrich and used as received. Phosphine and arsine ligands were obtained from Sigma-Aldrich or Strem, except for *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>, which were prepared by literature methods.<sup>13</sup> SbEt<sub>3</sub>, Sb<sup>i</sup>Pr<sub>3</sub><sup>14</sup> and Na[BAr<sup>F</sup>]<sup>15</sup> were made as described. CH<sub>2</sub>Cl<sub>2</sub> was dried by distillation from CaH<sub>2</sub> and diethyl ether and n-hexane from Na.

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 spectrometer over the range 4000–200 cm<sup>-1</sup>. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, <sup>27</sup>Al and <sup>119</sup>Sn NMR spectra were recorded from CDCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> solutions using a Bruker AV400 spectrometer and referenced to TMS via the residual solvent resonance, CFC<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>, [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> in H<sub>2</sub>O at pH = 1 or SnMe<sub>4</sub> as appropriate. Typically, [Cr(acac)<sub>3</sub>] was added as a relaxation agent when recording the <sup>119</sup>Sn spectra, except for those containing [AlCl<sub>4</sub>]<sup>-</sup>, when it appeared to react with the complexes, turning green. In these cases a 2 second pulse delay was used. Microanalyses were undertaken by London Metropolitan University.

**[SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>]:** A solution of AsEt<sub>3</sub> (0.058 g, 0.36 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a solution of SnCl<sub>4</sub> (0.047 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The colourless solution was left to stir for 1 h before the product was isolated by evaporation of the solvent under vacuum to afford a white solid. Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation of a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Yield 0.093 g, 88%. Required for C<sub>12</sub>H<sub>30</sub>As<sub>2</sub>Cl<sub>4</sub>Sn (584.7): C, 24.6; H, 5.2. Found: C, 24.5; H, 5.0 %. IR (Nujol/cm<sup>-1</sup>): ν = 288s (Sn-Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 295 K): δ = 2.34 (q, [12H], <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>2</sub>), 1.42 (t, [18H], <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 295 K): δ = 8.62 (CH<sub>2</sub>), 15.04 (CH<sub>3</sub>). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): n.o.; (CD<sub>2</sub>Cl<sub>2</sub>, 193 K): δ = -657.4.

**[SnBr<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>]:** A solution of AsEt<sub>3</sub> (0.144 g, 0.89 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added to a solution of SnBr<sub>4</sub> (0.195 g, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The pale yellow solution was left to stir for 1 h before the product was isolated by removal of the solvent to afford a yellow solid. Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation of a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Yield 0.175 g, 50%. Required for C<sub>12</sub>H<sub>30</sub>As<sub>2</sub>Br<sub>4</sub>Sn (762.5): C, 18.9; H, 4.0. Found: C, 19.0; H, 4.0 %. IR (Nujol/cm<sup>-1</sup>): ν = 210s (Sn-Br). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 2.35 (q, [12H], <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>2</sub>), 1.43 (t, [18H], <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 8.5 (CH<sub>2</sub>), 14.8 (CH<sub>3</sub>). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -1173.4; (CD<sub>2</sub>Cl<sub>2</sub>, 193 K): δ = -1125.3.

**[SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>(OTf)]:** [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (0.150 g, 0.26 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) to form a clear solution. To this TMSOTf (0.057 g, 0.26 mmol) was added in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the clear solution was stirred for 2 h. The solvent was removed and the white powder was dried *in vacuo*. Crystals suitable for single crystal X-ray diffraction were grown from slow evaporation of a solution of the compound in CH<sub>2</sub>Cl<sub>2</sub>. Yield 0.138 g, 77%. Required for C<sub>13</sub>H<sub>30</sub>As<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>O<sub>3</sub>SSn (698.1): C, 22.4, H, 4.3. Found C, 21.9; H, 4.2%. IR (Nujol/cm<sup>-1</sup>):  $\nu = 294s, 378w$  (Sn-Cl), 1156m (-OSO<sub>2</sub>), 1231m, 1200m (CF<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 1.39$  (t, [18H], <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, CH<sub>3</sub>), 2.38 (q, [12H], <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 9.0$  (CH<sub>2</sub>), 16.0 (CH<sub>3</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -78.7$  (s, CF<sub>3</sub>). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): n.o.; (CD<sub>2</sub>Cl<sub>2</sub>, 183 K):  $\delta = -620$  (s).

**[SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>(OTf)]:** [SnCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sup>16</sup> (0.300 g, 0.72 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). To this TMSOTf (0.016 g, 0.72 mmol) was added in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The solution was stirred for 16 h and the solvent and volatiles were removed and the resulting white powder dried *in vacuo*. The powder was then washed with diethyl ether (3 x 10 mL) and dried *in vacuo*. Crystals suitable for single crystal X-ray diffraction were grown by the slow evaporation of a saturated solution of the compound in CH<sub>2</sub>Cl<sub>2</sub>. Yield 0.215 g, 57%. Required for C<sub>7</sub>H<sub>18</sub>Cl<sub>3</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SSn (526.1): C, 16.0, H 3.5. Found C, 15.7; H, 3.4%. IR (Nujol/cm<sup>-1</sup>):  $\nu = 296m, 306m, 377w$  (Sn-Cl), 1173m (-OSO<sub>2</sub>), 1200m, 1235m (CF<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 1.83$  (m, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 10.09$  (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C} = 19.4 Hz, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 8.74$  (s, <sup>1</sup>J<sub>31P-117Sn} = 2814, <sup>1</sup>J<sub>31P-119Sn} = 2963 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -78.6$  (s, CF<sub>3</sub>). <sup>119</sup>Sn (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -516$  (t, <sup>1</sup>J<sub>P-119Sn} = 2963 Hz).</sub></sub></sub></sub>

**[SnCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>(OTf)]:** [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sup>16</sup> (0.08 g, 0.16 mmol) is dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). To this TMSOTf (0.036 g, 0.16 mmol) was added in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), resulting in a clear colourless solution which was stirred for 2 h. Solvent and volatiles were removed *in vacuo* and the resultant white powder was washed with diethyl ether (3 x 10 mL) and then dried *in vacuo*. Yield 0.065 g, 66%. Required for C<sub>13</sub>H<sub>30</sub>Cl<sub>3</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>SSn (610.2): C, 25.6; H, 5.0. Found, C, 25.4; H, 5.1%. IR (Nujol/cm<sup>-1</sup>):  $\nu = 289m, 301w, 374w$  (Sn-Cl), 1187m (-OSO<sub>2</sub>), 1235m (CF<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 1.30$  (m, [18H], CH<sub>3</sub>), 2.33 (m, [12H], CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 7.59$  (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C} = 2.93 Hz, CH<sub>2</sub>), 13.95 (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C} = 11 Hz, CH<sub>3</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -78.6$  (s, CF<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 28.45$ . <sup>31</sup>P{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 183 K):  $\delta = 33.58$  (s, <sup>1</sup>J<sub>31P-117Sn} = 2617 Hz, <sup>1</sup>J<sub>31P-119Sn} = 2734 Hz). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -535$ ; (CD<sub>2</sub>Cl<sub>2</sub>, 183 K):  $\delta = -535$  (t, <sup>1</sup>J<sub>31P-119Sn} = 2737 Hz).</sub></sub></sub></sub></sub>

**[SbEt<sub>3</sub>Cl(OTf)]:** SnCl<sub>4</sub> (0.100 g, 0.38 mmol) was dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. To this, SbEt<sub>3</sub> (0.160 g, 0.77 mmol) was added in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, resulting in the precipitation of a large amount of white solid. TMSOTf (0.085 g, 0.38 mmol) was added in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and the reaction stirred for 16 h. The liquid was filtered away from the unidentified solid and concentrated to dryness *in vacuo*, leading to a white solid. Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation

of a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Yield 0.064 g, 30%. Required for C<sub>7</sub>H<sub>15</sub>ClF<sub>3</sub>O<sub>3</sub>SSb (393.3): C, 21.4; H, 3.8 Found C, 21.7; H, 4.2%. IR (Nujol/cm<sup>-1</sup>): ν = 329m (Sb-Cl), 1167w (-OSO<sub>2</sub>), 1198w, 1235w (CF<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 1.62 (t, [9H], <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH<sub>3</sub>), 2.80 (q, [6H], <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 9.68 (CH<sub>2</sub>), 28.55 (CH<sub>3</sub>).

**[SnCl<sub>3</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>][AlCl<sub>4</sub>]:** [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}]<sup>4</sup> (0.150 g, 0.33 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and AlCl<sub>3</sub> (0.044 g, 0.33 mmol) was added. This resulted in a pale yellow clear solution which was stirred for a further 2 h. The solution was then concentrated to dryness *in vacuo* producing a white powder, which was then washed with n-hexane (3 x 10 mL) and the solid separated and dried *in vacuo* to leave a white powder. Yield: 0.120 g, 61%. Required for C<sub>10</sub>H<sub>16</sub>AlCl<sub>7</sub>P<sub>2</sub>Sn (591.9): C, 20.3; H, 2.7, Found C, 20.4; H, 2.8%. IR (Nujol/cm<sup>-1</sup>): ν = 322m, 342m (Sn-Cl), 451m, 497br ([AlCl<sub>4</sub>]<sup>-</sup>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 2.06 (t, <sup>2</sup>J + <sup>5</sup>J<sub>P-H</sub> = 4.5 Hz, [12H], CH<sub>3</sub>), 7.86-7.92 (m, [4H], Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 11.52 (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C</sub> = 16.4 Hz, CH<sub>3</sub>), 130.7-131.3, 134.2, 135.3 (Ar). <sup>27</sup>Al NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 102.8 (s, [AlCl<sub>4</sub>]<sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -24.7 (s, <sup>1</sup>J<sub>31P-117Sn</sub> = 930 Hz, <sup>1</sup>J<sub>31P-119Sn</sub> = 972 Hz). <sup>119</sup>Sn (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = -469 (t, <sup>1</sup>J<sub>31-119Sn</sub> = 972 Hz)

**[SnCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub>:** [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] (0.100 g, 0.22 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and to this AlCl<sub>3</sub> (0.058 g, 0.44 mmol) was added. This resulted in a pale yellow clear solution, which was stirred for a further 2 h. The solution was then concentrated to dryness *in vacuo* producing a white sticky solid, which was then washed with n-hexane (3 x 10 mL), the solid separated and dried *in vacuo* to leave a white sticky solid. Yield: 0.81 g 51%. Required for C<sub>10</sub>H<sub>16</sub>Al<sub>2</sub>Cl<sub>10</sub>P<sub>2</sub>Sn (725.4): C, 16.7; H, 2.2. Found C, 17.5; H, 2.7%. IR (Nujol/cm<sup>-1</sup>): ν = 294m, 310m (Sn-Cl), 452sh, 487s ([AlCl<sub>4</sub>]<sup>-</sup>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 2.18 (t, <sup>2</sup>J + <sup>5</sup>J<sub>PH</sub> = 4.5 Hz, [12H], CH<sub>3</sub>), 7.94-8.30 (m, [4H], Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 12.28 (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C</sub> = 16.1 Hz, CH<sub>3</sub>), 129.8-130.1, 134.4, 135.9 (Ar-H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -23.7 (<sup>1</sup>J<sub>31P-117Sn</sub> = 815 Hz, <sup>1</sup>J<sub>31P-119Sn</sub> = 853 Hz). <sup>27</sup>Al NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 102.9 (s, [AlCl<sub>4</sub>]<sup>-</sup>). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = -429 (t, <sup>1</sup>J<sub>31P-119Sn</sub> = 850 Hz).

**[SnCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>]:** [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] (0.200 g, 0.40 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and AlCl<sub>3</sub> (0.054 g, 0.40 mmol) was added. The suspension was stirred for 2 h leaving a clear and colourless solution, the solution was concentrated to dryness leaving a fine white powder which was washed with Et<sub>2</sub>O (3 x 10 mL) and dried *in vacuo* to yield a white powder. Yield: 0.160 g, 63%. Required for C<sub>10</sub>H<sub>16</sub>AlCl<sub>7</sub>P<sub>2</sub>Sn (630.04): C, 22.9; H, 4.8. Found C, 23.1; H, 5.3%. IR (Nujol/cm<sup>-1</sup>): ν = 280m, 289m (Sn-Cl), 484s, 503sh ([AlCl<sub>4</sub>]<sup>-</sup>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 1.36 (m, [18H], CH<sub>3</sub>), 2.32 (m, [12H], CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 7.34 (t, <sup>2</sup>J + <sup>4</sup>J<sub>31P-13C</sub> = 2.93 Hz, -CH<sub>3</sub>), 14.12 (t, <sup>1</sup>J + <sup>3</sup>J<sub>31P-13C</sub> = 22.45 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 35.22 (<sup>1</sup>J<sub>31P-117Sn</sub> = 2208 Hz, <sup>1</sup>J<sub>31P-119Sn</sub> = 2317 Hz);

(CD<sub>2</sub>Cl<sub>2</sub>, 183 K):  $\delta = 26.96$  ( $^1J_{31P-117Sn} = 2426$  Hz,  $^1J_{31P-119Sn} = 2520$  Hz).  $^{27}Al$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 103.2$  (s, [AlCl<sub>4</sub>]<sup>-</sup>).  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -350.2$  (br t,  $^1J_{31P-119Sn} = 2307$  Hz).

**[SnCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub>:** [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] (0.200 g, 0.40 mmol) was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 ml), to this AlCl<sub>3</sub> (0.107 g, 0.80 mmol) was added, the suspension was stirred for 2 h leaving a clear and colourless solution, the solution was concentrated to dryness and washed with Et<sub>2</sub>O (3 x 10 ml) then dried *in vacuo* leaving a sticky white solid which was dried *in vacuo*. Yield 0.201 g (66%) Anal. Required for C<sub>12</sub>H<sub>30</sub>Al<sub>2</sub>Cl<sub>10</sub>P<sub>2</sub>Sn (763.39) C, 18.9; H, 4.0. Found C, 19.0; H, 3.8, IR (Nujol/cm<sup>-1</sup>) = 289m, (Sn-Cl), 484s, ([AlCl<sub>4</sub>]<sup>-</sup>).  $^1H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295K):  $\delta = 1.39$  (m, [18H], CH<sub>3</sub>), 2.38 (m, [12H], CH<sub>2</sub>),  $^{13}C\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 7.50$  (t,  $^2J + ^4J_{31P-13C} = 2.93$  Hz, -CH<sub>3</sub>), 14.51 (t,  $^1J + ^3J_{31P-13C} = 13.2$  Hz),  $^{27}Al$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 103.0$ ,  $^{31}P\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 40.78$  ( $^1J_{31P-117Sn} = 2172$  Hz,  $^1J_{31P-119Sn} = 2274$  Hz).  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -301.4$  (br, t,  $^1J_{31P-119Sn} = 2291$  Hz).

**Reaction of [SnCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> + PEt<sub>3</sub>:** [SnCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (0.100 g, 0.13 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), to this PEt<sub>3</sub> (0.015 g, 0.22 mmol) was added in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). To this 10 drops of CD<sub>2</sub>Cl<sub>2</sub> is added. A portion of the solution was used for *in situ* NMR studies.

$^{27}Al$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 103.1$  (s, [AlCl<sub>4</sub>]<sup>-</sup>), 110.8 (d,  $^1J_{31P-27Al} = 267$  Hz, [AlCl<sub>3</sub>(PEt<sub>3</sub>)]).  $^{31}P\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -14.8$  (sextet,  $^1J_{27Al-31P} = 264$  Hz, [AlCl<sub>3</sub>(PEt<sub>3</sub>)]), 32.2 ( $^1J_{31P-117Sn} = 2312$  Hz,  $^1J_{31P-119Sn} = 2394$  Hz, new Sn-PEt<sub>3</sub> containing cation – see text).  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -449$  (t,  $^1J_{31P-119Sn} = 2394$  Hz).

**[SnCl<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>][BAR<sup>F</sup>]:** A Schlenk was charged with [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>] (0.100 g, 0.20 mmol) and Na[BAR<sup>F</sup>] (0.178 g, 0.20 mmol). To this CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added the resulting cloudy solution was stirred for 2 h, the solution was then filtered and concentrated to dryness *in vacuo* yielding a white solid. Yield: 0.201 g, 75%. Required for C<sub>44</sub>H<sub>42</sub>BCl<sub>3</sub>F<sub>24</sub>P<sub>2</sub>Sn (1324.3): C, 39.9, H, 3.2 Found C, 39.8, H, 3.3%.  $^1H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 1.35$  (m, [18H], CH<sub>3</sub>), 2.29 (m, [12H], CH<sub>2</sub>), 7.57 (s, [4H], [Bar<sup>F</sup>]), 7.72 (m, [8H], [Bar<sup>F</sup>]);  $^{19}F\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -63.0$  (s, -CF<sub>3</sub>)  $^{31}P\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 37.1$  ( $^1J_{31P-117Sn} = 2208$  Hz,  $^1J_{31P-119Sn} = 2311$  Hz);  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -379$  (t,  $^1J_{31P-119Sn} = 2311$  Hz).

**[SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>][BAR<sup>F</sup>]:** A Schlenk was charged with [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (0.100 g, 0.17 mmol) and Na[BAR<sup>F</sup>] (0.152 g, 0.17 mmol). To this CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added the resulting cloudy solution was stirred for 2 h and then filtered and concentrated to dryness *in vacuo* yielding a white solid. Yield: 0.162 g, 67%. Required for C<sub>44</sub>H<sub>42</sub>BCl<sub>3</sub>F<sub>24</sub>As<sub>2</sub>Sn (1412.2): C, 37.4, H, 3.0 Found C, 37.3, H, 2.8%.  $^1H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = 1.44$  (t,  $^3J_{HH} = 7.7$  Hz, [18H], CH<sub>3</sub>), 2.42 (q,  $^3J_{HH} = 7.7$  Hz, [12H], CH<sub>2</sub>), 7.57 (s, [4H], [Bar<sup>F</sup>]), 7.72 (m, [8H], [Bar<sup>F</sup>]);  $^{19}F\{^1H\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta = -63.0$  (s, -CF<sub>3</sub>);  $^{119}Sn$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 183 K):  $\delta = -388$  (br s).

**[SnCl<sub>3</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] [BAr<sup>F</sup>]**: A Schlenk was charged with [SnCl<sub>4</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}] (0.100 g, 0.17 mmol) and Na[BAr<sup>F</sup>] (0.152 g, 0.17 mmol) and to this CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added. The resulting cloudy solution was stirred for 2 h and then filtered and concentrated to dryness *in vacuo* yielding a white solid. Yield: 0.162 g, 67%. Required for C<sub>42</sub>H<sub>28</sub>BCl<sub>3</sub>F<sub>24</sub>P<sub>2</sub>Sn (1286.2): C, 39.2, H, 2.2 Found C, 39.3, H, 2.0%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 2.01 (t, <sup>2</sup>J +<sup>5</sup>J<sub>PH</sub> = 4.7 Hz, [12H], CH<sub>3</sub>), 7.57 (s, [4H], [BAr<sup>F</sup>]), 7.72 (m, [8H], [BAr<sup>F</sup>]), 7.82 (m, [4H], [BAr<sup>F</sup>]); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -63.0 (s, -CF<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -24.50 (<sup>1</sup>J<sub>31P-Sn</sub> = 1007 Hz); <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 183/298 K): δ = n.o.

**[SnBr<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>] [BAr<sup>F</sup>]**: A Schlenk was charged with [SnBr<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] (0.077 g, 0.1 mmol) and Na[BAr<sup>F</sup>] (0.090 g, 0.1 mmol) to this CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added; the resulting cloudy solution was stirred for 2 h and then filtered and concentrated to dryness *in vacuo* yielding a light yellow gum, which was then dissolved in Et<sub>2</sub>O (5 mL), then the solution was concentrated to dryness *in vacuo* yielding a light yellow solid. Yield: 0.091 g, 58%. Required for C<sub>44</sub>H<sub>42</sub>BBr<sub>3</sub>F<sub>24</sub>As<sub>2</sub>Sn (1448.2): C, 34.2, H, 2.7 Found C, 34.3, H, 2.9%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 1.39 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, [18H], CH<sub>3</sub>), 2.42 (br, [12H], CH<sub>2</sub>), 7.58 (s, [4H], [BAr<sup>F</sup>]), 7.73 (m, [8H], [BAr<sup>F</sup>]); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = 9.1 (s, -CH<sub>3</sub>), 15.9 (s, -CH<sub>2</sub>), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, <sup>1</sup>J<sub>11B-13C</sub> = 49.9 Hz); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K): δ = -62.8 (s, -CF<sub>3</sub>). <sup>119</sup>Sn NMR (CD<sub>2</sub>Cl<sub>2</sub>, 183/298 K): δ = n.o.

### X-Ray Experimental

Crystals of the complexes were grown from CH<sub>2</sub>Cl<sub>2</sub> solutions allowed to evaporate slowly in the glovebox. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013, or SHELX-2014/7.41.<sup>18</sup> H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. Details of the crystallographic parameters are given in Table S1 in the ESI. CCDC reference numbers for the crystallographic information files in cif format are CCDC 1916557 [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>], CCDC 1916558 [SnBr<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>], CCDC 1916559 [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>(OTf)], CCDC 1916560 [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>(OTf)], CCDC 1916561 [SnCl<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>][AlCl<sub>4</sub>]<sub>2</sub>, CCDC 1916562 [Et<sub>3</sub>AsCl][SnCl<sub>5</sub>(AsEt<sub>3</sub>)]. These can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: + 44 1223 336033.

### Results and Discussion

**Neutral tin(IV) halide complexes:** The neutral tin(IV) phosphine complexes used in this study were made by literature methods or minor modifications thereof, *viz.*  $[\text{SnCl}_4(\text{PEt}_3)_2]$ ,<sup>17</sup>  $[\text{SnCl}_4(\text{PMe}_3)_2]$ ,<sup>16</sup>  $[\text{SnBr}_4(\text{PMe}_3)_2]$ ,<sup>16</sup>  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ ,<sup>4</sup>  $[\text{SnCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)]$ ,<sup>4</sup> as was  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$ .<sup>16</sup> Their identity and purity were confirmed by comparison with literature data; key spectroscopic data are given in Table 1 for comparison purposes. Tin complexes of triethylarsine were reported as long ago as 1949,<sup>19</sup> but lacked any spectroscopic or structural data. The crystal structure of  $[\text{SnCl}_4(\text{AsEt}_3)_2]$  (Figure 1(a)) reveals it to be the *trans* isomer and that the d(Sn-Cl) are not significantly different to those in *trans*- $[\text{SnCl}_4(\text{PEt}_3)_2]$ <sup>17</sup> or *trans*- $[\text{SnCl}_4(\text{PMe}_3)_2]$ ,<sup>11</sup> but slightly longer than that in *trans*- $[\text{SnCl}_4(\text{AsPh}_3)_2]$ <sup>20</sup> (2.415(1), 2.424(1) Å). The d(Sn-As) of 2.65964(16) Å is significantly shorter than that in the triphenylarsine complex (2.7623(3) Å), consistent with the stronger donor power of the trialkyl arsine ligand. In *trans*- $[\text{SnBr}_4(\text{AsEt}_3)_2]$  (Figure 1(b)) the d(Sn-As) is 2.6773(3) Å, only very slightly longer than in the chloride.

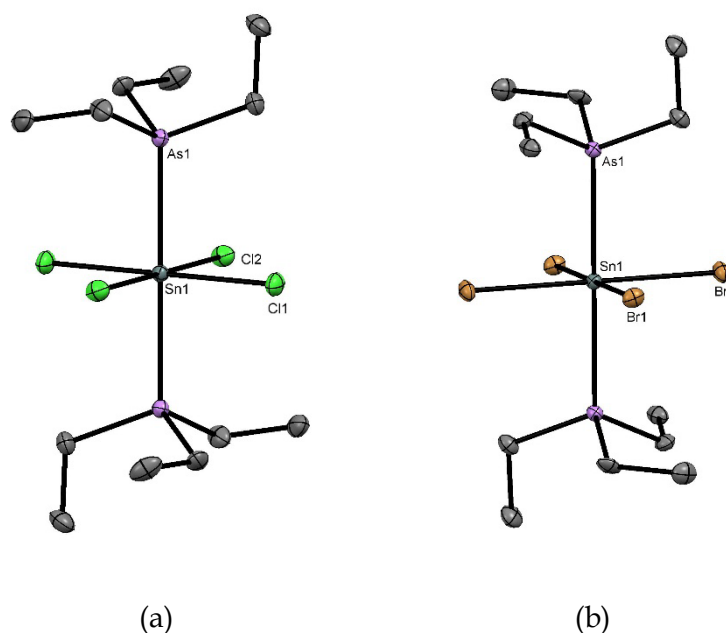


Fig. 1 (a) The structure of  $[\text{SnCl}_4(\text{AsEt}_3)_2]$  showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) are: Sn1–Cl1 = 2.4498(4), Sn1–Cl2 = 2.4544(4), Sn1–As1 = 2.65964(16), As1–Sn1–As1 = 180.0, Cl1–Sn1–Cl2 = 90.367(15), Cl1–Sn1–Cl1 = 180.0, Cl2–Sn1–Cl2 = 180.0; (b) The structure of  $[\text{SnBr}_4(\text{AsEt}_3)_2]$  showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) are: Sn1–Br1 = 2.6286(3), Sn1–Br2 = 2.6173(3), Sn1–As1 = 2.6773(3), As1–Sn1–As1 = 180.0, Br1–Sn1–Br2 = 89.298(11), Br1–Sn1–Br1 = 180.0, Br2–Sn1–Br2 = 180.0.

Attempts to isolate a complex of  $\text{AsEt}_3$  with  $\text{SnI}_4$  were not successful, as noted previously by others.<sup>19</sup>

Addition of a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{SbR}_3$  (R = Et or  $^i\text{Pr}$ ) to  $\text{CH}_2\text{Cl}_2$  solutions of  $\text{SnX}_4$  (X = Cl or Br) result in immediate precipitation of grey solids, which contain essentially no C/H (microanalysis), whilst the supernatant solutions contain  $\text{R}_3\text{SbX}_2$ , based upon comparisons of their  $^1\text{H}$  NMR spectra with literature

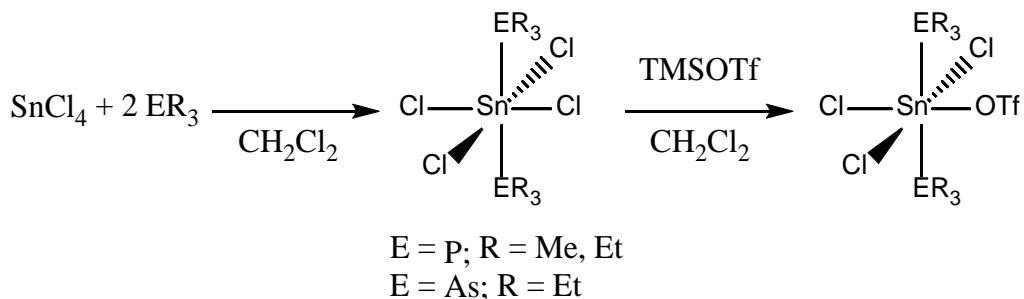


data.<sup>21</sup> and ESI This suggests that any Sn(IV)-stibine complexes are too unstable to isolate, and redox chemistry occurs [ $\text{SnX}_4 + \text{SbR}_3 \rightarrow \text{SnX}_2 + \text{R}_3\text{SbX}_2$ ]. Cunningham *et. al.*<sup>22</sup> reported that reaction of  $\text{SbPh}_3$  with  $\text{SnX}_4$  initially gave yellow solids which became white on washing with pentane. The white solids had  $^{119}\text{Sn}$  Mössbauer spectra consistent with  $\text{SnX}_2$ , indicating similar, but slower, redox chemistry occurring with the triarylstibine. The redox chemistry in these tin systems contrasts with the reactions of Group 13 trihalides with trialkylstibines, which gave simple adducts.<sup>6</sup>

### Reactions of $[\text{SnX}_4(\text{ER}_3)_2]$ (E = P, As) and $[\text{SnCl}_4(\text{L-L})]$ (L-L = *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>, Et<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PEt<sub>2</sub> or *o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>) with TMSOTf

The complexes  $[\text{SnX}_4(\text{ER}_3)_2]$  (X = Cl, ER<sub>3</sub> = PMe<sub>3</sub>, PEt<sub>3</sub>, AsEt<sub>3</sub>; X = Br, ER<sub>3</sub> = PMe<sub>3</sub>, AsEt<sub>3</sub>) were treated with one mol. equivalent of TMSOTf in anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution with a view to removing one chloride ligand (as TMSCl) with the aim to create a tin cation. Triflate can behave either as an anion or coordinate to the metal; in practice we found that that it coordinates to the tin in the present study.

For the chloride systems the reactions proceeded to completion in ~ 2 h to give good yields of moisture-sensitive white powders, identified by microanalysis as  $[\text{SnCl}_4(\text{ER}_3)_2(\text{OTf})]$  (Scheme 1). Curiously, the corresponding reactions with the tin(IV) bromide complexes did not occur, and after 24 h the NMR spectra of these systems showed only unchanged starting materials. Similarly, no reaction occurred between  $[\text{SnCl}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}]$ ,<sup>4</sup>  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ <sup>4</sup> or  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$ <sup>16</sup> with TMSOTf in CH<sub>2</sub>Cl<sub>2</sub> solution even after 3 d. For the systems which produced mono triflate complexes, use of more TMSOTf failed to give any evidence that a second chloride could be removed.



Scheme 1 Reactions with TMSOTf.

Colourless crystals of  $[\text{SnCl}_3(\text{PMe}_3)_2(\text{OTf})]$  and  $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$  were grown by slow evaporation of solutions in anhydrous CH<sub>2</sub>Cl<sub>2</sub>, and their X-ray structure analyses revealed the geometry shown in Fig. 2. The structures show six-coordinate tin centres with *mer*-chlorines, and *trans* pnictines with the triflate *trans* to chlorine. Comparison of the two structures shows that the  $d(\text{Sn}-\text{Cl}_{\text{transCl}})$  are not significantly different and in both cases are longer than  $d(\text{Sn}-\text{Cl}_{\text{transOTf}})$ . The  $d(\text{Sn}-\text{Cl}_{\text{transCl}})$  and  $d(\text{Sn}-\text{As})$  are also similar to those in  $[\text{SnCl}_4(\text{AsEt}_3)_2]$ . The  $d(\text{Sn}-\text{O})$  distances are ~2.26 Å, which fall at the lower

end of the range found in octahedral Sn(IV) triflates ( $\sim 2.2 - 2.6 \text{ \AA}$ )<sup>23</sup> and may be compared to the sum of the covalent radii of Sn and O ( $2.15 \text{ \AA}$ ).<sup>24</sup>

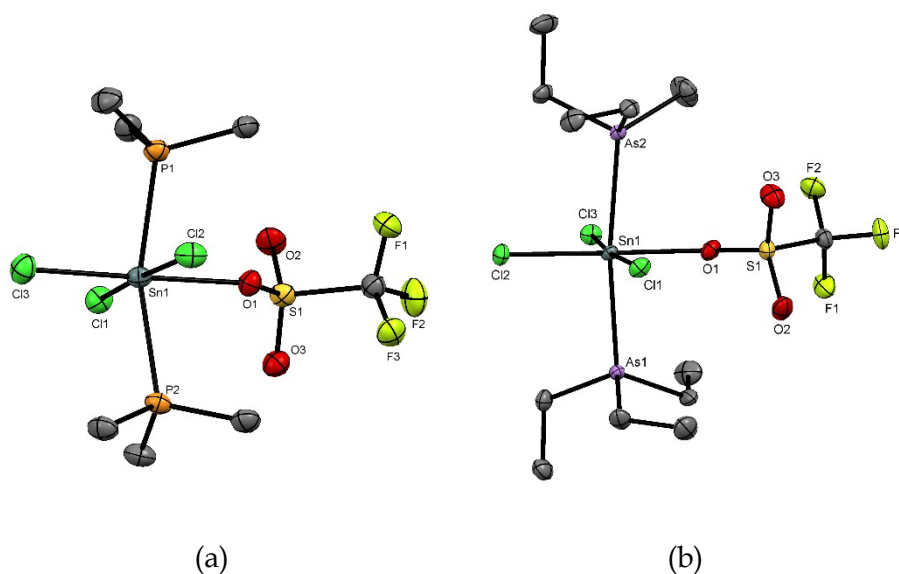


Fig. 2: (a) The structure of  $[\text{SnCl}_3(\text{PMe}_3)_2(\text{OTf})]$  showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are: Sn1–Cl1 = 2.4457(9), Sn1–Cl2 = 2.4558(9), Sn1–Cl3 = 2.4085(10), Sn1–P1 = 2.5496(9), Sn1–P2 = 2.5506(9), Sn1–O1 = 2.266(3), P1–Sn1–P2 = 164.16(3), Cl1–Sn1–Cl2 = 174.66(3), Cl3–Sn1–Cl1 = 92.67(3), Cl3–Sn1–Cl2 = 92.68(4), O1–Sn1–Cl1 = 89.25(7), O1–Sn1–Cl2 = 85.41(7), O1–Sn1–P1 = 82.17(7), O1–Sn1–P2 = 82.51(7); (b) The structure of  $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$ : Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are: Sn1–Cl1 = 2.4480(7), Sn1–Cl2 = 2.4168(8), Sn1–Cl3 = 2.4533(7), Sn1–As1 = 2.6451(4), Sn1–As2 = 2.6530(4), Sn1–O1 = 2.259(2), As1–Sn1–As2 = 172.239(12), Cl1–Sn1–Cl2 = 92.83(3), Cl3–Sn1–Cl1 = 173.76(3), Cl3–Sn1–Cl2 = 93.17(3), O1–Sn1–As2 = 86.28(6), O1–Sn1–As1 = 85.96(6), O1–Sn1–Cl1 = 88.46(6), O1–Sn1–Cl3 = 85.52(6).

Comparison of the NMR spectroscopic data (Table 1) shows that conversion of  $[\text{SnCl}_4(\text{PR}_3)_2]$  into  $[\text{SnCl}_3(\text{PR}_3)_2(\text{OTf})]$  results in modest high frequency shifts of the  $^{119}\text{Sn}$  and  $^{31}\text{P}$  resonances and a more marked increase in  $^1J_{\text{Sn-P}}$ . The  $^{119}\text{Sn}$  chemical shift also moves to high frequency in  $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$  compared to  $[\text{SnCl}_4(\text{AsEt}_3)_2]$ .

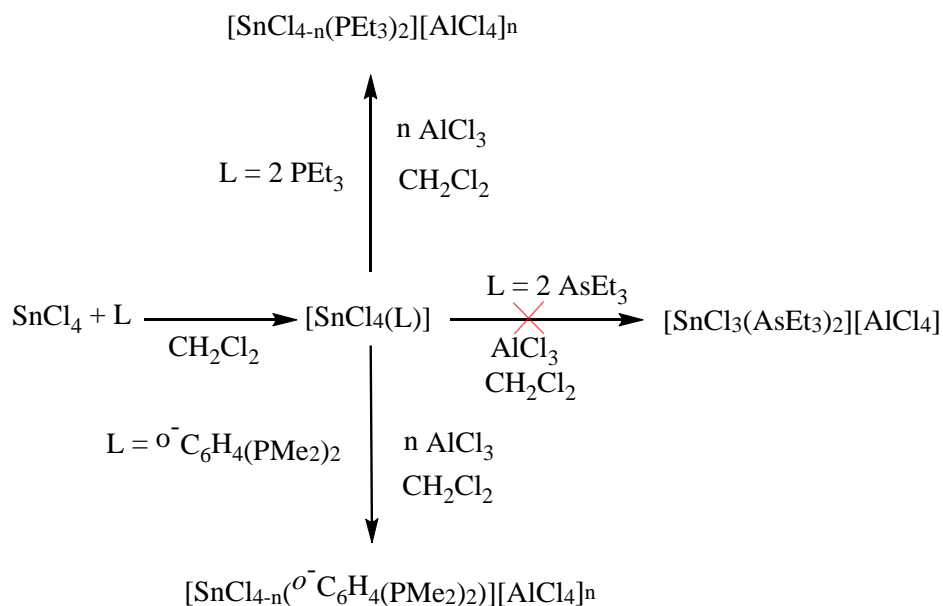
The reaction of  $\text{SnCl}_4$ ,  $\text{SbEt}_3$  and  $\text{TMSOTf}$  in  $\text{CH}_2\text{Cl}_2$  again resulted in redox chemistry, with  $[\text{Et}_3\text{SbCl}(\text{OTf})]$  isolated as one product in  $\sim 30\%$  yield, along with much insoluble grey solid, which had no significant C/H content and is most likely  $\text{SnCl}_2$  (*cf.* reference 22). Crystals of the former were grown from  $\text{CH}_2\text{Cl}_2$  solution and although the crystal quality was poor, confirmed them to be  $[\text{Et}_3\text{SbCl}(\text{OTf})]$ , which has a trigonal bipyramidal geometry with equatorial ethyl groups (see ESI).

### Reactions of $[\text{SnX}_4(\text{ER}_3)_2]$ and $[\text{SnCl}_4(\text{L-L})]$ with $\text{AlX}_3$

No examples of ‘self-ionisation’, such as  $[\text{SnX}_3(\text{ER}_3)_2]_2[\text{SnX}_6]$  or  $[\text{SnX}_2(\text{L-L})_2][\text{SnX}_6]$ , have been reported in reaction of  $\text{SnX}_4$  with pnictines,<sup>5</sup> i.e.  $\text{SnX}_4$  is not a sufficiently strong Lewis acid to abstract

a halide from a second tin centre in these systems. This is also consistent with ligands such as  $\text{MeC}(\text{CH}_2\text{AsMe}_2)_3$  failing to displace a halide from a neutral  $[\text{SnX}_4\{\kappa^2\text{-MeC}(\text{CH}_2\text{AsMe}_2)_3\}]$ ,<sup>4</sup> to form  $[\text{SnX}_3\{\kappa^3\text{-MeC}(\text{CH}_2\text{AsMe}_2)_3\}]^+$ . However, using the stronger Lewis acid,  $\text{AlCl}_3$ , has been successful in removing a chloride in some cases.<sup>11</sup>

The  $[\text{SnCl}_3(\text{PEt}_3)_2][\text{AlCl}_4]$  and  $[\text{SnCl}_2(\text{PEt}_3)_2][\text{AlCl}_4]_2$  were made by treatment of  $[\text{SnCl}_4(\text{PEt}_3)_2]$  with one and two mol. equivalents, respectively, of  $\text{AlCl}_3$  in anhydrous  $\text{CH}_2\text{Cl}_2$  (Scheme 2), and behave similarly to the previously reported<sup>11</sup>  $[\text{SnCl}_x(\text{PMe}_3)_2][\text{AlCl}_4]_y$  ( $x = 3, y = 1$ ;  $x = 2, y = 2$ ).



Scheme 2 Reactions of the tin complexes with  $\text{AlCl}_3$

Attempts to grow crystals from a  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{SnCl}_2(\text{PEt}_3)_2][\text{AlCl}_4]_2$  produced a few small colourless crystals, one of which was found on X-ray structure solution to be  $[\text{SnCl}_2(\text{PEt}_3)_3][\text{AlCl}_4]_2$  containing a *tris*(phosphine) dication (Fig. 3), presumably as a result of rearrangement in solution during recrystallisation.

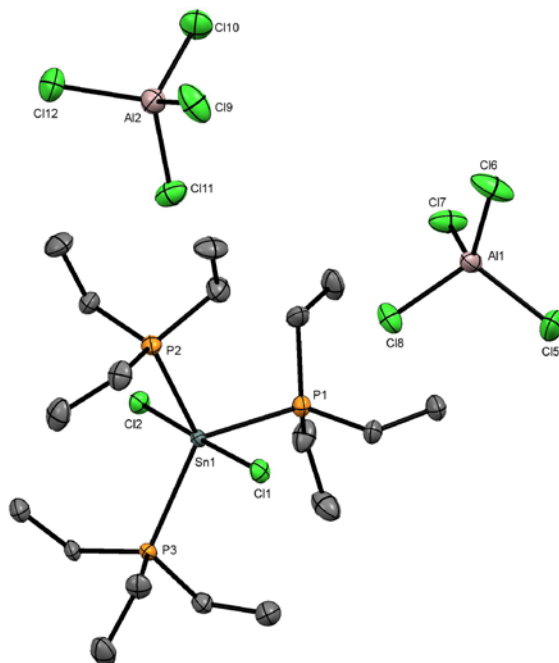


Fig. 3 The structure of  $[\text{SnCl}_2(\text{PEt}_3)_3][\text{AlCl}_4]_2$  showing the atom numbering scheme. Note there are two crystallographically independent  $[\text{SnCl}_2(\text{PEt}_3)_3][\text{AlCl}_4]_2$  units in the asymmetric unit. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are: Sn1–Cl1 = 2.4531(13), Sn1–Cl2 = 2.4589(13), Sn1–P1 = 2.5679(14), Sn1–P2 = 2.5610(13), Sn1–P3 = 2.5525(13), Cl2–Sn1–P3 = 91.10(4), Cl2–Sn1–P2 = 92.07(5), Cl2–Sn1–P1 = 86.01(4), Cl1–Sn1–Cl2 = 178.28(4), Cl1–Sn1–P3 = 90.52(4), Cl1–Sn1–P2 = 87.51(4), Cl1–Sn1–P1 = 92.63(4), P3–Sn1–P2 = 123.83(4), P3–Sn1–P1 = 122.85(4), P2–Sn1–P1 = 113.31(5).

The structure contains a trigonal bipyramidal cation with axial chlorides, the bond angles showing only small deviations from the idealised values, and in contrast to  $[\text{SnCl}_2(\text{PMe}_3)_2][\text{AlCl}_4]_2$ , there is no interaction of the tin centre with the tetrachloroaluminate anions. This is likely due to the steric effect caused by the presence of the third  $\text{PEt}_3$  ligand. The  $d(\text{Sn}-\text{Cl})$  are very similar to the  $d(\text{Sn}-\text{Cl}_{\text{transCl}})$  in the OTf complex in Fig. 3. There were insufficient crystals produced to obtain any spectroscopic data, so direct synthesis of a bulk sample was explored. However, addition of one mol. equivalent of  $\text{PEt}_3$  to  $[\text{SnCl}_2(\text{PEt}_3)_2][\text{AlCl}_4]_2$  in anhydrous  $\text{CH}_2\text{Cl}_2$  solution does not form the new cation  $[\text{SnCl}_2(\text{PEt}_3)_3]^{2+}$ . *In situ* NMR studies reveal a mixture of three main species (Experimental Section);  $[\text{AlCl}_4]^-$ ,  $[\text{AlCl}_3(\text{PEt}_3)]$  (identified by its characteristic NMR spectra<sup>25</sup>) and a new Sn- $\text{PEt}_3$  containing species. The  $^{119}\text{Sn}$  NMR spectrum shows a triplet  $^1J(^{119}\text{Sn}-^{31}\text{P})$  coupling and hence indicates only two phosphines coordinated to the tin centre, e.g.  $[\text{SnCl}_x(\text{PEt}_3)_2]^{n+}$ . The  $^{31}\text{P}$  and  $^{119}\text{Sn}$  chemical shifts do not correspond to those of  $[\text{SnCl}_3(\text{PEt}_3)_2][\text{AlCl}_4]$ .

The solution NMR data (Table 1) show that along the series  $[\text{SnCl}_4(\text{PEt}_3)_2]$ ,  $[\text{SnCl}_3(\text{PEt}_3)_2][\text{AlCl}_4]$ ,  $[\text{SnCl}_2(\text{PEt}_3)_2][\text{AlCl}_4]_2$ , the chemical shifts move to higher frequency in both the  $^{31}\text{P}$  and  $^{119}\text{Sn}$  spectra. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^{119}\text{Sn}$  chemical shifts of the cations also vary significantly with temperature and the

tin spectra have rather broad resonances, which probably reflects a variation in the interaction of the cations with the  $[\text{AlCl}_4]^-$  anions under different conditions.

The reaction of  $[\text{SnCl}_4(\text{AsEt}_3)_2]$  with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  did not proceed similarly to the reactions involving  $\text{PEt}_3$ . Monitoring the reaction by NMR spectroscopy identified a mixture of species present including starting materials and  $\text{Et}_3\text{AsCl}_2$ .<sup>26</sup> A few crystals grown from this mixture contained the chlorotriethylarsonium(V) cation and a pentachloro(triethylarsine)stannate(IV) anion,  $[\text{Et}_3\text{AsCl}][\text{Sn}(\text{AsEt}_3)\text{Cl}_5]$  (Fig. 4).

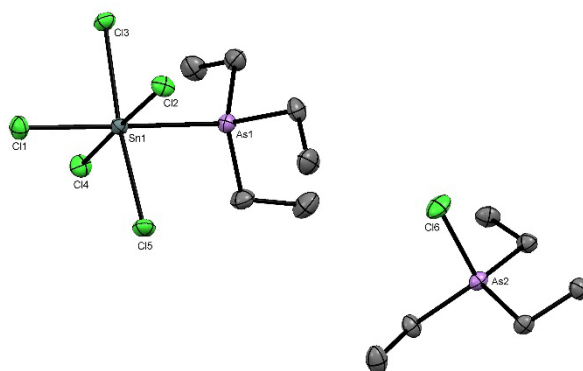


Fig. 4 The structure of  $[\text{Et}_3\text{AsCl}][\text{SnCl}_5(\text{AsEt}_3)]$  showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are:  $\text{Sn1-As1} = 2.6696(5)$ ,  $\text{Sn1-Cl3} = 2.4453(8)$ ,  $\text{Sn1-Cl4} = 2.4304(9)$ ,  $\text{Sn1-Cl2} = 2.4365(8)$ ,  $\text{Sn1-Cl1} = 2.3930(9)$ ,  $\text{Sn1-Cl5} = 2.4254(8)$ ,  $\text{Cl3-Sn1-As1} = 87.09(2)$ ,  $\text{Cl4-Sn1-As1} = 85.21(2)$ ,  $\text{Cl4-Sn1-Cl3} = 91.59(3)$ ,  $\text{Cl2-Sn1-As1} = 92.00(2)$ ,  $\text{Cl2-Sn1-Cl3} = 88.20(3)$ ,  $\text{Cl1-Sn1-Cl3} = 90.72(3)$ ,  $\text{Cl1-Sn1-Cl4} = 90.90(3)$ ,  $\text{Cl1-Sn1-Cl2} = 91.88(3)$ ,  $\text{Cl1-Sn1-Cl5} = 93.86(3)$ ,  $\text{Cl5-Sn1-As1} = 88.54(2)$ ,  $\text{Cl5-Sn1-Cl4} = 91.32(3)$ ,  $\text{Cl5-Sn1-Cl2} = 88.66(3)$ .

Arsine substituted halostannate anions do not seem to have been reported previously,<sup>5</sup> and the nearest literature example is the zwitterionic phosphine complex  $[\text{SnCl}_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{H})]$ .<sup>27</sup> Comparison of the key bond lengths with those in *trans*- $[\text{SnCl}_4(\text{AsEt}_3)_2]$  shows that the  $d(\text{Sn-As})$  and  $d(\text{Sn-Cl}_{\text{transCl}})$  are little different, although  $d(\text{Sn-Cl}_{\text{transAs}})$  is  $\sim 0.05 \text{ \AA}$  shorter. The reaction of *trans*- $[\text{SnBr}_4(\text{AsEt}_3)_2]$  with  $\text{AlBr}_3$  also produced a mixture of products, including  $\text{Et}_3\text{AsBr}_2$ .<sup>26</sup>

The reactions of  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$  with one and two mol. equivalents of  $\text{AlCl}_3$  in anhydrous  $\text{CH}_2\text{Cl}_2$  were also investigated. The products were identified by microanalysis as  $[\text{SnCl}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{AlCl}_4]$  and  $[\text{SnCl}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{AlCl}_4]_2$ . These very moisture-sensitive complexes were poorly soluble in  $\text{CH}_2\text{Cl}_2$  and attempts to grow crystals have been unsuccessful. Obtaining multinuclear NMR data was also hindered by their poor solubility in weakly coordinating organic solvents. However, the trends in chemical shifts and coupling constants within the series (Table 1) replicate those observed for  $[\text{SnCl}_x(\text{PEt}_3)_2][\text{AlCl}_4]_y$  ( $x = 4, y = 0$ ;  $x = 3, y = 1$ ;  $x = 2, y = 2$ ), with  $\delta^{119}\text{Sn}$  and  $\delta^{31}\text{P}$  NMR moving to high frequency on going from the neutral complex to the mono- and the di-

cations. The  $^1J(^{119}\text{Sn}-^{31}\text{P})$  also follow the same trend as the  $\text{PMe}_3$  complexes, with  $^1J_{31\text{P}-119\text{Sn}} [\text{SnCl}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]^+ > [\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}] > [\text{SnCl}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]^{2+}$ .

$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$  also reacted with  $\text{AlCl}_3$  in anhydrous  $\text{CH}_2\text{Cl}_2$  to form a poorly soluble white product, but the NMR spectra indicated a mixture of species present, which we were unable to identify.

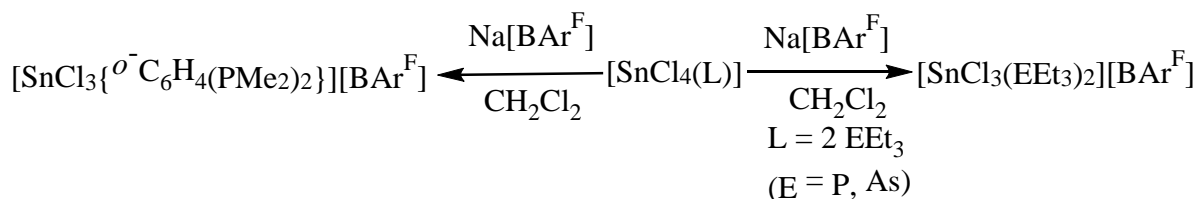
Table 1 Selected spectroscopic data<sup>a</sup>

Compound	$\delta(^{31}\text{P}\{\text{H}\})$	$\delta(^{119}\text{Sn})$	$^1J(^{119}\text{Sn}-^{31}\text{P})/\text{Hz}$	$\nu(\text{Sn-X})/\text{cm}^{-1}$	Reference
$[\text{SnCl}_4(\text{PMe}_3)_2]$	+1.6	-554	2635	321	11
$[\text{SnCl}_4(\text{PEt}_3)_2]$	+20.9	-572	2391	-	17
$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$	-28.1	-616	945	307, 296	4
$[\text{SnCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)]$	-4.9	-615	1049	318, 307, 282	4
$[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$	-	-675	-	323, 315, 304, 300	16
$[\text{SnCl}_4(\text{AsEt}_3)_2]$	-	-657 <sup>b</sup>	-	288	This work
$[\text{SnBr}_4(\text{AsEt}_3)_2]$	-	-1173 <sup>b</sup>	-	210	This work
$[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$	-	-620 <sup>b</sup>	-	294, 378	This work
$[\text{SnCl}_3(\text{AsEt}_3)_2][\text{BAr}^{\text{F}}]$	-	-388	-	-	This work
$[\text{SnCl}_3(\text{PMe}_3)_2(\text{OTf})]$	+8.7	-516	2963	296, 306	This work
$[\text{SnCl}_3(\text{PEt}_3)_2(\text{OTf})]$	+33.4 <sup>b</sup>	-535 <sup>b</sup>	2737 <sup>b</sup>	289, 301	This work
$[\text{SnCl}_3(\text{PEt}_3)_2][\text{AlCl}_4]$	+35.5	-350	2307	280, 289	This work
$[\text{SnCl}_2(\text{PEt}_3)_2][\text{AlCl}_4]_2$	+40.8	-300	2274	289	This work
$[\text{SnCl}_3(\text{PEt}_3)_2][\text{BAr}^{\text{F}}]$	+37.1	-379	2311	286	This work
$[\text{SnCl}_3(\text{PMe}_3)_2][\text{AlCl}_4]$	+10.8	-456	2725	-	11
$[\text{SnCl}_2(\text{PMe}_3)_2][\text{AlCl}_4]_2$	+16.9	-333	2591	-	11
$[\text{SnCl}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{AlCl}_4]$	-24.7	-469	972	322, 342	This work
$[\text{SnCl}_2\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{AlCl}_4]_2$	-23.7	-429	875	294, 305	This work

a. NMR data from  $\text{CH}_2\text{Cl}_2$  solution at 293 K, except b. 193 K.

### Reactions of $[\text{SnX}_4(\text{EEt}_3)_2]$ and $[\text{SnCl}_4(\text{L-L})]$ with $\text{Na}[\text{BAr}^{\text{F}}]$

Addition of  $\text{Na}[\text{BAr}^{\text{F}}]$  to a  $\text{CH}_2\text{Cl}_2$  solution  $[\text{SnX}_4(\text{EEt}_3)_2]$  ( $\text{E} = \text{P}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{E} = \text{As}$ ;  $\text{X} = \text{Cl}$ ) or  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$  (Scheme 3) readily formed the  $[\text{BAr}^{\text{F}}]^-$  salts,  $[\text{SnX}_3(\text{EEt}_3)_2][\text{BAr}^{\text{F}}]$  and  $[\text{SnCl}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{BAr}^{\text{F}}]$ , with precipitation of  $\text{NaX}$ . The NMR spectroscopic data for the cations match those of the  $[\text{AlCl}_4]^-$  salts discussed above, and using  $\text{Na}[\text{BAr}^{\text{F}}]$  as the halide abstractor allowed generation of the  $[\text{SnBr}_3(\text{PEt}_3)_2]^+$  cation that proved elusive with the other halide abstractors. Using excess  $\text{Na}[\text{BAr}^{\text{F}}]$  did not lead to further halide abstraction.



Scheme 3 Reactions of the tin complexes with Na[BAr<sup>F</sup>]

### DFT studies

Computational studies of the tin complexes were undertaken to supplement the experimental data. Ground state geometries of [SnCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>], [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>], [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>], [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>(OTf)], [SnCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>],<sup>17</sup> [SnCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>],<sup>11</sup> [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>(OTf)], [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> were optimised alongside the uncoordinated ligands AsEt<sub>3</sub> and PEt<sub>3</sub> using DFT with the B3LYP functional and a basis set with a Stuttgart–Dresden effective core potential on Sn and As atoms and with an all-electron double- $\zeta$  basis set on all electrons in H, C, O, F, P, Al, S, and Cl atoms. Comparison of DFT results for the [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>][AlCl<sub>4</sub>] and [SnCl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>] against those reported,<sup>11</sup> was used to test the suitability of the basis set – see ESI.

The bond lengths from the calculated ligands are similar to those from available experimental data (Table S2) and show that the average C–E–C angles from AsEt<sub>3</sub> and PEt<sub>3</sub> (98.5 and 100.4°, respectively) are slightly wider than those found in AsMe<sub>3</sub> (97.0°) and PMe<sub>3</sub> (98.8°). The average As–C bond distances from the DFT analysis (~1.98 Å) are similar to those from experimental data (~1.94 Å) for the tin complexes, showing a shortening in comparison to ‘free’ AsEt<sub>3</sub> (As–C = 2.01 Å). The P–C bond distances also follow this trend, with a shortening from the phosphine complexes (DFT: 1.87–1.89 Å; X-ray: ~1.79 Å), compared to the free PMe<sub>3</sub> and PEt<sub>3</sub> (1.90–1.92 Å; X-ray: 1.84 Å). This, when combined with the widening of the C–As–C (DFT: 105.33–106.2 °; X-ray: 105.9–106.0 °) and C–P–C angles (DFT: 106.3–109.1 °; X-ray: 107.1–109.1 °) of the complexes, against the values for the ‘free’ ligands (AsEt<sub>3</sub>: 98.5 °; PMe<sub>3</sub>: 98.8 ° and PEt<sub>3</sub>: 100.4 °), matches the trends seen for trialkylstibine ligands upon coordination to Group 13 metal halides,<sup>6</sup> although the effect here is much smaller. The widening of the C–E–C angle corresponds to an increased *s*-character in the E–C bond and increased *p*-character in the lone pair. The comparable data from the halo tin-arsine and phosphine complexes shows the free ligands have *s*-character of AsEt<sub>3</sub>: 12.20; PMe<sub>3</sub>: 15.08; PEt<sub>3</sub>: 15.57%, which doubles to 25.3–25.9% upon coordination.

Calculating the ground state structure of the [SnCl<sub>4</sub>(AsEt<sub>3</sub>)<sub>2</sub>] and [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>(OTf)] complexes, alongside DFT calculations of the ionic [SnCl<sub>3</sub>(AsEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex, show that there is very little change in the bond lengths/angles and this is consistent with reported data for [SnCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Burford’s complexes are also noted for a significant decrease in the P–Sn–P angle with increasing charge,<sup>11</sup> the

neutral  $[\text{SnCl}_4(\text{AsEt}_3)_2]$  complex (X-ray: 180; DFT: 179.9 °) and the cationic  $[\text{SnCl}_3(\text{AsEt}_3)_2]^+$  species show a similar trend (DFT: 174 °).

Notably, while the HOMO and LUMO energies in the neutral tetrahalide and triflate complexes are not significantly different, those of the cationic species are some 4 eV lower in energy, consistent with the latter displaying higher Lewis acidity (Table S7). Furthermore, using the  $\text{AsEt}_3$  complexes as examples, the HOMO is concentrated on the  $\text{SnCl}_4$  unit in the  $[\text{SnCl}_4(\text{AsEt}_3)_2]$ , with some delocalisation onto the  $\text{AsEt}_3$  ligands in  $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$ , and this is even more obvious in  $[\text{SnCl}_3(\text{AsEt}_3)_2]^+$  (Fig. 5).



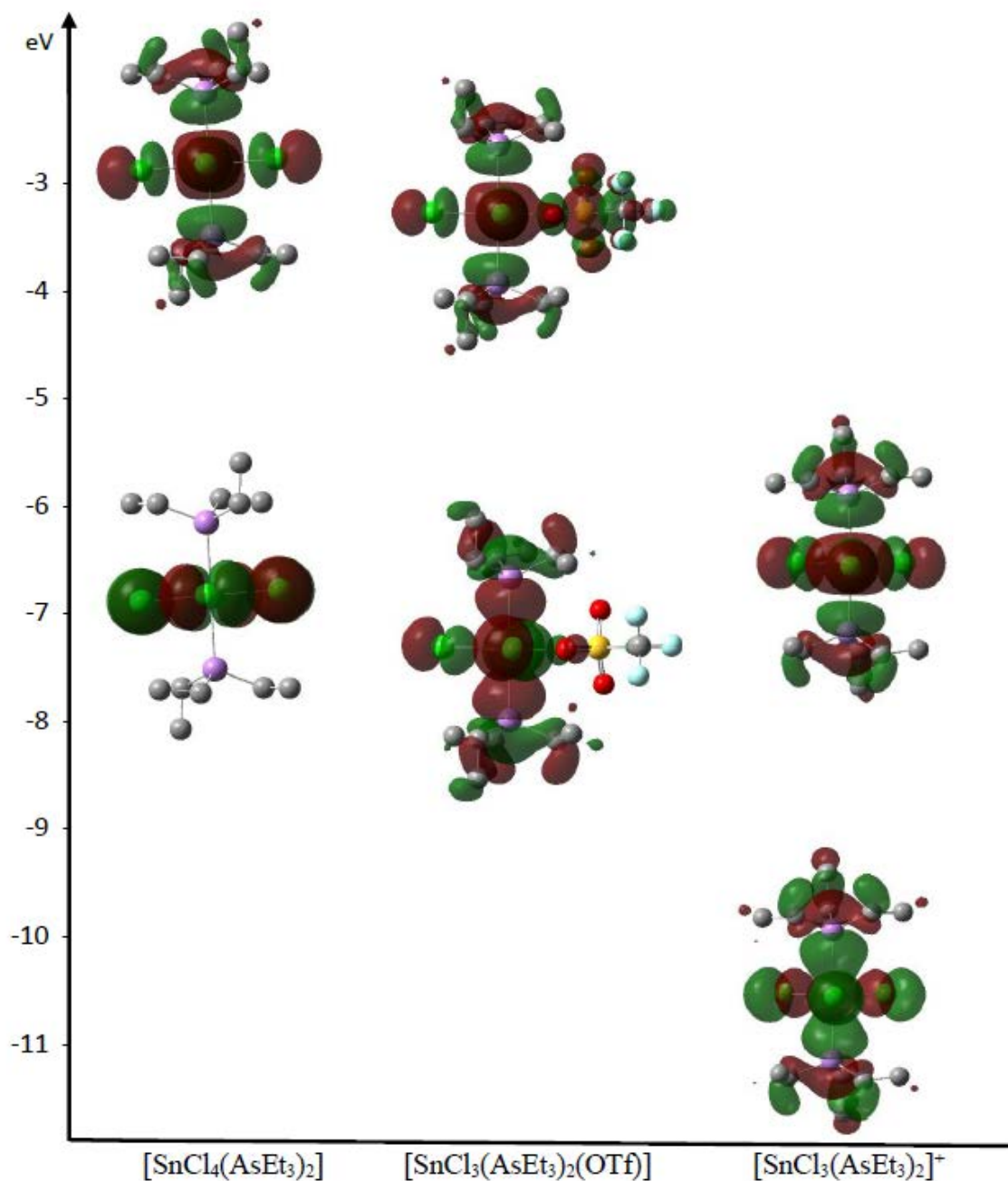


Fig. 5 Representation of the LUMO and HOMO of  $[\text{SnCl}_4(\text{AsEt}_3)_2]$ ,  $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$  and  $[\text{SnCl}_3(\text{AsEt}_3)_2]^+$  determined by DFT analysis, showing their relative energies.

### Conclusions

This study has confirmed the high stability of tin tetrahalide complexes with neutral phosphine and arsine ligands and has demonstrated the formation of some complexes with  $\text{Sn}^{\text{IV}}:\text{X}$  ratio of 1:3 or 1:2.

In the case of  $\text{SbEt}_3$ , we found that  $\text{SnCl}_4$  causes chlorination of the stibine, consistent with the greater stability of  $\text{Sb}(\text{V})$  over  $\text{As}(\text{V})$  (although  $\text{P}(\text{V})$  is also more stable than  $\text{As}(\text{V})$ , the stronger basicity of the  $\text{PR}_3$  ligands means that coordination is favoured over chlorination in this system).

Replacement of chloride by triflate to form  $[\text{SnCl}_3(\text{ER}_3)_2(\text{OTf})]$  is possible for  $\text{ER}_3 = \text{PMe}_3, \text{PEt}_3, \text{AsEt}_3$ , but not with complexes of chelating bidentate ligands. This may indicate that reversible dissociation of the neutral ligand plays a role in the substitution. The failure of corresponding  $[\text{SnBr}_4(\text{ER}_3)_2]$  to react with TMSOTf was unexpected, although formation of TMSBr is less favoured energetically.

Aluminium trichloride is able to abstract chloride ligands from  $[\text{SnCl}_4(\text{PEt}_3)_2]$  and  $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$  to form mono- and di-cationic Sn(IV) complexes, but these reactions do not occur with arsine ligands, possibly due to the weaker donor arsines having less affinity for the hard tin(IV) cations. On the other hand, using the large, weakly coordinating  $[\text{BAR}^{\text{F}}]^-$  anion does lead smoothly to the formation of  $[\text{SnCl}_3(\text{EEt}_3)_2][\text{BAR}^{\text{F}}]$  for  $\text{E} = \text{P}$  and  $\text{As}$ ,  $[\text{SnBr}_3(\text{PEt}_3)_2][\text{BAR}^{\text{F}}]$ , as well as affording  $[\text{SnCl}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}][\text{BAR}^{\text{F}}]$ .

In practice, the  $\text{Na}[\text{BAR}^{\text{F}}]$  works better as a halide abstractor to form the monocations (but does not form dications), whereas  $\text{AlCl}_3$  can compete for coordination to the weakly bound arsine ligand, whilst it is clear that the triflate anion can coordinate readily to Sn(IV).

DFT studies have shown that bonding and orbital components in the triflate complexes are very similar to those for the tetrachlorides, while the HOMO and LUMO energies are somewhat lower (by *ca.* 4 eV) for the cations compared to the neutral species, indicating that the cationic species are stronger Lewis acids.

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### Conflicts of Interest

The authors have no conflicts to declare.

### Electronic Supporting Information

ESI contains the multinuclear NMR and IR spectra associated with each of the new compounds described, together with the X-ray crystallographic parameters and full details of the DFT calculations.

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