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

Victoria K. Greenacre, Rhys P. King, William Levason and Gillian Reid*

The reaction of trans-[SnCl₄(PR₃)₂] (R = Me or Et) with trimethylsilyl triflate (TMSOTf) in CH₂Cl₂ solution substitutes one chloride to form [SnCl₃(PR₃)(OTf)], addition of excess TMSOTf does not substitute further chlorides. The complexes have been fully characterised by microanalysis, IR and multinuclear NMR (¹H, ¹³C(¹H), ¹⁹F(¹H), ³¹P(¹H), ¹¹⁹Sn) spectroscopy. The crystal structure of [SnCl₄(PMe₂)₂(OTf)] revealed mer-chlorines and trans-phosphines. In contrast, trans-[SnBr₄(PR₃)₂], [SnCl₄(PEt₃)₂(PEt₃)₂], [SnCl₄(o-C₆H₄(PMe₂))₃] and [SnCl₄(o-C₆H₄(AsMe₂))] did not react with TMSOTf in CH₂Cl₂ solution even after 3 days. The arsine complexes, [SnX₄(AsEt₃)₂] (X = Cl, Br), were confirmed as trans-isomers by similar spectroscopic and structural studies, while attempts to isolate [Sn₄(AsEt₃)₂] were unsuccessful and reaction of SnX₄ with SbR₃ (R = Et, iPr) resulted in reduction to SnX₂ and formation of R₃SbX₂. trans-[SnCl₄(AsEt₃)₂] is converted by TMSOTf into [SnCl₃(PEt₃)(OTf)], whose X-ray structure reveals the same geometry found in the phosphine analogues, with the trflate coordinated. The salts, [SnCl₄(PEt₃)₂][AlCl₄] and [SnCl₄(PEt₃)₂][AlCl₄] were made by treatment of [SnCl₄(PEt₃)₂] with one and two mol. equivalents, respectively, of AlCl₃ in anhydrous CH₂Cl₂, whereas reaction of [SnCl₄(AsEt₃)₂] with AlCl₃ produced a mixture including Et₃AsCl₂ and [Et₃AsCl][Sn(AsEt₃)₂Cl₂] (the latter identified crystallographically). In contrast, using Na[BArF] (BArF = [B{3,5-(CF₃)₂C₆H₃}₄]) produced [SnCl₄(PEt₃)₂][BArF] and also allowed clean isolation of the arsine analogue, [SnCl₃(AsEt₃)₂][BArF]. [SnCl₄(o-C₆H₄(PMe₂))₃] also reacts with AlCl₃ in CH₂Cl₂ to form [SnCl₃(o-C₆H₄(PMe₂))(AsMe₂)][AlCl₄] and [SnCl₄(o-C₆H₄(PMe₂))(AsMe₂)][AlCl₄]. Multinuclear NMR spectroscopy on the [AlCl₄]⁻ salts show that δ¹³P and δ¹¹⁹Sn move progressively to high frequency on conversion from the neutral to the mono- and di-cations, whilst J¹¹⁹Sn⁻¹³¹P follow the trend: [SnCl₄(o-C₆H₄(PMe₂))(AsMe₂)][AlCl₄] > [SnCl₄(o-C₆H₄(PMe₂))(AsMe₂)][AlCl₄]. DFT studies on selected complexes show only small changes in ligand geometries and bond lengths between the halide and trflate complexes, consistent with the X-ray crystallographic data reported and the HOMO and LUMO energies are relatively unperturbed upon the introduction of (coordinated) trflate, 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. In addition to neutral complexes [MLₙXₚ₋ₚ] [M = transition metal, X = halide, L = neutral ligand], related cations [MLₙXₚ₋ₚ⁺] or [MLₙXₚ₋₋₂]⁺ (c, d ≥ a) are commonly known, formed either spontaneously in the presence of excess L, or upon the addition of large, weakly coordinating anions. In some cases complexes of the type [MLₙXₚ][MXₚ⁻] 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’ LₙXₚ] (M’ = p-block metal) with much stronger M-X than M-L bonding. 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, SnX₄, typify this pattern in that the majority of complexes are octahedral with neutral ligands filling two coordination sites. Rare exceptions are provided by 1,4,7-tri-
methyl-1,4,7-triazacyclonane, 1,3,5-trimethyl-1,3,5-triazacyclohexane and 1,4,7-trithiacyclonane (L2), which generate the ‘self-ionisation’ complexes, [SnX4(L2)]+[SnX4] (X = Cl or Br), although more flexible acyclic polydentate ligands, such as MeC(CH2AsMe2)3, behave as bidentate ligands, as in [SnX4(k2- MeC(CH2AsMe2)3)].

Complexes of the tin(n) halides, SnX4 (X = Cl or Br), with neutral phosphine and arsine ligands have been explored in considerable detail and almost all are of the octahedral trans-[SnX4(ER3)] or cis-[SnX4(bidentate)] (bidentate = diphosphine or diarsine) types. SnI4 is a weaker Lewis acid and forms similar, but less stable adducts, whilst complexes of SnF4 have been much less studied.

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. MacDonald et al. obtained [SnCl3(PMe3)2][AlCl4] and [SnCl3(PMe3)2][AlCl4] by treatment of trans-[SnCl4(PMe3)2] with one or two mol. equivalents of AlCl3, respectively. The former has a distorted trigonal bipyramidal geometry with trans axial PMe3 ligands. The dication has trans PMe3 groups, and two cis interactions from the [AlCl4]− anions completing a very distorted octahedron. The Sn–Cl distances decrease along the series [SnCl4(PMe3)2] > [SnCl3(PMe3)2] > [SnCl2(PMe3)2]. In the present work we have explored the reaction of tin(n) 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 ([CF3SO3]−) via treatment with trimethylsilyltriflate, [AlX4]− via addition of aluminium trihalides and using the large diffuse [BaP+]− anion, via addition of its Na+ salt [BaP− = [B(3,5-(CF3)2C6H3)3]2+].

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(n) halides, TMSOTf, and aluminium halides were obtained from Sigma-Aldrich or Strem, except for C6H4(AsMe2)2, which were prepared by literature methods. Phosphine and arsine ligands were obtained from Sigma-Aldrich and used as received. Phosphine and arsine ligands were obtained from Sigma-Aldrich or Strem, except for C6H4(AsMe2)2 and C6H4(H2AsMe2), which were prepared by literature methods. SbBr3, SbPr3, and Na[BaP−] were made as described. CH2Cl2 was dried by distillation from CaH2 and diethyl ether and n-hexane from Na.

Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000–200 cm−1. 1H, 13C{1H}, 19F{1H}, 31P{1H}, 27Al and 119Sn NMR spectra were recorded from CDC13 or CH2Cl2/CDCl3 solutions using a Bruker AV400 spectrometer and referenced to TMS via the residual solvent resonance, CFCl3, 85% H3PO4, [Al(H2O)6]3+ in H2O at pH = 1 or SnMe4 as appropriate. Typically, [Cr(acac)3] was added as a relaxation agent when recording the 119Sn spectra, except for those containing [AlCl4]−, when it is known to react with the complexes, turning green. In these cases a 2 seconds pulse delay was used.

Microanalyses were undertaken by London Metropolitan University.
added in CH₂Cl₂ (5 mL). The solution was stirred for 16 h and the solid and volatiles were removed and the resulting white powder dried in vacuo. The powder was then washed with diethyl ether (3 × 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 CH₂Cl₂. Yield 0.215 g, 57%. Required for C₁₇H₁₈Cl₃F₃O₃P₂Sn (526.1): C, 25.6; H, 5.0.

[SbEt₃Cl(OTf)]SnCl₄ (0.100 g, 0.38 mmol) was dissolved in 5 mL of CH₂Cl₂. The solution was stirred for 2 h leaving a clear and colourless solution; the liquid was filtered away from the unidentified solid and concentrated to dryness in vacuo producing a white sticky solid, which was then washed with n-hexane (3 × 10 mL), the solid separated and dried in vacuo to leave a white sticky powder. Yield: 0.160 g, 63%. Required for C₁₀H₁₆AlCl₇P₂Sn (591.9): C, 20.3; H, 2.7, Found C, 20.4; H, 2.8%. IR (Nujol/cm⁻¹): ν = 2322m, 342m (Sn–Cl), 451m, 497br (SnCl₄).¹H NMR (CD₂Cl₂, 295 K): δ = 2.06 (t, J = 3.3Hz, 1H), 2.50 (t, J = 3.3Hz, 1H), 7.26–7.27 (m, [4H], Ar–H). ¹³C¹H NMR (CD₂Cl₂, 295 K): δ = 112.6 (s, [AlCl₄]), 117.9 (s, [AlCl₄]), 31P¹H NMR (CD₂Cl₂, 295 K): δ = 102.8 (s, [AlCl₄]).²⁷Al NMR (CD₂Cl₂, 295 K): δ = −24.7 (s, J₃₁P–Al = 930 Hz, J₃₁P–Al = 972 Hz).²⁷Sn NMR (CD₂Cl₂, 298 K): δ = −469 (s, J₃₁P–Sn = 972 Hz).

[SnCl₄(o-C₆H₄(PMe₃)₂)][AlCl₄]

[SnCl₄(o-C₆H₄(PMe₃)₂)] (0.100 g, 0.22 mmol) was suspended in CH₂Cl₂ (5 mL) and to this AlCl₃ (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 × 10 mL), the solid separated and dried in vacuo to leave a white sticky powder. Yield: 0.81 g, 51%. Required for C₁₀H₁₆AlCl₁₀P₂Sn (725.4): C, 16.7; H, 2.2. Found C, 17.5; H, 2.7%. IR (Nujol/cm⁻¹): ν = 294m, 310m (Sn–Cl), 452sh, 487s ([AlCl₄]).¹H NMR (CD₂Cl₂, 295 K): δ = 2.18 (t, J = 3.3Hz, 1H), 2.20 (s, 2H), 2.32 (m, 12H, CH₂). ¹³C¹H NMR (CD₂Cl₂, 295 K): δ = 31.5 (s, J₃₁P–Al = 930 Hz, J₃₁P–Al = 972 Hz).²⁷Al NMR (CD₂Cl₂, 295 K): δ = 102.9 (s, [AlCl₄]).²⁷Sn NMR (CD₂Cl₂, 298 K): δ = −429 (s, J₃₁P–Sn = 850 Hz.).

[SnCl₄(PEt₃)]²⁺[AlCl₆]

[SnCl₄(PEt₃)] (0.200 g, 0.40 mmol) was suspended in CH₂Cl₂ (5 mL) and AlCl₃ (0.054 g, 0.40 mmol) was added. The suspension was stirred for 2 h leaving a clear and colourless solution; the solution was then concentrated to dryness leaving a white fine powder which was washed with Et₂O (3 × 10 mL) and dried in vacuo to yield a white powder. Yield: 0.160 g, 63%. Required for C₁₀H₁₆AlCl₁₀P₂Sn (610.2): C, 21.7; H, 4.2%. IR (Nujol/cm⁻¹): ν = 289m, 310m (Sn–Cl), 452sh, 487s ([AlCl₄]).¹H NMR (CD₂Cl₂, 295 K): δ = 3.8. Found C, 20.4; H, 2.8%. IR (Nujol/cm⁻¹): ν = 2322m, 342m (Sn–Cl), 451m, 497br (SnCl₄).¹H NMR (CD₂Cl₂, 295 K): δ = 2.06 (t, J = 3.3Hz, 1H), 2.50 (t, J = 3.3Hz, 1H), 7.26–7.27 (m, [4H], Ar–H). ¹³C¹H NMR (CD₂Cl₂, 295 K): δ = 112.6 (s, [AlCl₄]), 117.9 (s, [AlCl₄]), 31P¹H NMR (CD₂Cl₂, 295 K): δ = 102.8 (s, [AlCl₄]).²⁷Al NMR (CD₂Cl₂, 295 K): δ = −24.7 (s, J₃₁P–Al = 930 Hz, J₃₁P–Al = 972 Hz).²⁷Sn NMR (CD₂Cl₂, 298 K): δ = −469 (s, J₃₁P–Sn = 972 Hz).
3.8, IR (Nujol/cm\(^{-1}\)) = 289m, (Sn–Cl), 484s, ([AlCl\(_4\)]\(^{-}\)). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 1.39\) (m, [18H], CH\(_3\)), 2.38 (m, [12H], CH\(_2\)), 53\(^1\)\(_1\)\(_{\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 7.50\) (t, \(J_{\text{HH}} = 2.93\) Hz, –CH\(_3\)), 14.51 (t, \(J_{\text{HH}} = 13.2\) Hz). \(^2\)\(_7\)Al NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 103.0\). \(^{31}\)P\(_1\)\(_{\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 40.8\) (\(J_{\text{PHP}} = 2.93\) Hz, \(J_{\text{PHP}} = 13.2\) Hz). \(^{13}\)Sn NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = -301.4\) (t, \(J_{\text{HH}} = -2291\) Hz).

**Reaction of [SnCl\(_2\)(PEt\(_3\))\(_2\)]\([AlCl_4]\) with PEt\(_3\)**

[SnCl\(_2\)(PEt\(_3\))\(_2\)]\([AlCl_4]\) (0.100 g, 0.20 mmol) was dissolved in CH\(_2\)Cl\(_2\) (3 mL), to this PEt\(_3\) (0.015 g, 0.02 mmol) was added in CH\(_2\)Cl\(_2\) (2 mL). To this 10 drops of CD\(_2\)Cl\(_2\) is added. A portion of the solution was used for in situ NMR studies.

\(27\)Al NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 103.1\) (s, [AlCl\(_4\)]\(^{-}\)), 110.8 (d, \(J_{\text{PHP}} = 27.1\) Hz, [AlCl\(_4\)]\(^{-}\)). \(^{31}\)P\(_1\)\(_{\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = -14.8\) (sexet, \(J_{\text{PHP}} = 264\) Hz, [AlCl\(_4\)]\(^{-}\)). \(^{13}\)Sn NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = -449\) (t, \(J_{\text{HH}} = -2394\) Hz).

**[SnCl\(_4\)(AsEt\(_3\))\(_2\)]\([BArF]\)**

A Schlenk was charged with [SnCl\(_4\)(AsEt\(_3\))\(_2\)] (0.100 g, 0.20 mmol) and Na[BAr\(_F\)] (0.178 g, 0.20 mmol). To this CH\(_2\)Cl\(_2\) (5 mL) was added. The resulting cloudy solution was stirred for 2 h, then filtered and concentrated to dryness in vacuo yielding a light yellow gum, which was then dissolved in Et\(_2\)O (5 mL), then the solution was concentrated to dryness in vacuo yielding a light yellow solid. Yield: 0.091 g, 58%. Required C\(_{44}\)H\(_{42}\)As\(_2\)BCl\(_3\)F\(_{24}\)Sn (1412.2): C, 37.4, H, 3.0. Found C, 37.3, H, 3.0.

\(13\)C\(_{1}\)\(_{\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 1.35\) (m, [18H], CH\(_3\)), 2.38 (br, [12H], CH\(_2\)), 7.58 (s, [4H], [BarF]), 7.73 (m, [8H], [BarF]). \(^{119}\)Sn NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = 9.1\) (s, –CH\(_2\)), 15.9 (s, –CH\(_3\)), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, \(J_{\text{PHP}} = 49.9\) Hz). \(^{19}\)F\(_{1}\)\(_{\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 295 K): \(\delta = -62.8\) (s, –CF\(_3\)). \(^{119}\)Sn NMR (CD\(_2\)Cl\(_2\), 183/298 K): \(\delta = n\).n.o.

**X-Ray experimental**

Crystals of the complexes were grown from CH\(_2\)Cl\(_2\) 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 (\(\lambda = 0.71073\) Å) rotating anode generator with VHF Varimax optics (70 \(\mu\)m focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELXL/S/L97, SHELX-2013, or SHELX-2014/7/41. \(\text{H}\) 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\(_4\)(AsEt\(_3\))\(_2\)], CCDC 1916558 [SnBr\(_4\)(AsEt\(_3\))\(_2\)], CCDC 1916559 [SnCl\(_4\)(PMe\(_3\))\(_2\)(OTf)], CCDC 1916560 [SnCl\(_4\)(AsEt\(_3\))\(_2\)(OTf)], CCDC 1916561 [SnCl\(_4\)(PMe\(_3\))\(_2\)] [AlCl\(_4\)], CCDC 1916562 [Et\(_3\)AsCl][SnCl\(_4\)(AsEt\(_3\))\(_2\)].

**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:-[SnCl\(_4\)(PMe\(_3\))\(_2\)], \[^{17}\]SnCl\(_4\)(PMe\(_3\))\(_2\), \[^{18}\]SnBr\(_4\)(PMe\(_3\))\(_2\), \[^{19}\]SnCl\(_4\)(PMe\(_3\))\(_2\), \[^{20}\]SnCl\(_4\)(PMe\(_3\))\(_2\), \[^{21}\]SnCl\(_4\)(PMe\(_3\))\(_2\), \[^{22}\]SnCl\(_4\)(PMe\(_3\))\(_2\) and [SnCl\(_4\)(PMe\(_3\))\(_2\)] as was [SnCl\(_4\)(PMe\(_3\))\(_2\)]. Their identity and purity were confirmed by comparison with literature data; key spectroscopic data are in Table S1 for comparison purposes. Tins complexes of triethylarsine were reported as long ago as 1949, \[^{19}\] but lacked any spectroscopic or structural data. The crystal structure of [SnCl\(_4\)(AsEt\(_3\))\(_2\)] (Fig. 1[a]) reveals it to be the trans isomer and that the d(Sn–Cl) are not significantly different to those in
Table 1  Selected spectroscopic data

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<th>Compound</th>
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<th>δ(^{119})Sn</th>
<th>1(^J)((^{119})Sn–(^{31})P)/Hz</th>
<th>ν(Sn–X)/cm(^{-1})</th>
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\(^{a}\) NMR data from CH\(_2\)Cl\(_2\) solution at 293 K, except. \(^{b}\) 193 K.

Fig. 1  (a) The structure of [SnCl\(_4\)(AsEt\(_3\))] 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 (°) are: Sn1–Cl1 = 2.4498(4), Sn1–Cl2 = 2.6173(3), 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 [SnBr\(_4\)(AsEt\(_3\))] 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 (°) 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.

Reactions of [SnX\(_4\)(ER\(_3\))\(_2\)] (E = P, As) and [SnCl\(_4\)(L–L)] (L–L = \(\sigma\)-C\(_6\)H\(_4\)(PM\(_3\))\(_2\), Et\(_2\)P(CH\(_2\))\(_2\)PEt\(_2\) or \(\sigma\)-C\(_6\)H\(_4\)(AsMe\(_3\))\(_2\)) with TMSOTf

The complexes [SnX\(_4\)(ER\(_3\))\(_2\)] X = Cl, ER\(_3\) = PM\(_3\), PME\(_3\), AsEt\(_3\); X = Br, ER\(_3\) = PME\(_3\), AsEt\(_3\); were treated with one mol. equiv. of TMSOTf in anhydrous CH\(_2\)Cl\(_2\) solution with a view to removing one chloride ligand (as TMSCl) to create a tin cation. Triflate can behave either as an anion or coordinate to the metal; in practice we found 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 [SnCl\(_4\)(ER\(_3\))\(_2\)(OTf)] (Scheme 1). Curiously, the corresponding reactions with the tin(n) 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 [SnCl\(_4\)(Et\(_2\)P(CH\(_2\))\(_2\)PEt\(_2\))] or [SnCl\(_4\)(\(\sigma\)-C\(_6\)H\(_4\)(AsMe\(_3\))\(_2\))] with TMSOTf in CH\(_2\)Cl\(_2\) 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.

Addition of a CH\(_2\)Cl\(_2\) solution of SbR\(_3\) (R = Et or \(\text{^{1}P}\)) to CH\(_2\)Cl\(_2\) solutions of 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 R\(_3\)SbX\(_2\), based upon comparisons of their \(^{1}\)H NMR spectra with literature data and ESL.\(^{11}\) This suggests that any Sn(n)–stibine complexes are too unstable to isolate, and redox chemistry occurs [SnX\(_4\) + SbR\(_3\) \(\rightarrow\) SnX\(_4\) + R\(_3\)SbX\(_2\)]. Cunningham \textit{et al.} reported that reaction of SbPh\(_3\) with SnX\(_4\) initially gave yellow solids which became white on washing with pentane. The white solids had \(^{119}\)Sn Mössbauer spectra consistent with 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 triarylithiostibines, which gave simple adducts.\(^{6}\)
Colourless crystals of \([\text{SnCl}_3(\text{PMe}_3)_2]([\text{OTf}]\) and \([\text{SnCl}_4(\text{AsEt}_3)_2]([\text{OTf}]\) were grown by slow evaporation of solutions in anhydrous \(\text{CH}_2\text{Cl}_2\), 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 \(d(\text{Sn}-\text{Cl}_{\text{trans}Cl})\) are not significantly different and in both cases are longer than \(d(\text{Sn}-\text{Cl}_{\text{trans}OTf})\). The \(d(\text{Sn}-\text{Cl}_{\text{trans}Cl})\) and \(d(\text{Sn}-\text{As})\) are also similar to those in \([\text{SnCl}_4(\text{AsEt}_3)_2]_2\). The \(d(\text{Sn}-\text{O})\) distances are \(\sim 2.26\ \text{Å}\), which fall at the lower end of the range found in octahedral Sn(IV) tri-

Reactions of \([\text{SnX}_4(\text{ER}_3)_2]\) and \([\text{SnCl}_4(\text{L}_2)]\) with \(\text{AlCl}_3\)

No examples of ‘self-ionisation’, such as \([\text{SnX}_3(\text{ER}_3)_2][\text{SnX}_4]\) or \([\text{SnX}_2(\text{L}_2)][\text{SnX}_4]\), have been reported in reaction of \(\text{SnX}_4\) with pnictines, 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 \([\text{SnX}_4(\text{k}^2\text{MeC}(\text{CH}_2\text{AsMe}_2)_3)]\), to form \([\text{SnX}_3(\text{k}^2\text{MeC}(\text{CH}_2\text{AsMe}_2)_3)]\). However, using the stronger Lewis acid, \(\text{AlCl}_3\), has been successful in removing a chloride in some cases.\(^{11}\)

The \([\text{SnCl}_4(\text{PEt}_3)_2][\text{AlCl}_4]\) and \([\text{SnCl}_4(\text{PET}_3)_2][\text{AlCl}_4]\) 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\(^{11}\) \([\text{SnCl}_4(\text{PEt}_3)_2][\text{AlCl}_4]\) \((x = 3, y = 1; x = 2, y = 2)\).

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

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 \([\text{SnCl}_3(\text{PEt}_3)_2][\text{AlCl}_4]\), 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 \(d(\text{Sn}-\text{Cl}_{\text{trans}Cl})\) 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

\[\text{Scheme 2} \quad \text{Reactions of the tin complexes with AlCl}_3\]
of PEt₃ to [SnCl₄(PEt₃)₂][AlCl₄] in anhydrous CH₂Cl₂ solution does not form the new cation [SnCl₂(PEt₃)₃]²⁺. In situ NMR studies reveal a mixture of three main species (Experimental section); [AlCl₄]⁻, [AlCl₃(PEt₃)]⁻ (identified by its characteristic NMR spectra) and a new Sn-PEt₃ containing species. The $^{119}$Sn NMR spectrum shows a triplet $^3J$(¹¹⁹Sn⁻⁻⁻¹³¹P) coupling and hence indicates only two phosphines coordinated to the tin centre, e.g. [SnCl₄(PEt₃)₂]²⁻. The $^{31}$P and $^{119}$Sn chemical shifts do not correspond to those of [SnCl₃(PEt₃)]²⁻.[AlCl₄].

The solution NMR data (Table 1) show that along the series [SnCl₄(PEt₃)], [SnCl₃(PEt₃)][AlCl₄], [SnCl₂(PEt₃)₂][AlCl₄], the chemical shifts move to higher frequency in both the $^{31}$P and $^{119}$Sn spectra. The $^{31}$P(¹¹⁹Sn) and $^{119}$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 [AlCl₄]⁻ anions under different conditions.

The reaction of [SnCl₄(AsEt₃)₂] with AlCl₃ in CH₂Cl₂ did not proceed similarly to the reactions involving PEt₃. Monitoring the reaction by NMR spectroscopy identified a mixture containing starting materials and Et₃AsCl₂. A few crystals grown from this mixture contained the chlorotriethylarsionium(v) cation and a pentachloro(triethylarsine)stannane(v) anion, [Et₃AsCl][Sn(AsEt₃)Cl₅] (Fig. 4).

Arsine substituted halostannate anions do not seem to have been reported previously,²⁷ and the nearest literature example is the zwitterionic phosphine complex [SnCl₅(Ph₂PCH₂PPh₂H)]⁻.²⁷ Comparison of the key bond lengths with those in trans-[SnCl₄(AsEt₃)₂] shows that the

d(Sn–As) and d(Sn–Cl₅trans) are little different, although d(Sn–Cl₅trans) is ~0.05 Å shorter. The reaction of trans-[SnBr₄(AsEt₃)₂] with AlBr₃ also produced a mixture of products, including Et₃AsBr₂.²⁶

The reactions of [SnCl₄(o-C₆H₄(PMe₂)₂)] with one and two mol. equivalents of AlCl₃ in anhydrous CH₂Cl₂ were also investigated. The products were identified by microanalysis as [SnCl₄(o-C₆H₄(PMe₂)₂)]²⁻[AlCl₄] and [SnCl₄(o-C₆H₄(PMe₂)₂)]²⁻[AlCl₄]. These very moisture-sensitive complexes were poorly soluble in CH₂Cl₂ 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 [SnCl₄(PEt₃)][AlCl₄] (x = 4, y = 0; x = 3, y = 1; x = 2, y = 2), with $^δ$¹¹⁹Sn and $^δ$³¹P NMR moving to high frequency on going from the neutral complex to the mono- and the di-cations. The $^3J$(¹¹⁹Sn⁻⁻⁻¹³¹P) also follow the same trend as the PMe₃ complexes, with $^3J$(¹¹⁹Sn⁻⁻⁻¹³¹P) > [SnCl₄(o-C₆H₄(PMe₂)₂)]²⁻ > [SnCl₄(o-C₆H₄(PMe₂)₂)]²⁻ > [SnCl₄(o-C₆H₄(PMe₂)₂)]²⁻.²⁸

[SnCl₄(o-C₆H₄(AsMe₂)₂)] also reacted with AlCl₃ in anhydrous CH₂Cl₂ to form a poorly soluble white product, but the NMR spectra indicated a mixture of species present, which we were unable to identify.

Reactions of [SnX₄(EEt₃)₂] and [SnCl₄(L–L)] with Na[BArF]²⁹

Addition of Na[BArF]²⁻ to a CH₂Cl₂ solution [SnX₄(EEt₃)₂] (E = P; X = Cl or Br; E = As; X = Cl) or [SnCl₄(o-C₆H₄(PMe₂)₂)] (Scheme 3) readily formed the [BArF]⁻ salts, [SnX₄(EEt₃)]²⁻[BArF]²⁻ and [SnCl₄(o-C₆H₄(PMe₂)₂)][BArF]²⁻, with precipitation of NaX.

Scheme 3 Reactions of the tin complexes with Na[BArF]²⁻.
The NMR spectroscopic data for the cations match those of the [AlCl₄]⁻ salts discussed above, and using Na[BArF⁷] as the halide abstractor allowed generation of the [SnBr₃(AsEt₃)₂]⁺ cation that proved elusive with the other halide abstractors. Using excess Na[BArF⁷] did not lead to further halide abstraction.

**DFT studies**

Computational studies of the tin complexes were undertaken to supplement the experimental data. Ground state geometries of [SnCl₃(PMe₃)₂][AlCl₄], [SnCl₃(AsEt₃)₂], [SnCl₄(AsEt₃)₂(OTf)], [SnCl₄(PEt₃)₁], [SnCl₄(PMe₃)]⁺, [SnCl₄(PMe₃)]⁻ were optimised alongside the uncoordinated ligands AsEt₃ and PEt₃ 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-ζ basis set on all electrons in H, C, O, F, P, Al, S, and Cl atoms. Comparison of DFT results for the [SnCl₄(PMe₃)]⁻ and [SnCl₄(PMe₃)]⁺ against those reported,¹¹ was used to test the suitability of the computational methods.

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 AsEt₃ and PEt₃ (98.5 and 100.4°, respectively) are slightly wider than those found in AsMe₃ (97.0°) and PMe₃ (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’ AsEt₃ (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 PMe₃ and PEt₃ (1.90–1.92 Å; X-ray: 1.84 Å). This, when combined with the widening of the C–As–C (DFT: 105.3–106.2°; 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 (AsEt₃: 98.5°; PMe₃: 98.8° and PEt₃: 100.4°), matches the trends seen for trialkylstibine ligands upon coordination to Group 13 metal halides,⁶ 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 tinarsine and phosphine complexes shows the free ligands have s-character of AsEt₃: 12.20; PMe₃: 15.08; PEt₃: 15.57%, which doubles to 25.3–25.9% upon coordination.

Calculating the ground state structure of the [SnCl₄(AsEt₃)₂] and [SnCl₃(AsEt₃)₂(OTf)] complexes, alongside DFT calculations of the ionic [SnCl₄(AsEt₃)₂]⁺ complex, show that there is very little change in the bond lengths/angles and this is consistent with reported data for [SnCl₄(PMe₃)]⁻. Burford’s complexes are also noted for a significant decrease in the P–Sn–P angle with increasing charge,¹¹ the neutral [SnCl₄(AsEt₃)₂] complex (X-ray: 180; DFT: 179.9°) and the cationic [SnCl₄(AsEt₃)₂]⁺ species show a similar trend (DFT: 174°).

Notably, while the HOMO and LUMO energies in the neutral tetrahalide and triflate cations 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 AsEt₃ complexes as examples, the HOMO is concentrated on the SnCl₄ unit in the [SnCl₄(AsEt₃)₂], with some delocalisation onto the AsEt₃ ligands in [SnCl₄(AsEt₃)₂(OTf)], and this is even more obvious in [SnCl₄(AsEt₃)₂]⁺ (Fig. 5).

**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 Sn⁴⁺:X ratio of 1:3 or 1:2.

In the case of SbEt₃, we found that SnCl₄ causes chlorination of the stibine, consistent with the greater stability of Sb(v) over As(v) (although P(v) is also more stable than As(v), the stronger basicity of the PR₃ ligands means that coordination is favoured over chlorination in this system).

Replacement of chloride by triflate to form [SnCl₄(ER₃)(OTf)] is possible for ER₃ = PMe₃, PEt₃, AsEt₃, 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 [SnBr₄(ER₃)]₂ to react with TMSOTf was unexpected, although formation of TMSBr is less favoured energetically.

Aluminium trichloride is able to abstract chloride ligands from [SnCl₄(PEt₃)₂] and [SnCl₄(o-C₆H₄(PMe₂)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 [BArF]$^-$ anion does lead smoothly to the formation of [SnCl$_3$(Et$_3$N)$_2$][BArF] for E = P and As, [SnBr$_3$(AsEt$_3$)$_2$][BArF], as well as affording [SnCl$_3$(0-C$_6$H$_4$(PMe$_2$)$_2$)$_2$][BArF].

In practice, the Na[BArF]$^-$ works better as a halide abstractor to form the monocations (but does not form dications), whereas 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).

**Conflicts of interest**

The authors have no conflicts to declare.

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**References**


6 V. K. Greenacre, W. Levason and G. Reid, Organometallics, 2018, 37, 2123.


