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17097Neutral 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 trimethylsilyltriflate (TMSOTf) in CH₂Cl₂ solution substitutes one chloride to form [SnCl₃(PR₃)₂(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 [SnCl₃(PMe₃)₂(OTf)] revealed *mer*-chlorines and *trans*-phosphines. In contrast, *trans*-[SnBr₄(PR₃)₂], [SnCl₄(Et₂P(CH₂)₂PEt₂)], [SnCl₄(*o*-C₆H₄(PMe₂)₂)] and [SnCl₄(*o*-C₆H₄(AsMe₂)₂)] 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 [SnI₄(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(AsEt₃)₂(OTf)], whose X-ray structure reveals the same geometry found in the phosphine analogues, with the triflate coordinated. The salts, [SnCl₃(PEt₃)₂][AlCl₄] and [SnCl₂(PEt₃)₂][AlCl₄]₂ 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)Cl₅] (the latter identified crystallographically). In contrast, using Na[BAR^F] (BAR^F = [B(3,5-(CF₃)₂C₆H₃)₄][−]) produced [SnCl₃(PEt₃)₂][BAR^F] and also allowed clean isolation of the arsine analogue, [SnCl₃(AsEt₃)₂][BAR^F]. [SnCl₄(*o*-C₆H₄(PMe₂)₂)] also reacts with AlCl₃ in CH₂Cl₂ to form [SnCl₃(*o*-C₆H₄(PMe₂)₂)][AlCl₄] and [SnCl₂(*o*-C₆H₄(PMe₂)₂)][AlCl₄]₂. Multinuclear NMR spectroscopy on the [AlCl₄][−] salts show that $\delta^{31}\text{P}$ and $\delta^{119}\text{Sn}$ move progressively to high frequency on conversion from the neutral complex to the mono- and the di-cations, whilst ¹J(¹¹⁹Sn–³¹P) follow the trend: [SnCl₃(*o*-C₆H₄(PMe₂)₂)]⁺ > [SnCl₄(*o*-C₆H₄(PMe₂)₂)] > [SnCl₂(*o*-C₆H₄(PMe₂)₂)]²⁺. 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.

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Introduction

Much of the coordination chemistry of the transition metal ions with neutral ligands is based around metal halide complexes.¹ 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 ≥ a) are commonly known,

formed either spontaneously in the presence of excess L, or upon the addition of large, weakly coordinating anions.¹ 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.¹ 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.² Rare exceptions are provided by 1,4,7-tri-

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methyl-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),³ although more flexible acyclic polydentate ligands, such as $MeC(CH_2AsMe_2)_3$, behave as bidentate ligands, as in $[SnX_4\{\kappa^2-MeC(CH_2AsMe_2)_3\}]$.⁴

Complexes of the tin(IV) halides, SnX_4 ($X = Cl$ or Br), with neutral phosphine and arsine ligands have been explored in considerable detail⁵ and almost all are of the octahedral *trans*- $[SnX_4(ER_3)_2]$ or *cis*- $[SnX_4(bidentate)]$ (bidentate = diphosphine or diarsine) types. SnI_4 is a weaker Lewis acid and forms similar, but less stable adducts,⁵ whilst complexes of SnF_4 have been much less studied.^{4,5} Reported examples of stibine complexes of p-block halides are extremely rare.^{5,6}

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.^{7–12} MacDonald *et al.*¹¹ 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 ($[BAR^F]^- = [B\{3,5-(CF_3)_2C_6H_3\}_4]^-$).

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*- $C_6H_4(PMe_2)_2$ and *o*- $C_6H_4(AsMe_2)_2$, which were prepared by literature methods.¹³ $SbEt_3$, Sb^iPr_3 ¹⁴ and $Na[BAR^F]$ ¹⁵ were made as described. CH_2Cl_2 was dried by distillation from CaH_2 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 , $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$, ^{27}Al and ^{119}Sn NMR spectra were recorded from $CDCl_3$ or CH_2Cl_2/CD_2Cl_2 solutions using a Bruker AV400 spectrometer and referenced to TMS *via* the residual solvent resonance, $CFCl_3$, 85% H_3PO_4 , $[Al(H_2O)_6]^{3+}$ in H_2O at pH = 1 or $SnMe_4$ as appropriate.

Typically, $[Cr(acac)_3]$ was added as a relaxation agent when recording the ^{119}Sn spectra, except for those containing $[AlCl_4]^-$, when it appeared to react with the complexes, turning green. In these cases a 2 seconds pulse delay was used. Microanalyses were undertaken by London Metropolitan University.

$[SnCl_4(AsEt_3)_2]$

A solution of $AsEt_3$ (0.058 g, 0.36 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $SnCl_4$ (0.047 g, 0.18 mmol) in CH_2Cl_2 (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_2Cl_2 solution of the compound. Yield 0.093 g, 88%. Required for $C_{12}H_{30}As_2Cl_4Sn$ (584.7): C, 24.6; H, 5.2. Found: C, 24.5; H, 5.0%. IR (Nujol/ cm^{-1}): $\nu = 288s$ (Sn–Cl). 1H NMR ($CDCl_3$, 295 K): $\delta = 2.34$ (q, [12H], $^3J_{HH} = 7.6$ Hz, CH_2), 1.42 (t, [18H], $^3J_{HH} = 7.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): $\delta = 8.62$ (CH_2), 15.04 (CH_3). ^{119}Sn NMR (CD_2Cl_2 , 298 K): n.o.; (CD_2Cl_2 , 193 K): $\delta = -657.4$.

$[SnBr_4(AsEt_3)_2]$

A solution of $AsEt_3$ (0.144 g, 0.89 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $SnBr_4$ (0.195 g, 0.45 mmol) in CH_2Cl_2 (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_2Cl_2 solution of the compound. Yield 0.175 g, 50%. Required for $C_{12}H_{30}As_2Br_4Sn$ (762.5): C, 18.9; H, 4.0. Found: C, 19.0; H, 4.0%. IR (Nujol/ cm^{-1}): $\nu = 210s$ (Sn–Br). 1H NMR (CD_2Cl_2 , 295 K): $\delta = 2.35$ (q, [12H], $^3J_{HH} = 7.6$ Hz, CH_2), 1.43 (t, [18H], $^3J_{HH} = 7.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 295 K): $\delta = 8.5$ (CH_2), 14.8 (CH_3). ^{119}Sn NMR (CD_2Cl_2 , 295 K): $\delta = -1173.4$; (CD_2Cl_2 , 193 K): $\delta = -1125.3$.

$[SnCl_3(AsEt_3)_2(OTf)]$

$[SnCl_4(AsEt_3)_2]$ (0.150 g, 0.26 mmol) was dissolved in CH_2Cl_2 (10 mL) to form a clear solution. To this TMSOTf (0.057 g, 0.26 mmol) was added in CH_2Cl_2 (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_2Cl_2 . Yield 0.138 g, 77%. Required for $C_{13}H_{30}As_2Cl_3F_3O_3SSn$ (698.1): C, 22.4, H, 4.3. Found C, 21.9; H, 4.2%. IR (Nujol/ cm^{-1}): $\nu = 294s$, 378w (Sn–Cl), 1156m ($-OSO_2$), 1231m, 1200m (CF_3). 1H NMR (CD_2Cl_2 , 295 K): $\delta = 1.39$ (t, [18H], $^3J_{HH} = 7.8$ Hz, CH_3), 2.38 (q, [12H], $^3J_{HH} = 7.8$ Hz, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 295 K): $\delta = 9.0$ (CH_2), 16.0 (CH_3). $^{19}F\{^1H\}$ NMR (CD_2Cl_2 , 295 K): $\delta = -78.7$ (s, CF_3). ^{119}Sn NMR (CD_2Cl_2 , 298 K): n.o.; (CD_2Cl_2 , 183 K): $\delta = -620$ (s).

$[SnCl_3(PMe_3)_2(OTf)]$

$[SnCl_4(PMe_3)_2]^{16}$ (0.300 g, 0.72 mmol) was suspended in CH_2Cl_2 (5 mL). To this TMSOTf (0.016 g, 0.72 mmol) was



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3.8, IR (Nujol/cm⁻¹) = 289m, (Sn–Cl), 484s, ([AlCl₄]⁻). ¹H NMR (CD₂Cl₂, 295 K): δ = 1.39 (m, [18H], CH₃), 2.38 (m, [12H], CH₂), ¹³C{¹H}NMR (CD₂Cl₂, 295 K): δ = 7.50 (t, ²J + ⁴J_{31P–13C} = 2.93 Hz, –CH₃), 14.51 (t, ¹J + ³J_{31P–13C} = 13.2 Hz), ²⁷Al NMR (CD₂Cl₂, 295 K): δ = 103.0, ³¹P{¹H} NMR (CD₂Cl₂, 295 K): δ = 40.8 (¹J_{31P–117Sn} = 2172 Hz, ¹J_{31P–119Sn} = 2274 Hz). ¹¹⁹Sn NMR (CD₂Cl₂, 298 K): δ = –301.4 (br, t, ¹J_{31P–119Sn} = 2291 Hz).

Reaction of [SnCl₂(PEt₃)₂][AlCl₄]₂ + PEt₃

[SnCl₂(PEt₃)₂][AlCl₄]₂ (0.100 g, 0.13 mmol) was dissolved in CH₂Cl₂ (3 mL), to this PEt₃ (0.015 g, 0.22 mmol) was added in CH₂Cl₂ (2 mL). To this 10 drops of CD₂Cl₂ is added. A portion of the solution was used for *in situ* NMR studies.

²⁷Al NMR (CD₂Cl₂, 295 K): δ = 103.1 (s, [AlCl₄]⁻), 110.8 (d, ¹J_{31P–27Al} = 267 Hz, [AlCl₃(PEt₃)₂]). ³¹P{¹H} NMR (CD₂Cl₂, 295 K): δ = –14.8 (sextet, ¹J_{27Al–31P} = 264 Hz, [AlCl₃(PEt₃)₂]), 32.2 (¹J_{31P–117Sn} = 2312 Hz, ¹J_{31P–119Sn} = 2394 Hz, new Sn–PEt₃ containing cation – see text). ¹¹⁹Sn NMR (CD₂Cl₂, 298 K): δ = –449 (t, ¹J_{31P–119Sn} = 2394 Hz).

[SnCl₃(PEt₃)₂][BAR^F]

A Schlenk was charged with [SnCl₄(PEt₃)₂] (0.100 g, 0.20 mmol) and Na[BAR^F] (0.178 g, 0.20 mmol). To this CH₂Cl₂ (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 C₄₄H₄₂BCl₃F₂₄P₂Sn (1324.3): C, 39.9, H, 3.2 Found C, 39.8, H, 3.3%. ¹H NMR (CD₂Cl₂, 295 K): δ = 1.35 (m, [18H], CH₃), 2.29 (m, [12H], CH₂), 7.57 (s, [4H], [BAR^F]), 7.72 (m, [8H], [BAR^F]); ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): δ = –63.0 (s, –CF₃). ³¹P{¹H} NMR (CD₂Cl₂, 295 K): δ = 37.1 (¹J_{31P–117Sn} = 2208 Hz, ¹J_{31P–119Sn} = 2311 Hz); ¹¹⁹Sn NMR (CD₂Cl₂, 298 K): δ = –379 (t, ¹J_{31P–119Sn} = 2311 Hz).

[SnCl₃(AsEt₃)₂][BAR^F]

A Schlenk was charged with [SnCl₄(AsEt₃)₂] (0.100 g, 0.17 mmol) and Na[BAR^F] (0.152 g, 0.17 mmol). To this CH₂Cl₂ (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 C₄₄H₄₂As₂BCl₃F₂₄Sn (1412.2): C, 37.4, H, 3.0 Found C, 37.3, H, 2.8%. ¹H NMR (CD₂Cl₂, 295 K): δ = 1.44 (t, ³J_{HH} = 7.7 Hz, [18H], CH₃), 2.42 (q, ³J_{HH} = 7.7 Hz, [12H], CH₂), 7.57 (s, [4H], [BAR^F]), 7.72 (m, [8H], [BAR^F]); ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): δ = –63.0 (s, –CF₃); ¹¹⁹Sn NMR (CD₂Cl₂, 183 K): δ = –388 (br s).

[SnCl₃{*o*-C₆H₄(PMe₂)₂}][BAR^F]

A Schlenk was charged with [SnCl₄{*o*-C₆H₄(PMe₂)₂}] (0.100 g, 0.17 mmol) and Na[BAR^F] (0.152 g, 0.17 mmol) and to this CH₂Cl₂ (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 C₄₂H₂₈BCl₃F₂₄P₂Sn (1286.2): C, 39.2, H, 2.2 Found C, 39.3, H, 2.0%. ¹H NMR (CD₂Cl₂, 295 K): δ = 2.01 (t, ²J + ⁵J_{PH} = 4.7 Hz, [12H], CH₃), 7.57 (s, [4H], [BAR^F]), 7.72 (m, [8H], [BAR^F]), 7.82 (m, [4H], [BAR^F]); ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): δ = –63.0 (s,

–CF₃); ³¹P{¹H} NMR (CD₂Cl₂, 295 K): δ = –24.5 (¹J_{31P–Sn} = 1007 Hz); ¹¹⁹Sn NMR (CD₂Cl₂, 183/298 K): δ = n.o.

[SnBr₃(AsEt₃)₂][BAR^F]

A Schlenk was charged with [SnBr₄(AsEt₃)₂] (0.077 g, 0.1 mmol) and Na[BAR^F] (0.090 g, 0.1 mmol) to this CH₂Cl₂ (5 mL) was added; the resulting cloudy solution was stirred for 2 h, filtered and concentrated to dryness *in vacuo* yielding a light yellow gum, which was then dissolved in Et₂O (5 mL), then the solution was concentrated to dryness *in vacuo* yielding a light yellow solid. Yield: 0.091 g, 58%. Required for C₄₄H₄₂As₂BBR₃F₂₄Sn (1448.2): C, 34.2, H, 2.7. Found C, 34.3, H, 2.9%. ¹H NMR (CD₂Cl₂, 295 K): δ = 1.39 (t, ³J_{HH} = 7.6 Hz, [18H], CH₃), 2.42 (br, [12H], CH₂), 7.58 (s, [4H], [BAR^F]), 7.73 (m, [8H], [BAR^F]); ¹³C{¹H}NMR (CD₂Cl₂, 295 K): δ = 9.1 (s, –CH₃), 15.9 (s, –CH₂), 118.1(s), 123.8(s), 126.5(s), 129.3(m), 135.4(s), 162.3(q, ¹J_{11B–13C} = 49.9 Hz); ¹⁹F{¹H} NMR (CD₂Cl₂, 295 K): δ = –62.8 (s, –CF₃). ¹¹⁹Sn NMR (CD₂Cl₂, 183/298 K): δ = n.o.

X-Ray experimental

Crystals of the complexes were grown from CH₂Cl₂ 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-2014/7.41.¹⁸ 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 [SnCl₄(AsEt₃)₂], CCDC 1916558 [SnBr₄(AsEt₃)₂], CCDC 1916559 [SnCl₃(PMe₃)₂(OTf)], CCDC 1916560 [SnCl₃(AsEt₃)₂(OTf)], CCDC 1916561 [SnCl₂(PEt₃)₃][AlCl₄]₂, CCDC 1916562 [Et₃AsCl][SnCl₅(AsEt₃)₃].†

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.* [SnCl₄(PEt₃)₂],¹⁷ [SnCl₄(PMe₃)₂],¹⁶ [SnBr₄(PMe₃)₂],¹⁶ [SnCl₄{*o*-C₆H₄(PMe₂)₂}],⁴ [SnCl₄(Et₂PCH₂CH₂PET₂)],⁴ as was [SnCl₄{*o*-C₆H₄(AsMe₂)₂}].¹⁶ 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 1949,¹⁹ but lacked any spectroscopic or structural data. The crystal structure of [SnCl₄(AsEt₃)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^a

Compound	$\delta(^{31}\text{P}\{^1\text{H}\})$	$\delta(^{119}\text{Sn})$	$^1J(^{119}\text{Sn}-^{31}\text{P})/\text{Hz}$	$\nu(\text{Sn-X})/\text{cm}^{-1}$	Ref.
$[\text{SnCl}_4(\text{PMe}_3)_2]$	+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 ^b	—	288	This work
$[\text{SnBr}_4(\text{AsEt}_3)_2]$	—	−1173 ^b	—	210	This work
$[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$	—	−620 ^b	—	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 ^b	−535 ^b	2737 ^b	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	−301	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	853	294, 305	This work

^a NMR data from CH_2Cl_2 solution at 293 K, except. ^b 193 K.

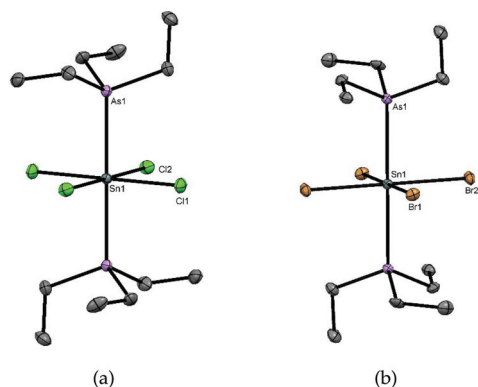


Fig. 1 (a) The structure of $[\text{SnCl}_4(\text{AsEt}_3)_2]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Sn1–Cl1 = 2.4498(4), Sn1–Cl2 = 2.4544(4), Sn1–As1 = 2.65964(16), As1–Sn1–As1 = 180.0, 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 (°) 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.

trans- $[\text{SnCl}_4(\text{PET}_3)_2]$ ¹⁷ or *trans*- $[\text{SnCl}_4(\text{PMe}_3)_2]$,¹¹ but slightly longer than that in *trans*- $[\text{SnCl}_4(\text{AsPh}_3)_2]$ ²⁰ (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 trialkylarsine ligand. In *trans*- $[\text{SnBr}_4(\text{AsEt}_3)_2]$ (Fig. 1(b)) the *d*(Sn–As) is 2.6773(3) Å, only very slightly longer than in the chloride.

Attempts to isolate a complex of AsEt_3 with SnI_4 were not successful, as noted previously by others.¹⁹

Addition of a CH_2Cl_2 solution of SbR_3 (R = Et or ⁱPr) to CH_2Cl_2 solutions of SnX_4 (X = Cl or Br) result in immediate precipitation of grey solids, which contain essentially no C/H

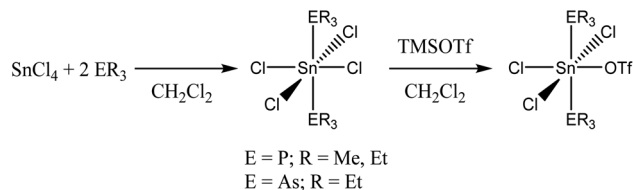
(microanalysis), whilst the supernatant solutions contain R_3SbX_2 , based upon comparisons of their ¹H NMR spectra with literature data and ESI.[†] This suggests that any Sn(IV) -stibine complexes are too unstable to isolate, and redox chemistry occurs $[\text{SnX}_4 + \text{SbR}_3 \rightarrow \text{SnX}_2 + \text{R}_3\text{SbX}_2]$. Cunningham *et al.*²² reported that reaction of SbPh_3 with SnX_4 initially gave yellow solids which became white on washing with pentane. The white solids had ¹¹⁹Sn 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 trialkylstibines, which gave simple adducts.⁶

Reactions of $[\text{SnX}_4(\text{ER}_3)_2]$ (E = P, As) and $[\text{SnCl}_4(\text{L-L})]$ (L–L = *o*-C₆H₄(PMe₂)₂, Et₂P(CH₂)₂PET₂ or *o*-C₆H₄(AsMe₂)₂) with TMSOTf

The complexes $[\text{SnX}_4(\text{ER}_3)_2]$ (X = Cl, ER₃ = PMe₃, PET₃, AsEt₃; X = Br, ER₃ = PMe₃, AsEt₃) were treated with one mol. equivalent of TMSOTf in anhydrous CH_2Cl_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 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 $[\text{SnCl}_4\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PET}_2\}]$,⁴ $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}]$ ⁴ or $[\text{SnCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$ ¹⁶ with TMSOTf in CH_2Cl_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.





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_2Cl_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 $d(\text{Sn}-\text{Cl}_{\text{transCl}})$ 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 $\text{Sn}(\text{IV})$ triflates ($\sim 2.2\text{--}2.6$ Å)²³ and may be compared to the sum of the covalent radii of Sn and O (2.15 Å).²⁴

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}Sn and ^{31}P resonances and a more marked increase in $J_{\text{Sn-P}}$. The ^{119}Sn chemical shift also moves to high frequency in $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$ compared to $[\text{SnCl}_4(\text{AsEt}_3)_2]$.

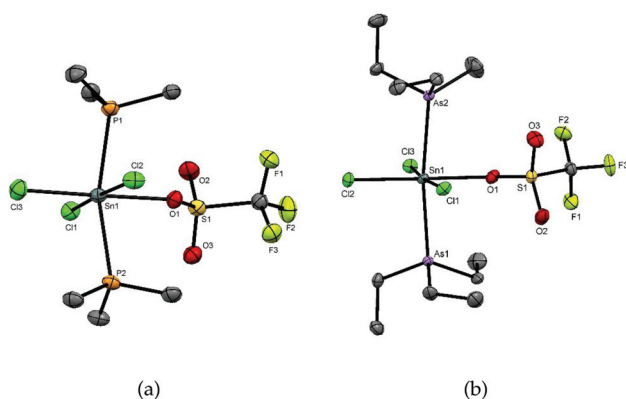


Fig. 2 (a) The structure of $[\text{SnCl}_3(\text{PMe}_3)_2(\text{OTf})]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: $\text{Sn1}-\text{Cl1} = 2.4457(9)$, $\text{Sn1}-\text{Cl2} = 2.4558(9)$,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

The reaction of SnCl_4 , SbEt_3 and TMSOTf in CH_2Cl_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 SnCl_2 (cf. ref. 22). Crystals of the former were grown from CH_2Cl_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†).

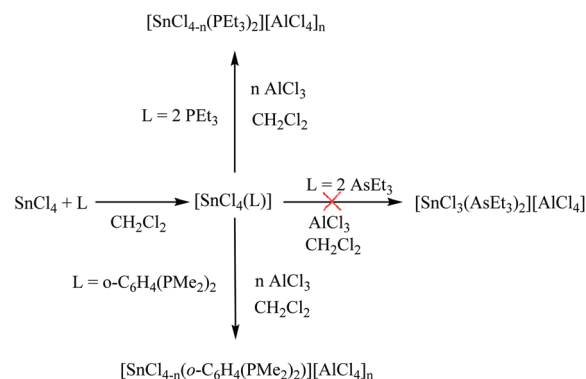
Reactions of $[\text{SnX}_4(\text{ER}_3)_2]$ and $[\text{SnCl}_4(\text{L-L})]$ with AlX_3

No examples of 'self-ionisation', such as $[\text{SnX}_3(\text{ER}_3)_2]_2[\text{SnX}_6]$ or $[\text{SnX}_2(\text{L-L})_2]_2[\text{SnX}_6]$, have been reported in reaction of SnX_4 with pnictines,⁵ i.e. 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 $[\text{SnX}_4\{\kappa^2\text{-MeC}(\text{CH}_2\text{AsMe}_2)_2\}]$,⁴ to form $[\text{SnX}_3\{\kappa^3\text{-MeC}(\text{CH}_2\text{AsMe}_2)_3\}]^+$. However, using the stronger Lewis acid, AlCl_3 , has been successful in removing a chloride in some cases.¹¹

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 AlCl_3 in anhydrous CH_2Cl_2 (Scheme 2), and behave similarly to the previously reported¹¹ $[\text{SnCl}_x(\text{PMe}_3)_2][\text{AlCl}_4]_y$ ($x = 3, y = 1$; $x = 2, y = 2$).

Attempts to grow crystals from a CH_2Cl_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.

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 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

Scheme 2 Reactions of the tin complexes with AlCl_3 .

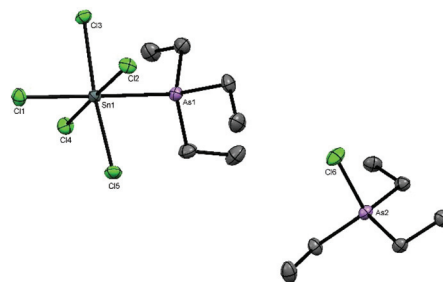


Fig. 4 The structure of $[\text{Et}_3\text{AsCl}][\text{SnCl}_5(\text{AsEt}_3)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Sn1–As1 = 2.6696(5), Sn1–Cl3 = 2.4453(8), Sn1–Cl4 = 2.4304(9), Sn1–Cl2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

$d(\text{Sn-As})$ and $d(\text{Sn-Cl}_{\text{transCl}})$ are little different, although $d(\text{Sn-Cl}_{\text{transAs}})$ is ~ 0.05 Å shorter. The reaction of *trans*-[SnBr₄(AsEt₃)₂] with AlBr₃ also produced a mixture of products, including Et₃AsBr₂.²⁶

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}P and ^{119}Sn spectra. The $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{AlCl}_4]^-$ anions under different conditions.

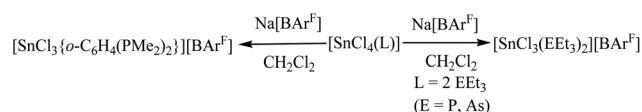
The reaction of $[\text{SnCl}_4(\text{AsEt}_3)_2]$ with AlCl_3 in CH_2Cl_2 did not proceed similarly to the reactions involving PET_3 . Monitoring the reaction by NMR spectroscopy identified a mixture of species present including starting materials and Et_3AsCl_2 .²⁶ A few crystals grown from this mixture 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).

Arsine substituted halostannate anions do not seem to have been reported previously,⁵ and the nearest literature example is the zwitterionic phosphine complex $[\text{SnCl}_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{H})]^{.27}$ Comparison of the key bond lengths with those in *trans*- $[\text{SnCl}_4(\text{AsEt}_3)_2]$ shows that the

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

Addition of Na[Bar^F] 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 [Bar^F][−] salts, [SnX₃(EET₃)₂][Bar^F] and [SnCl₃{o-C₆H₄(PMe₂)₂}][Bar^F], with precipitation of NaX.



Scheme 3 Reactions of the tin complexes with Na[BAr^F].

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 $[\text{SnBr}_3(\text{AsEt}_3)_2]^+$ cation that proved elusive with the other halide abstractors. Using excess $\text{Na}[\text{BAR}^{\text{F}}]$ did not lead to further halide abstraction.

DFT studies

Computational studies of the tin complexes were undertaken to supplement the experimental data. Ground state geometries of $[\text{SnCl}_3(\text{PMe}_3)_2][\text{AlCl}_4]$, $[\text{SnCl}_4(\text{AsEt}_3)_2]$, $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$, $[\text{SnCl}_4(\text{PET}_3)_2]$,¹⁷ $[\text{SnCl}_4(\text{PMe}_3)_2]$,¹¹ $[\text{SnCl}_3(\text{PMe}_3)_2(\text{OTf})]$, $[\text{SnCl}_3(\text{PMe}_3)_2]^+$ were optimised alongside the uncoordinated ligands AsEt_3 and PET_3 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 $[\text{SnCl}_3(\text{PMe}_3)_2][\text{AlCl}_4]$ and $[\text{SnCl}_4(\text{PMe}_3)_2]$ against those reported,¹¹ 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_3 and PET_3 (98.5 and 100.4°, respectively) are slightly wider than those found in AsMe_3 (97.0°) and PMe_3 (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_3 (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_3 and PET_3 (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_3 : 98.5°; PMe_3 : 98.8° and PET_3 : 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 tin-arsine and phosphine complexes shows the free ligands have *s*-character of AsEt_3 : 12.20; PMe_3 : 15.08; PET_3 : 15.57%, which doubles to 25.3–25.9% upon coordination.

Calculating the ground state structure of the $[\text{SnCl}_4(\text{AsEt}_3)_2]$ and $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$ complexes, alongside DFT calculations of the ionic $[\text{SnCl}_3(\text{AsEt}_3)_2]^+$ complex, show that there is very little change in the bond lengths/angles and this is consistent with reported data for $[\text{SnCl}_3(\text{PMe}_3)_2]^+$. Burford’s complexes are also noted for a significant decrease in the P–Sn–P angle with increasing charge,¹¹ 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

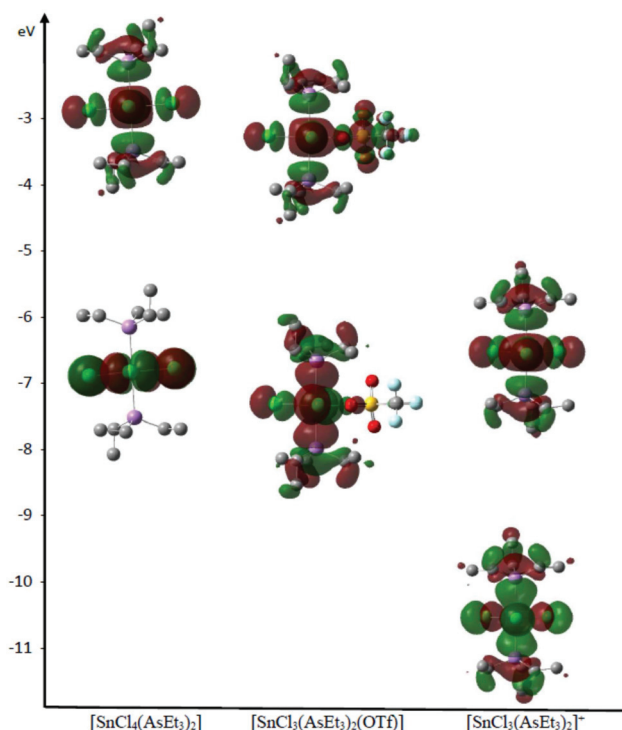


Fig. 5 Representation of the LUMO and HOMO of $[\text{SnCl}_4(\text{AsEt}_3)_2]$, $[\text{SnCl}_3(\text{AsEt}_3)_2(\text{OTf})]$ and $[\text{SnCl}_3(\text{AsEt}_3)_2]^+$ determined by DFT analysis, showing their relative energies.

energy, consistent with the latter displaying higher Lewis acidity (Table S7†). Furthermore, using the AsEt_3 complexes as examples, the HOMO is concentrated on the SnCl_4 unit in the $[\text{SnCl}_4(\text{AsEt}_3)_2]$, with some delocalisation onto the 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).

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 Sn^{IV} :X ratio of 1 : 3 or 1 : 2.

In the case of SbEt_3 , we found that 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 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 $\text{ER}_3 = \text{PMe}_3$, PET_3 , 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 As , $[\text{SnBr}_3(\text{AsEt}_3)_2][\text{BAR}^{\text{F}}]$, 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 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.

Conflicts of interest

The authors have no conflicts to declare.

Acknowledgements

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