

Tin(IV) halide complexes of AsPh₃: The structures of *trans*-SnCl₄(AsPh₃)₂ and SnBr₄(AsPh₃)·AsPh₃†

Mary F. Mahon,^a Natalia L. Moldovan,^b Kieran C. Molloy,^{*,a} Alexandra Muresan,^b Ioan Silaghi-Dumitrescu^b and Luminita Silaghi-Dumitrescu^b

^a Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

^b Department of Chemistry, Babes-Bolyai University, RO-3400, Cluj-Napoca, Romania

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The structures of two 1 : 2 adducts between tin(IV) halides and AsPh₃ have been determined. SnCl₄(AsPh₃)₂ adopts a six-coordinate geometry at tin in which the two organoarsine donors are mutually *trans*. In contrast, SnBr₄(AsPh₃)₂ is five-coordinate at tin and only one arsine is directly bonded to the metal, in an axial site of the trigonal bipyramid. The second AsPh₃ group has a close contact with the axially bound bromine [As...Br: 3.567(3) Å], which is a unique structural variation that depicts an intermediate in a halogen-transfer reaction between Group 14 and Group 15 elements. AACVD using SnCl₄(AsPh₃)₂ generates a film containing SnO₂ and a second crystalline material which is possibly SnCl₂, but which contains no arsenic.

Introduction

As part of our general interest in the deposition of metal phosphides^{1–3} by MOCVD we have had cause to re-examine some of the fundamental chemistry of adducts formed between R₃E (E = P, As) and main group metal halides. It is now clear that not all of the species previously reported as simple adducts MX_n·(ER₃)_y contain 2e M–E interactions. This is best exemplified by the work of Godfrey, du Mont and others who have shown that the “adducts” arising from reactions of germanium(IV) halides with tertiary phosphines, GeX₄·PR₃, are halophosphonium salts [R₃PX]⁺[GeX₃][–], in which halogen transfer is accompanied by oxidation of phosphorus and reduction of germanium.^{4,5} A similar phenomenon is also seen in tin chemistry, where reaction of SnI₄ and Cy₃P leads to the isolation of both [Cy₃PI]⁺[SnI₃][–] and [Cy₃PI]⁺[SnI₅][–]. Here, analogous halogen transfer occurs, though the anion which co-crystallises was found to contain either Sn(II) or Sn(IV) rather than just the lower oxidation state.⁶

Structural characterisations of simple tertiary phosphine adducts of SnX₄ are surprisingly rare [SnI₄(PPR₃)₂,⁷ SnCl₄(PEt₃)₂,⁸ SnCl₄·dppe⁹ (dppe = bis-diphenylphosphinoethane)] while no analogous Ge(IV) halide adducts have been crystallographically confirmed. Structural characterisation of tertiary arsine adducts containing either of the two Group 14 elements is equally sparse, with high quality data available only for SnI₄[1,2-(Me₂As)₂C₆H₄]¹⁰ and GeCl₄(AsMe₃)₂,⁴ a poorly resolved structure for the organotin adduct Ph₃SnNO₃(AsPh₃)¹¹ has also been published. Thus, while there are a number of synthetic and spectroscopic studies of SnX₄/AsR₃ compounds,^{12–14} their structural integrity is open to question. Moreover, as adduct formation is one of the key steps in the deposition, by MOCVD, of metal pnictide thin films from MX_n and ER₃, a greater understanding of the interactions between the two species is desirable. In this paper we report on the structures of the nominally 2 : 1 adducts formed between SnX₄ (X = Cl, Br) and AsPh₃, with an unexpected result. In addition, the use of SnCl₄(AsPh₃)₂ in CVD experiments has been explored.

Experimental

General

Elemental analyses were performed using an Exeter Analytical CE 440 analyser, SEM was carried out on a JEOL JSM-6310 microscope while quantitative EDXS measurements were made on a JEOL JXA-8600 electron probe microanalyser. XRD was performed using a Bruker D8 diffractometer on which coupled θ – 2θ scans were carried out. Thermogravimetric studies were performed on a Perkin Elmer TGA7 analyser; samples were loaded as quickly as possible in air then the temperature increased under a flow of dry N₂ gas.

Synthesis of SnCl₄(AsPh₃)₂ (1)^{12,14}

AsPh₃ (4.70 g, 15.32 mmol) in dichloromethane (30 ml) was added slowly to a solution of SnCl₄ (2.00g, 7.66 mmol) in the same solvent (30 ml). An immediate yellowish precipitate is formed. Analysis, found (calc. for C₃₆H₃₀As₂Cl₄Sn): C 49.4 (49.5), H 3.46 (3.43)%; mp 158 °C (lit.¹⁴ 160–162 °C). Crystals suitable for X-ray diffraction were obtained by concentrating the filtrate by half and cooling the remaining solution in a refrigerator.

Synthesis of SnBr₄(AsPh₃)·(AsPh₃) (2)

A solution of SnBr₄ (1.1 mmol) in hexane was added to a solution of AsPh₃ (2.2 mmol) in the same solvent (total volume 40 ml). After 6 h stirring, a small amount of sticky white solid was separated by cannula filtration. The filtrate was cooled to –5 °C which resulted in a crop of yellow-brown crystals of **2** (mp 82–84 °C). Analysis, found (calc. for C₃₆H₃₀As₂Br₄Sn): C 41.7 (41.1), H 3.15 (2.88)%.

Crystallography

Crystallographic data for compounds **1** and **2** are summarised in Table 1. In both cases, data collections were implemented on a Nonius KappaCCD diffractometer at 150(2) (**1**) or 170(2) K (**2**). Non-hydrogen atoms were refined anisotropically without exception. All data were corrected for Lorentz, polarisation, extinction and absorption. Refinement was based on F^2 .

For **2**, good unit cell parameter e.s.d.s belie a poor data set from a crystal which exhibited split diffraction spots clearly visible in the data frames. This reflects the sample quality, which did not clearly extinguish polarised light under the microscope

† Electronic supplementary information (ESI) available: SEM of the film deposited by AACVD using (**1**) as the precursor: (Fig. 6) showing the underlay with the larger crystallites superimposed, (Fig. 7) showing the particulate nature of the film and the film thickness; SEM showing ill-formed crystallites deposited on the surface of the layer of SnO₂ (Fig. 8). See <http://www.rsc.org/suppdata/dt/b4/b411342j/>

Table 1 Crystallographic data for **1** and **2**

	(1)	(2)
Empirical formula	C ₁₈ H ₁₅ AsCl ₂ Sn _{0.5}	C ₁₈ H ₁₅ AsBr ₂ Sn _{0.5}
Formula weight	872.94	1050.77
Wavelength/Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.6020(6)	13.0280(5)
<i>b</i> /Å	9.6230(5)	13.2010(4)
<i>c</i> /Å	10.6270(7)	13.4930(6)
<i>a</i> /°	111.806(3)	63.853(1)
<i>β</i> /°	107.329(3)	63.562(2)
<i>γ</i> /°	94.693(5)	64.848(2)
<i>V</i> /Å ³	849.53(9)	1788.1(1)
<i>Z</i>	1	2
<i>μ</i> (Mo-K α)/mm ⁻¹	3.025	7.045
θ range/°	3.60–27.55	3.53–27.62
Reflections collected	9775	37057
Independent reflections	3877 [<i>R</i> (int) = 0.0401]	8103 [<i>R</i> (int) = 0.1366]
Reflections observed (>2 σ)	3217	4483
Goodness-of-fit on <i>F</i> ²	1.058	0.994
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0331, 0.0753	0.0845, 0.2163
Final <i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0443, 0.0807	0.1604, 0.2527

[i.e. exhibited signs of twinning]. High residual peaks in the difference electron density map [4.074 e Å⁻³ at 1.04 Å from Sn(1) and 1.617 Å from Br(3), -1.915 e Å⁻³ at 0.927 Å from Sn(1)] along with higher than average e.s.d.s on atomic positions have been manifested as a result of these shortcomings. Nonetheless, the refinement affords unambiguous assignment of the solid state structure for this compound.

CCDC reference numbers 245840 (for compound **1**) and 245841 (for compound **2**).

See <http://www.rsc.org/suppdata/dt/b4/b411342j/> for crystallographic data in CIF or other electronic format.

Aerosol-assisted CVD

Films were grown using aerosol-assisted chemical vapour deposition (AACVD) on glass microscope slides under a N₂ atmosphere at 1 bar pressure, using a horizontal cold wall reactor; details of the reactor assembly have been given elsewhere.¹⁵ In a typical experiment, 0.2 g of **1** dissolved in THF (15 ml) was used as precursor, and delivered to a pyrex glass slide substrate, held at 430 °C, by an N₂ carrier gas (0.8 L min⁻¹) over a 20 min period.

Results and discussion

Structural chemistry

SnX₄·2AsPh₃ [X = Cl (**1**), Br (**2**)] have been prepared by literature routes. While data for (**1**) are consistent with earlier reports, the mp of (**2**) (82–84 °C) differs from that quoted by others (104 °C).^{12,14} Both compounds have some solubility in organic solvents and reasonably low melting points; TGA of (**1**) (Fig. 1) indicates that complete weight loss takes place by 330 °C, starting at around the melting point (160 °C). These characteristics indicate the viability of (**1**) as a CVD precursor, in either conventional or aerosol-assisted modes.

The structures of both (**1**) and (**2**) have been determined. Compound (**1**) adopts a centrosymmetric, octahedral *trans*-(Ph₃As)₂SnCl₄ geometry (Fig. 2), as is found in GeCl₄(AsMe₂)₂,⁴ the only other Group 14 adduct for which direct comparison can be made. The Sn–As bond [2.7623(3) Å] compares with those of 2.716(2), 2.752(2) in SnI₄[o-C₆H₄(AsMe₂)₂],¹⁰ the only other reported tin–tertiary arsine adduct.†

† The structure of Ph₃SnNO₃(AsPh₃) has been reported¹¹ but reliable bond length data were precluded by disorder.

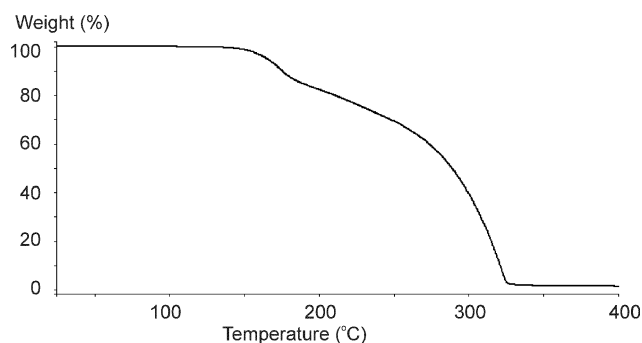


Fig. 1 TGA of (**1**).

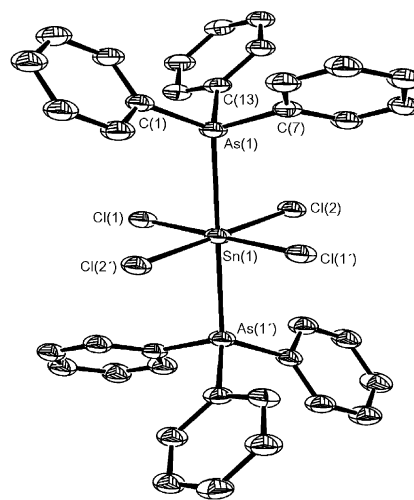


Fig. 2 The structure of (**1**) showing the labelling scheme; thermal ellipsoids are at the 30% probability level. Selected geometric data: Sn(1)–Cl(2) 2.4153(8), Sn(1)–Cl(1) 2.4239(7), Sn(1)–P(1) 2.7623(3) Å; Cl(1)–Sn(1)–Cl(1') 180, Cl(1)–Sn(1)–Cl(2) 90.09(3), Cl(1)–Sn(1)–Cl(2') 89.91(3), Cl(1)–Sn(1)–P(1) 90.46(2), Cl(1)–Sn(1)–P(1') 89.54(2), Cl(2)–Sn(1)–Cl(2') 180, Cl(2)–Sn(1)–P(1) 93.75(2), Cl(2)–Sn(1)–P(1') 86.25(2), P(1)–Sn(1)–P(1') 180°. Atoms with primed labels are related to those in the asymmetric unit by an inversion centre at tin.

Compound (**2**), despite an analogous empirical formula, adopts an entirely different structure. Although crystal quality in this case was low and the final Fourier map contained significant areas of residual density, the spatial arrangement of SnBr₄ with respect to the two Lewis bases is clear: the formulation is a

1 : 1 adduct $\text{SnBr}_4(\text{AsPh}_3)$ with a second AsPh_3 separated from the tin (Fig. 3). The 1 : 1 adduct component adopts a trigonal bipyramidal geometry with bromine and arsenic in axial positions. The Sn–Br(eq) [av. 2.485(1) Å] are notably shorter than the analogous bond to the axial bromine [Sn(1)–Br(4) 2.522(2) Å] while the Sn–As bond in (2) [2.780(1) Å] is longer than in (1) [2.7623(3) Å], which would be expected considering the differing Lewis acidity of the two tin(IV) halides. It is the longest such interaction reported to date, even in comparison with bonds to weaker acceptors such as SnI_4 or instances where tin adopts a higher coordination number,¹⁰ both factors which should lead to a weakening of the interaction. However, the most significant feature in the solid-state structure of (2) is the close approach of a second Lewis base to the axially-disposed bromine of the 1 : 1 adduct [Br(4)⋯As(2) 3.567(3) Å; Sn(1)–Br(4)⋯As(2) 172.1(1)°].

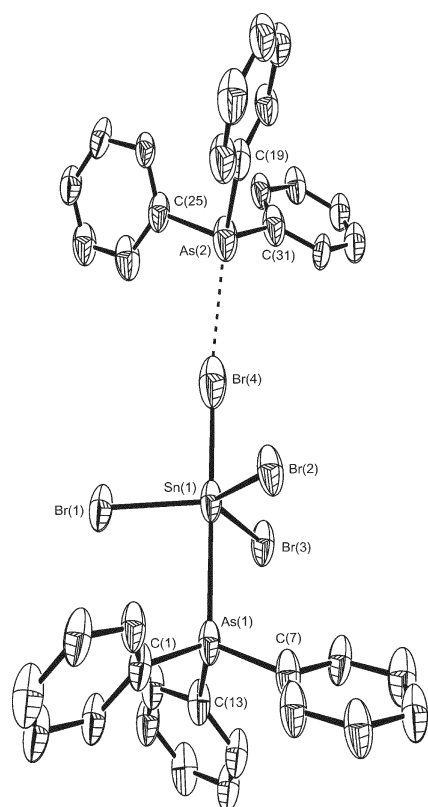


Fig. 3 The structure of (2) showing the labelling scheme; thermal ellipsoids are at the 30% probability level. Selected geometric data: Sn(1)–Br(1) 2.484(1), Sn(1)–Br(2) 2.486(2), Sn(1)–Br(3) 2.484(2), Sn(1)–Br(4) 2.522(2), Sn(1)–P(1) 2.780(1) Å; Br(1)–Sn(1)–Br(2) 120.02(6), Br(1)–Sn(1)–Br(3) 119.35(6), Br(1)–Sn(1)–Br(4) 93.75(5), Br(1)–Sn(1)–P(1) 86.35(4), Br(2)–Sn(1)–Br(3) 119.50(5), Br(2)–Sn(1)–Br(4) 93.66(5), Br(2)–Sn(1)–P(1) 86.11(5), Br(3)–Sn(1)–Br(4) 93.16(6), Br(3)–Sn(1)–P(1) 86.96(5), Br(4)–Sn(1)–P(1) 179.78(6)°.

We have attempted to rationalise the interplay of “2 : 1” and “1 : 1 + 1” adduct formation through DFT calculations performed at the B3LYP level¹⁶ as implemented in Gaussian 98¹⁷ on both (1) and (2) and their AsH_3 analogues. The standard Lanl2dz basis set has been extended with the polarization functions (p, d) recently optimised for the main group elements.¹⁸ Table 2 includes the total and relative energies of (1) and (2), as well as of the models derived from these systems by replacing the Ph_3As ligands with AsH_3 (1a, 2a), obtained after full geometry optimisation.

These data show that the planar arrangement of four halogens is less favourable when AsH_3 coordinates to either SnBr_4 or to SnCl_4 , though the relative instability of *trans*- $\text{SnBr}_4(\text{AsH}_3)_2$ (1a-Br) is greater (53.92 kJ mol^{−1}) than for *trans*- $\text{SnCl}_4(\text{AsH}_3)_2$ (2a: 27.07 kJ mol^{−1}). This could be related to the barrier for the deformation of a trigonal pyramid to square planar geometry, which, presumably, like the better-known tetrahedral to square planar rearrangement,¹⁹ increases in EX_4 systems when the electronegativity of X decreases. Calculations based on Ph_3As “adducts” also show that *trans*- $\text{SnBr}_4(\text{AsPh}_3)_2$ (2) is more stable than *trans*- $\text{SnBr}_4(\text{AsPh}_3)_2$ (1-Br) by 9.91 kJ mol^{−1} while *trans*- $\text{SnCl}_4(\text{AsPh}_3)_2$ (1) is favoured by almost the same amount (9.00 kJ mol^{−1}) over *trans*- $\text{SnBr}_4(\text{AsPh}_3)_2$ (1-Br), both in accord with the crystallography presented in this paper. The latter calculations reinforce the suggestion that metal bromides are more likely to favour the 1 : 1 + 1 arrangement over 1 : 2 adducts, but that the nature of the donor substituents in ER_3 must also exert an influence. We note that the optimised structures of (1) and (2) incorporate relatively short intramolecular (Ph)H⋯X separations (H⋯Cl: 2.85 Å; H⋯Br: 3.01 Å) which are at the lower limit of the sum of the van der Waals radii (2.95, 3.05 Å for Cl and Br, respectively).²⁰ These types of contacts are apparent in the X-ray diffraction data [1: Cl(1)⋯HC(18) 2.74, Cl(2)⋯HC(6) 2.86, Cl(2)⋯HC(12) 2.94 Å; 2: Br(1)⋯HC(18) 3.16, Br(3)⋯HC(12) 3.20; Br(2)⋯HC(2) 3.23 Å] and it is possible that these hydrogen-bonding interactions play a part in stabilising each of the two structures. Moreover, their cooperative effect in the case of (1) might be responsible for the square planar geometry of halogens around the tin atom but that this is insufficient to alter the thermodynamically-favoured trigonal pyramidal arrangement of bromines in (2).

Table 3 shows further calculations on the two structural types for GeX_4 adducts of ER_3 . The calculations again show that bromine destabilises the 2 : 1 adduct relative to the 1 : 1 + 1 structure, but in addition that both E and R must also have a structural influence. Thus, the calculations predict that 1 : 1 + 1 is favoured for Ph_3As while the reverse is true for Me_3As , irrespective of the nature of the halogen. The results are consistent with the fact that $\text{GeCl}_4/\text{Me}_3\text{As}$ generate a crystallographically proven 2 : 1 adduct, with modest correlation between observed and calculated metrical data [Ge–X obs(calc): X = Cl 2.307, 2.341 (2.339); X = As 2.472 (2.563) Å]. No reaction was observed experimentally, however, between GeCl_4 and Ph_3As .⁴

Table 2 B3LYP/Lanl2dz(dp) calculated energies for 1, 2 and related systems

System	Total energy/a.u.	Relative energy/kJ mol ^{−1}
$\text{AsH}_3 \cdots \text{SnCl}_3\text{--Cl} \cdots \text{AsH}_3$ (2a-Cl) ^a	−79.2319647	0.0
$\text{AsH}_3 \cdots \text{SnCl}_4 \cdots \text{AsH}_3$ (1a) ^a	−79.2216908	27.07
$\text{AsH}_3 \cdots \text{SnBr}_3\text{--Br} \cdots \text{AsH}_3$ (2a) ^a	−72.0913296	0.0
$\text{AsH}_3 \cdots \text{SnBr}_4 \cdots \text{AsH}_3$ (1a-Br) ^a	−72.0707733	53.92
$\text{AsPh}_3 \cdots \text{SnCl}_3\text{--Cl} \cdots \text{AsPh}_3$ (2-Cl) ^b	−1465.3449938	9.00
$\text{AsPh}_3 \cdots \text{SnCl}_4 \cdots \text{AsPh}_3$ (1)	−1465.3484264	0.0
$\text{AsPh}_3 \cdots \text{SnBr}_3\text{--Br} \cdots \text{AsPh}_3$ (2)	−1458.1965223	0.0
$\text{AsPh}_3 \cdots \text{SnBr}_4 \cdots \text{AsPh}_3$ (1-Br) ^c	−1458.1927430	9.91

^a 1a, 2a etc. relate to the AsH_3 analogues of analogous structures labelled 1, 2 etc. ^b Structure 2 but with chlorine in place of bromine. ^c Structure 1 but with bromine in place of chlorine.

Table 3 B3LYP/Lan12dz(dp) calculated energies for GeX₄/ER₃ systems

System	Total energy/a.u.	Relative energy/kJ mol ⁻¹
AsMe ₃ ...GeCl ₃ -Cl...AsMe ₃ ^a	-315.5138506	42.85
AsMe ₃ ...GeCl ₄ ...AsMe ₃	-315.5301853	0.00
AsMe ₃ ...GeBr ₃ -Br...AsMe ₃ ^a	-308.3604367	29.66
AsMe ₃ ...GeBr ₄ ...AsMe ₃	-308.3717457	0.00
AsPh ₃ ...GeCl ₃ -Cl...AsPh ₃	-1465.7234433	0.00
AsPh ₃ ...GeCl ₄ ...AsPh ₃ ^b	-1465.7047335	49.07
AsPh ₃ ...GeBr ₃ -Br...AsPh ₃	-1458.5739458	0.00
AsPh ₃ ...GeBr ₄ ...AsPh ₃ ^b	-1458.5426998	81.97
PMe ₃ ...GeCl ₃ -Cl...PMe ₃ ^a	-316.2312721	48.00
PMe ₃ ...GeCl ₄ ...PMe ₃	-316.2495714	0.00
PMe ₃ ...GeBr ₃ -Br...PMe ₃ ^a	-309.0770607	32.21
PMe ₃ ...GeBr ₄ ...PMe ₃	-309.0893392	0.00

^a Structure analogous to **2**. ^b Structure analogous to **1**.

For phosphorus the correlation between theory and experiment is less consistent. Calculations for GeX₄/Me₃P always predict a preference for the 2 : 1 adduct even though no such structures, irrespective of the nature of R, have been crystallographically authenticated.⁴ The inclusion of solvent effects does not affect the relative energies of the two structural types, so clearly some further refinement of the model is required.

Despite the latter GeX₄/Me₃P calculations discussed above, it appears likely that (**2**) represents an intermediate in the halogen transfer from tin to arsenic and the formation of species such as [Ph₃AsBr]⁺[SnBr₃]⁻. Moreover, (**2**) also suggests that a 1 : 1 adduct is also an intermediate in this transfer reaction, despite the fact that the final reaction product fails to retain the donor→metal linkage. Thus, we suggest that a 1 : 1 adduct is formed initially, and, on approach of a second equivalent of base, the MX₄ component undergoes a trigonal pyramid to square planar rearrangement (2 : 1 adduct formation) or, if this is energetically disfavoured, halogen transfer ensues followed by loss of R₃E from the [(R₃E)MX₃]⁻ anion to leave [R₃EX]⁺[MX₃]⁻ as the product isolated.

In summary, halogen-transfer/redox reactions appear to be common in Group 14/15 “adduct” chemistry, and salts are more frequently encountered than true adducts. It is noteworthy that the only crystallographically authenticated 2 : 1 adducts of general formula MX₄(ER₃)₂ prepared by adding the Group 15 donor to MX₄ occur when X = Cl [GeCl₄(AsMe₃)₂,⁴ SnCl₄(PEt₃)₂],⁸ strongly implicating the halogen in determining the course of reaction. No MBr₄ or MI₄ adducts have been prepared by this route, seemingly because structure (**2**) is favoured and leads to halogen transfer. In contrast, SnI₄(PPrⁿ)₂⁷ was synthesised from tin powder and ⁿPr₃PI₂, which offers a different mechanistic route and bypasses the intermediate SnI₄(PPrⁿ) which would promote halogen transfer; the authors of this latter work note in their paper the difficulty encountered in preparing SnI₄(ER₃)₂ by conventional routes.⁷ However, the halogen alone is not solely responsible for the reaction pathway as all of the species GeCl₄(PR₃) are of structure [R₃PX]⁺[GeCl₃]⁻.

To our knowledge, triorgano(halo)arsonium cations have not previously been reported with halo-tin or -germanium anions, though reaction of Ph₃As with GaI₃ is known to generate both an adduct, (Ph₃As)GaI₃ and a salt, [Ph₃AsI]⁺[GaI₄]⁻,²¹ again suggesting that the former is a precursor to the latter.

Materials chemistry

Phosphine adducts of metal halides have been extensively used for the CVD of metal phosphides *e.g.* TiCl₄(PR₃)₂ for the deposition of TiP,^{2,22} though analogous arsenic adducts have been less well studied.^{23,24} Indeed, the deposition of metal arsenide films, with the exception of MAs (M = Al, Ga, In),^{25,26} appears to be an almost barren area of study. Single-source

precursors [Co(CO)₂(AsHBU₂)(NO)]²⁷ and [Co(CO)₃(AsEt₃)₂]²⁸ have been used to generate CoAs.

AACVD, using (**1**) (0.2 g) in THF (15 ml) as precursor and a glass slide heated to 430 °C as substrate, has been carried out. The resulting film exhibited a coloured refringence pattern and was strongly adhered to the substrate. The film is composed of a discontinuous layer upon which larger crystallites are seen (Fig. 4). The underlay is composed of spherical particles of approximate 0.2 μm with an overall film thickness of *ca.* 0.35–0.40 μm (ESI†). EDXS indicated that these particles contain tin but not arsenic; small amounts of chlorine are also visible, though this may originate from the underlying glass as a large signal due to silicon is also apparent. The larger particles (up to 6 μm in length) show well-defined faces (ESI†) and contain tin and large amounts of chlorine, but again no arsenic. The X-ray diffraction pattern of the composite film (Fig. 5) contains one sharp diffraction peak and a series of minor ones. The major peak corresponds to the most intense line in the literature pattern for SnCl₂ (*d*_{obs}: 2.778, *d*_{lit}: 2.775 Å, PDF 181265, no indexing given) while the minor pattern can be indexed to SnO₂ (PDF 770449). The sharp intense diffraction peak is consistent with a sizable and highly-oriented crystallite and the match with SnCl₂ is also consistent with the high chlorine content noted in the EDXS of a single crystallite. We have noted that these large crystallites also appear to melt below the substrate temperature (430 °C), where we have observed, on occasion,

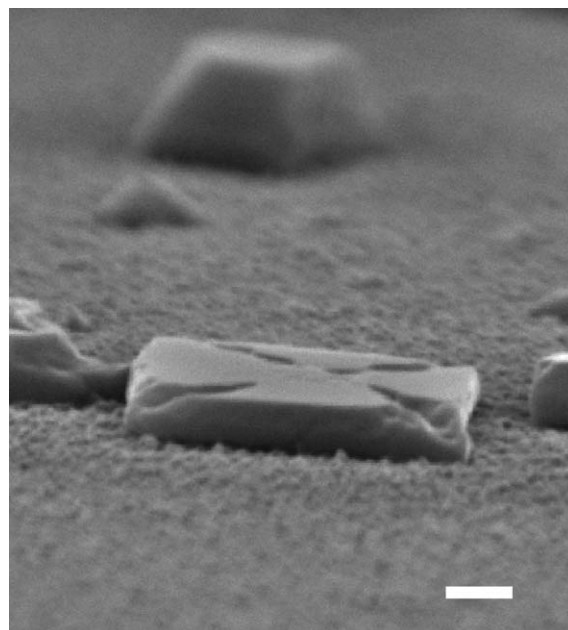


Fig. 4 SEM showing the large crystallites deposited on the surface of the layer of SnO₂; bar = 1 μm.

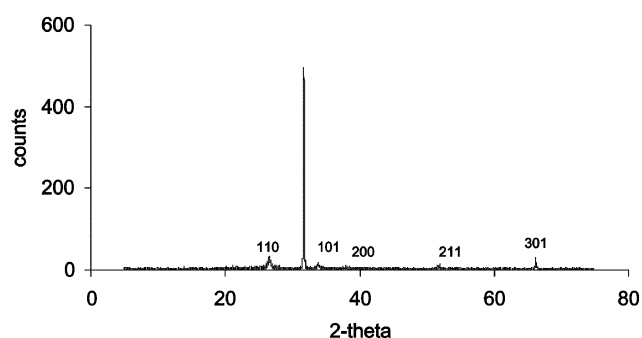


Fig. 5 XRD of the film deposited by AACVD using (1) as precursor; indexed lines refer to SnO_2 (PDF 770449) while the major diffraction line is consistent with SnCl_2 (PDF 181265).

that cooling of the film post-deposition has lead to ill-defined agglomerates superimposed on the SnO_2 layer (ESI^\dagger); SnCl_2 melts at 246°C . The only other match with a plausible chlorine-containing species with d_{obs} of 2.778 \AA is NaSn_2Cl_5 ($d_{\text{obs}} = 2.776\text{ \AA}$; PDF 830318). In contrast to the intense sharp reflection at d_{obs} of 2.778 \AA , the broader, weaker signals due to SnO_2 suggest a smaller particle size, consistent with the SEM.

These results imply that decomposition of (1) does not involve loss of PhCl (leaving the Sn-As bond intact), but by sequential loss of Ph_3AsCl_2 and/or Ph_3As . Both SnCl_2 and Sn^0 will be generated by these processes and give rise to the formation of a film containing SnCl_2 and SnO_2 , the latter by oxidation of Sn^0 . Furthermore, the simultaneous reduction at tin and oxidation at arsenic which accompanies halogen transfer is reflected in the structural chemistry of this family of compounds, where both this report and related studies^{4–6} reveal that adduct formation and halogen transfer seem to occur with similar likelihood. We have previously noted other instances where precursors with pre-defined Sn-E bonds have failed to generate SnE films *e.g.* $\text{Sn}(\text{SPh})_4$ generates Sn_3O_4 , again *via* Sn^0 , after the elimination of two equivalents of RSSR and reduction at tin.²⁹

Conclusions

While triphenylarsine forms a 2 : 1 adduct with SnCl_4 which adopts a centrosymmetric, octahedral *trans*-(Ph_3As)₂ SnCl_4 structure, the analogous “2 : 1 adduct” involving SnBr_4 involves a 1 : 1 trigonal bipyramidal (Ph_3As) SnBr_4 moiety associated with a second Ph_3As moiety through a long $\text{Br} \cdots \text{As}$ interaction. As other “adducts” of MX_4 ($\text{M} = \text{Ge}, \text{Sn}$; $\text{X} = \text{halogen}$) have previously been shown to be, in fact, salts *e.g.* $[\text{R}_3\text{PX}]^+[\text{MX}_3]^-$, this latter structure offers a unique insight into the mechanism of redox halogen transfer in these Group 14–15 compounds.

AACVD using *trans*-(Ph_3As)₂ SnCl_4 yields a film comprising of SnO_2 along with large crystallites which are probably SnCl_2 , by a decomposition mechanism which seems to involve loss of Ph_3AsCl_2 and Ph_3As from the tin.

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