Syntheses, X-ray structures and CVD of titanium(IV) arsine complexes†‡

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Five titanium arsine compounds have been synthesised *via* the reaction of $TiCl_4$ with $AsPh_3$ (1 : 1 and 1 : 2 equivalents), or one equivalent of $Ph_2AsCH_2AsPh_2$, $^tBuAsH_2$ and $As(NMe_2)_3$. In general, 1 : 1 and 1 : 2 adducts of the type $[TiCl_4(L)_n]$ ($n = 1$, L = $AsPh_3$, $Ph_2AsCH_2AsPh_2$, and $^tBuAsH_2$; $n = 2$, L = $AsPh_3$), were isolated and characterised. However, the reaction of $TiCl_4$ with $As(NMe_2)_3$ resulted in a novel exchange between a Cl and an NMe_2 group, yielding the product $[TiCl_3(NMe_2)(\mu\text{-}NMe_2)_2AsCl]$. The crystal structure of $[TiCl_3(NMe_2)(\mu\text{-}NMe_2)_2AsCl]$ has been determined and showed that the titanium and arsenic atoms are linked *via* two bridging NMe_2 groups. Additionally, crystal structures for the 1 : 1 and 1 : 2 adducts, $[TiCl_4(AsPh_3)]$ and $[TiCl_4(AsPh_3)_2]$ have been obtained, with Ti–As bond lengths of 2.7465(13) and 2.7238(7) Å observed respectively. The decomposition of the compounds has been investigated using thermogravimetric analysis, aerosol-assisted and low pressure chemical vapour deposition.

Introduction

Metal arsenides are known to exhibit a wide range of functional properties, and display band gap characteristics which are currently exploited within a range of photonic devices including lasers and light emitting diodes (LEDs). Apart from key III/V materials (*e.g.* GaAs, InAs), CoAs,[1] and MnAs,[2,3] knowledge surrounding metal arsenide thin films, particularly *via* chemical vapour deposition (CVD), remains limited; typically with only bulk material formation known. It is well understood that arsenide compounds are considerably less stable and volatile than their phosphorus counterparts,[4] which has until recently limited research into arsenic containing thin films. However, recent advances within CVD technology and the development of single-source precursors, has now facilitated research into this area.

Single-source precursors circumvent problems associated with precursor volatility when used with aerosol assisted (AA)CVD, and additionally enable high levels of stoichiometric control due to the existence of pre-formed bonds.[5] Single-source precursors have already proven successful in the deposition of III/V materials,[6] along with transition metal phosphide thin films. CrP films have been deposited *via* single-source pyrolysis routes (for instance that of $[Cr(CO)_5(PH_3)]$ to produce CrP films),[7] and additionally within CVD where examples include the low pressure (LP)CVD of $[Co(CO)_2\{P(^tBu)_2H\}(NO)]$[1] and $[TiCl_4(L)_n]$ ($n = 2$, L = $Cy^{hex}PH_2$; $n = 1$, L = dppm)[8,9] to yield CoP and TiP films respectively.

Single-source precursors available for the deposition of transition metal arsenide thin films are limited, with CoAs successfully being deposited *via* (MO)CVD of $[Co_2(CO)_6(\mu\text{-}As_2)]$,[1] and $[Co(CO)_4\{AsN(^tBu)CH_2CH_2N(^tBu)\}]$.[10] Therefore, we were interested in developing simple arsine adducts of titanium(IV) for potential application as single-source precursors to titanium arsenide films. Surprisingly, little structural data are available for complexes of this type. We have been studying a range of group 15 containing metal complexes and assessing their ability to form metal pnictide thin films *via* CVD including TaN and NbN,[11,12] TiN and TiNxCy,[13–15] and TiP.[8,9] Here we report the synthesis and characterisation of five titanium arsine adducts synthesised from the reaction of $TiCl_4$ with n$AsPh_3$ (n = 1, 2), $Ph_2AsCH_2AsPh_2$, $^tBuAsH_2$ and $As(NMe_2)_3$. Additionally, the use of some of the complexes in CVD experiments has been explored.

Experimental

General procedures and instrumentation

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an Mbraun Unilab glovebox. All solvents used were stored in alumina columns and dried such that the water concentration was 5–10 ppm. Elemental analysis was conducted using an EA-440 horizontal load analyser supplied by Exeter analytical. ^1H NMR was recorded using a Brüker AMX400 spectrometer. All spectra were recorded using C_6D_6, which was dried and degassed over molecular sieves prior to use; ^1H chemical shifts are reported relative to $SiMe_4$ (δ 0.00). Mass spectra were recorded using a Micromass ZABSE instrument. Thermogravimetric analysis (TGA) was conducted using a Netzsch STA 449C instrument, with samples sealed using aluminium sample pans. Due to the air sensitive nature of the samples, TGA was conducted under a flow of helium gas; heating rates of 10 °C min^{-1} were used in all instances. The reagents $AsPh_3$ and $Ph_2AsCH_2AsPh_2$ were supplied by Sigma Aldrich, and $As(NMe_2)_3$ and $^tBuAsH_2$ by SAFC Hitech Ltd.; with all reagents being used without further purification.

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Synthesis of [$TiCl_4(AsPh_3)$] (1)

A clear colourless solution of $AsPh_3$ (0.83 g, 2.7 mmol) in toluene (20 cm^3) was added with stirring to a 1 M orange-red solution of $TiCl_4$ in toluene (2.7 cm^3, 2.7 mmol). The solution turned dark red immediately on the addition of the $AsPh_3$ solution. The reaction mixture was allowed to stir for approximately 30 min, prior to solvent removal under vacuum to yield a purple-pink solid (**1**) (yield 85%, mpt 126 °C). Analysis found (calc. for $C_{18}H_{15}AsCl_4Ti$): C 41.78% (43.60); H 3.24% (3.05). ^{1}H NMR δ (ppm) (C_6D_6) 7.58 (m, 6H, *m*-C_6H_5), 7.13 (m, 9H, *o*-C_6H_5 and *p*-C_6H_5). Mass Spec. *m/z* (Cl+, methane): 152 [AsPh]H^+, 229 [$AsPh_2$]H^+, 306 [$AsPh_3$]H^+, 330, 353 [$TiAsPh_3$]H^+, 360, 424 [$TiCl_2AsPh_3$]H^+, 430, 458 [$AsPh_2$][$AsPh_2$]H^+, 493 [$TiCl_4AsPh_3$]H^+, 535 [$AsPh_2$][$AsPh_3$]H^+, 612 [$AsPh_3$][$AsPh_3$]H^+, 687. Mp 126 °C. Crystals of **1** were isolated *via* dichloromethane–hexane layering recrystallisation and characterised by X-ray crystallography.

Synthesis of [$TiCl_4(AsPh_3)_2$] (2)

A 1M orange-red solution of $TiCl_4$ in toluene (1.3 cm^3, 1.3 mmol) was added to a colourless solution of $AsPh_3$ (0.8 g, 2.61 mmol) in toluene (20 cm^3) with stirring. The solution turned dark red immediately on addition of the $TiCl_4$ solution. The reaction mixture was allowed to stir for approximately 30 min, prior to refluxing under nitrogen for 24 h. After cooling to room temperature, the solvent was removed under vacuum to yield a purple-pink solid (**2**) (yield 85%, mpt 88–90 °C). Analysis found (calc. for $C_{36}H_{30}As_2Cl_4Ti$): C 50.60% (53.90); H 3.78% (3.77). ^{1}H NMR δ (ppm) (C_6D_6) 7.43 (m, 12H, *m*-C_6H_5), 7.02 (m, 18H, *o*-C_6H_5 and *p*-C_6H_5). Mass Spec *m/z* (Cl+, methane): 152 [AsPh]H^+, 229 [$AsPh_2$]H^+, 306 [$AsPh_3$]H^+, 335, 458, 535. Crystals of **2** were isolated *via* dichloromethane–hexane layering recrystallisation and characterised by X-ray crystallography.

Reaction of $TiCl_4$ and $Ph_2AsCH_2AsPh_2$ (3)

A pale-yellow solution of $Ph_2AsCH_2AsPh_2$ (1.28 g, 2.7 mmol) in toluene (20 cm^3) was added with stirring to a red-orange 1M solution of $TiCl_4$ in toluene (2.7 cm^3, 2.7 mmol). A dark red-orange suspension formed immediately on addition of the $Ph_2AsCH_2AsPh_2$ solution. The reaction mixture was allowed to stir for approximately 30 min, prior to the removal of solvent under vacuum to yield a bright orange solid (**3**) (yield 86.2%, mpt 116–118 °C). Analysis found (calc. for $C_{25}H_{22}As_2Cl_4Ti$): C 45.08% (45.36); H 3.30% (3.35). Mass Spec. *m/z*/(Cl+, methane): 105, 155, 167 [$AsPhCH_2$]H^+, 191 [$TiCl_4$]H^+, 229 [$AsPh_2$]H^+, 245, 260, 306 [$AsPh_3$]H^+, 313 [$TiClAsPh_2$]H^+, 330, 395 [Ph_2AsCH_2AsPh]H^+, 472 [$Ph_2AsCH_2AsPh_2$]H^+, 501 [$TiCl_2As_2Ph_3$]H^+, 563, 639, 701, 869. Compound **3** was found to be insoluble in a variety of solvents (*e.g.* dichloromethane, hexane, and toluene) and no satisfactory ^{1}H NMR could be obtained.

Reaction of $TiCl_4$ and ^{t}BuAsH_2 (4)

^{t}BuAsH_2 (0.36 cm^3, 0.36 g, 2.69 mmol) was added to an orange-red 1M solution of $TiCl_4$ in toluene (2.7 cm^3, 2.7 mmol) which was cooled to −78 °C. The solution turned bright red immediately on addition of the ^{t}BuAsH_2 solution. The reaction mixture was allowed to stir while warming to room temperature, during which the deep red colour intensified. Once the reaction mixture had reached room temperature, it was cooled to −70 °C for approximately four weeks, after which a dark brown solid was observed. Excess reagents and solvents were carefully removed under vacuum, ensuring maximum product extraction was obtained; a small quantity of brown solid remained (**4**) (yield 16%). ^{1}H NMR δ (ppm) (C_6D_6) 3.0 (broad s, 2H, AsH_2), 1.3 (s, 9H, ^{t}BuAs).

Synthesis of [$TiCl_3(NMe_2)(\mu\text{-}NMe_2)_2AsCl$] (5)

A clear colourless solution of $As(NMe_2)_3$ (0.5 cm^3, 0.62 g, 3 mmol) in toluene (10 cm^3) was added *via* cannula to a red-orange 1M solution of $TiCl_4$ in toluene (2.7 cm^3, 2.7 mmol). The solution turned dark green immediately on addition of the $As(NMe_2)_3$ solution. After the addition, the reaction mixture was allowed to stir for approximately 30 min prior to the removal of solvent under vacuum to yield a dark-green solid (**5**) (yield 98%, mpt 95–97 °C). Analysis found (calc. for $C_6H_{18}AsCl_4N_3Ti$): C 18.50% (18.16); H 4.81% (4.57); N 10.70% (10.59). ^{1}H NMR δ (ppm) (C_6D_6) 3.7 (s, 6H, terminal NMe_2), 2.7 (s, 12H, μ-NMe_2). Mass Spec. *m/z* (Cl+, methane): 84 [TiCl]H^+, 105 [AsN_2]H^+, 110 [TiClNC]H^+, 120 [$AsNMe_2$]H^+, 136 [$AsNNMe_2$]H^+, 145 [$TiCl_2NC$]H^+, 154 [$TiCl_3$]H^+, 163 [$TiCl_2NMe_2$]H^+, 170, 190 [$TiCl_4$]H^+, 199 [$TiCl_3NMe_2$]H^+, 208 [$As(NMe_2)_3$]H^+, 216, 227, 254, 264, 300, 352, 365, 371, 406. Mp 95 °C. Crystals of **5** were isolated *via* dichloromethane–hexane layering recrystallisation and characterised by X-ray crystallography.

Crystallography

In all instances, single crystals were obtained *via* dichloromethane–hexane layering recrystallisation. A summary of the crystal data, data collection and refinement for compounds **1**, **2** and **5** is given in Table 2. Crystals were mounted on a glass fibre with silicon grease from Fomblin® vacuum oil. Datasets were collected on a Brüker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda 1 = 0.71073$ Å) at 150(2) K. Data reduction and integration was carried out with SAINT+,[16] and absorption corrections applied using SADABS.[17] All solutions and refinements were performed using PLATON,[18] the WinGX package and all software packages within.[19] All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogens were added using a riding model. The $AsPh_3$ group in **2** was disordered over two positions but the occupancy factors were not fixed during refinement cycles. CCDC reference numbers 762189 (compound **1**), 762190 (compound **2**) and 762191 (compound **5**).

Aerosol-assisted (AA)CVD

All AACVD depositions were conducted on 90 mm × 45 mm × 4 mm float-glass coated with a 50 nm thick SiCO barrier layer to stop diffusion of ions from the glass, as supplied by Pilkington. All substrate was cleaned using petroleum ether (60–80 °C) and 2-propanol and allowed to air dry prior to use. All depositions were conducted using a horizontal cold wall reactor, with substrates mounted onto a graphite heating block containing a Whatman cartridge heater, with temperature control achieved using a Pt–Rh thermocouple. A Vicks VE5520E Humidifier was used to produce the aerosol mist. Prior to the conduction of AACVD, equipment

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**, **2** and **5**; where $^{i} = -x + 1, -y + 2, -z + 2$

Compound	Selected Bond lengths (Å)		Selected Angles (°)	
(**1**)	Ti(1)–As(1) 2.7465(13) Ti(1)–Cl(1) 2.244(2) Ti(1)–Cl(2) 2.185(2)	Ti(1)–Cl(3) 2.220(2) Ti(1)–Cl(4) 2.193(2)	Cl(1)–Ti(1)–As(1) 175.41(8) Cl(2)–Ti(1)–As(1) 83.95(6)	Cl(3)–Ti(1)–As(1) 81.02(6) Cl(4)–Ti(1)–As(1) 82.86(6)
(**2**)	Ti(1)–As(1) 2.7238(7) Ti(1)–Cl(2) 2.2719(11)	Ti(1)–Cl(1) 2.2713(11)	Cl(1)–Ti(1)–As(1) 86.68(4) Cl(1)–Ti(1)–As(1^{i}) 93.32(4) As(1)–Ti(1)–As(1^{i}) 180.0	Cl(2)–Ti(1)–As(1) 90.36(4) Cl(2)–Ti(1)–As(1^{i}) 89.64(4)
(**5**)	N(1)–Ti(1) 2.323(2) N(2)–Ti(1) 2.417(2) N(3)–Ti(1) 1.864(2) Cl(1)–Ti(1) 2.3110(8)	Cl(2)–Ti(1) 2.3814(8) Cl(3)–Ti(1) 2.3004(8) Cl(4)–As(1) 2.2075(7)	As(1)–N(1)–Ti(1) 93.89(8) N(1)–Ti(1)–N(2) 69.62(7) N(2)–As(1)–N(1) 89.60(9)	As(1)–N(2)–Ti(1) 91.90(8) N(3)–Ti(1)–N(2) 165.86(9) N(2)–As(1)–Cl(4) 99.97(7)

Table 2 Crystallographic data for compounds **1**, **2** and **5**

Compound	(**1**)	(**2**)	(**5**)
Chemical formula	$C_{18}H_{15}AsCl_4Ti$	$C_{36}H_{30}As_2Cl_4Ti$	$C_6H_{18}AsCl_4N_3Ti$
Formula weight	495.92	802.14	396.85
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	9.5026(19)	9.686(3)	9.5866(16)
b/Å	11.324(2)	9.789(3)	15.623(3)
c/Å	18.683(4)	10.237(3)	9.8386(16)
α (°)	90	108.824(5)	90
β (°)	92.501(4)	111.489(5)	92.562(3)
γ (°)	90	92.081(5)	90
V/Å^3	2008.5(7)	841.7(5)	1472.1(4)
Z	4	1	4
D_c/Mg m^{-3}	1.640	1.582	1.791
T/K	150(2)	150(2)	150(2)
μ/mm^{-1}	2.591	2.548	3.514
λ/Å	0.71073	0.71073	0.71073
No. of data collected	16527	6969	12201
No. of unique data	4787	3757	3496
Goodness of fit on F^2	1.182	1.053	1.126
R_{int}	0.0609	0.028	0.0258
Final $R(\lvert F \rvert)$ for $F_0 2\sigma(F_0)$	0.0809	0.0461	0.0322
Final $R(F^2)$ for all data	0.1496	0.1188	0.0672

and substrate were allowed to heat to the required temperature under a flow of nitrogen. The compounds were either used as synthesised or created *in situ*, with delivery to substrate *via* N_2 carrier gas (1 L min^{-1}). After conduction of the AACVD, the substrates were allowed to cool under a flow of nitrogen, prior to their removal and subsequent storage in air.

Low pressure (LP)CVD

All LPCVD depositions were conducted on vertically halved glass microscope slides with approximate dimensions 1.2 cm × 7 cm, which were cleaned using petroleum ether (60–80 °C) and 2-propanol and allowed to air dry prior to use. LPCVD was conducted within a tube furnace, with approximately 0.5 g of compound used in all instances. The substrates were placed horizontally up the length of the tube furnace, with LPCVD conducted at 600 °C under vacuum.

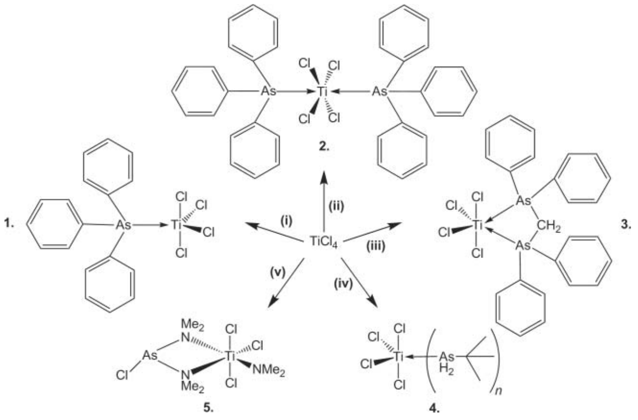
Film characterisation

X-Ray powder diffraction patterns were obtained using a Brüker AXS D8 discover machine using monochromatic Cu-Kα radiation. Wavelength dispersive X-ray analysis (WDX) was conducted using a Philips XL30ESEM machine. Scanning electron microscopy (SEM) was performed using a JSM-6301F scanning field emission machine.

Results and discussion

Synthesis and characterisation

Treatment of $TiCl_4$ with one or two equivalents of an arsine, L, resulted in the immediate formation of a dark-red colour and after work-up isolation of $[TiCl_4(L)_n]$ (L = $AsPh_3$, n = 1 (**1**), n = 2 (**2**); L = $Ph_2AsCH_2AsPh_2$, n = 1 (**3**)) in high yield (> 85%). Complexes **1** and **2** have been characterised by ^{1}H NMR spectroscopy, the results of which indicate that a monomeric complex $[TiCl_4(L)_n]$ has been isolated in all reactions (Scheme 1). Unfortunately, ^{1}H NMR of **3** could not be obtained due to the insolubility of this compound. However, analytical data were obtained for compounds **1–3**. The carbon and hydrogen analyses for **3** were satisfactory. However, for compounds **1** and **2**, although



Scheme 1 Schematic illustrating the synthesis of compounds **1–5** *via* the reaction of $TiCl_4$ with: (i) $AsPh_3$, (ii) $2AsPh_3$, (iii) $Ph_2AsCH_2AsPh_2$, (iv) $^tBuAsH_2$ and (v) $As(NMe_2)_3$.

the hydrogen analysis was satisfactory, the carbon analysis was low. This has been observed previously with some related phosphine adducts of $TiCl_4$, which was thought to be due to the formation of either titanium phosphide with carbon impurities or metal carbide during the thermal decomposition stage of the microanalysis procedure.[9] Therefore, it is possible that the % C for **1** and **2** are low due to the formation of metal carbide. In order to investigate whether the compounds are monomeric and if a *cis* or *trans* isomer had formed (for compound **2** when $n = 2$, L = $AsPh_3$), the structures of compounds **1** and **2** have been determined. The crystal structure of **1** was determined by single crystal X-ray diffraction and the results are shown in Fig. 1; selected bond lengths and angles are given in Table 1. Compound **1** crystallised into the monoclinic space group $P2_1/c$. It is monomeric in the solid state with the titanium atom adopting a distorted trigonal bipyramidal geometry. Three Cl atoms occupy the equatorial positions while the As atom of the $AsPh_3$ group and one Cl atom reside in the axial positions. A Ti–As bond length of 2.7465(13) Å was observed, which is approximately equal to the sum of the independent atomic radii (1.47 and 1.25 Å) (Fig. 1) indicating that the donor ligand is bound relatively weakly.

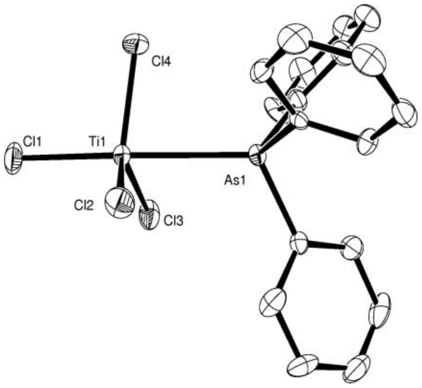


Fig. 1 ORTEP representation of $[TiCl_4AsPh_3]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

The structure of compound **2** was determined by single crystal X-ray crystallography, the results are shown in Fig. 2; selected bond lengths and angles are given in Table 1. Compound **2** lies on an inversion centre and crystallised into the triclinic space group $P\bar{1}$. Compound **2** adopts a centrosymmetric, octahedral *trans*-$(Ph_3As)_2TiCl_4$ geometry, as previously observed for both the $SnCl_4$ and $OsBr_4$ triphenylarsine adducts.[20,21] A related diphenylphosphine adduct of $TiCl_4$ was also shown to crystallise as the *trans* isomer.[9] An average Ti–As bond distance of 2.7238(7) Å was observed in compound **2**, which is similar to that found in **1**. Compounds **1** and **2** both demonstrate Ti–As bond lengths similar to that previously observed for the titanium bromide chelating arsine complex $[TiBr_4\{MeC(CH_2AsMe_2)_3\}]$ (approximately 2.68 Å), with the Ti–Cl bond lengths in **2** (approximately 2.27 Å) found to be in agreement with that previously reported for the six coordinate titanium chloride chelating phosphine complex $[TiCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ (2.28 Å approximately).[22] All other bond distances and angles are similar to related complexes and the octahedral coordination geometry around the titanium metal atom found in **2** was expected.

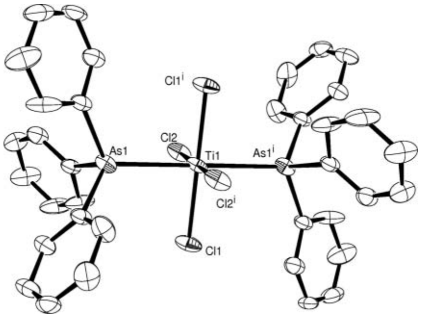


Fig. 2 ORTEP representation of $[TiCl_4(AsPh_3)_2]$ (**2**) showing one of two orientations of the disordered $AsPh_3$ group. Thermal ellipsoids at the 50% probability level and hydrogen atoms are omitted for clarity.

Titanium tetrachloride readily forms adducts of the type $[TiCl_4(L)_n]$, with donor ligands,[23] and compounds **1** and **2** have been previously described briefly in the literature;[24] however, to the best of our knowledge their structures have not been reported. The coordination numbers of $[TiCl_4(L)_n]$ adducts are generally 5 or 6 but in a few cases 8 coordination has been isolated.[25] For example, the reaction of titanium(IV) halides with chelating phosphine and arsine ligands afforded both 6- and 8-coordinate complexes. In general, 6-coordinate species were obtained when sterically demanding ligands, such as $Ph_2PCH_2PPh_2$ and $o\text{-}C_6H_4(PPh_3)_2$, were used, whereas 8-coordinate complexes were isolated with phosphines and arsines with relatively small cone angles at the metal, *e.g.* $o\text{-}C_2H_4(PMe_2)_2$ and $o\text{-}C_6H_4(AsMe_2)_2$.[25,26] A search of the Cambridge structural data base revealed that compounds **1** and **2** are the first crystallographically characterised $[TiCl_4(AsR_x)_n]$ structures without a chelating arsine ligand.

Unfortunately, X-ray quality crystals of $[TiCl_4(Ph_2AsCH_2AsPh_2)]$ (**3**), could not be obtained. It is assumed that due to the chelating nature of the ligand in **3** that a 6-coordinate geometry would be adopted, similar to that observed in the analogous phosphine complex $[TiCl_4(Ph_2PCH_2PPh_2)]$.[22] It was not possible to elucidate the geometry of **3** using IR spectroscopy due to the highly air sensitive nature of the complex resulting in partial decomposition during the analysis, or analyse the compound by ^1H NMR due to its insolubility.

Compounds **1–3** involve the use of tertiary arsines and a chelating arsine. We were particularly interested in investigating what effect changing the arsine ligand could have on the structure of the product obtained. Furthermore, changing the arsine could affect any film resulting from the use of these complexes, particularly since the presence of the phenyl group in **1–3** could lead to carbon contamination. We therefore decided to investigate the reaction of $TiCl_4$ with a primary arsine, which could result in a better decomposition route and potentially less carbon incorporation within the film. The primary arsine, $^tBuAsH_2$,[27] has been employed successfully both in dual- and single-source routes to GaAs and therefore we investigated the use of this ligand. Treatment of $TiCl_4$ with $^tBuAsH_2$ in toluene at −78 °C resulted in the immediate formation of a dark-red solution. The resulting complex is extremely volatile and attempts to remove the solvent *in vacuo* resulted in the loss of the compound to the vacuum trap. In order to overcome this problem the solution was kept at -70 °C and after approximately four weeks a dark brown solid was isolated in low yield. The ^1H NMR of the solid suggests an adduct, [TiCl$_4$(^{t}BuAsH$_2$)$_n$] (**4**) has been formed. Thus, peaks were observed at 1.3 and 3.0 ppm in a 9 : 2 ratio corresponding to the ^{t}Bu and AsH$_2$ protons respectively. However, the ^{1}H NMR of **4** clearly shows the formation of an adduct with an upfield shift in the peaks for the arsine ligand in **4**, in comparison to the free arsine. Unfortunately, the high volatility and air sensitive nature of compound **4** meant that further sample manipulation was difficult.

Tris(dimethylamino)arsine has also been successfully employed in the formation of GaAs.[27–29] We were therefore interested in attempting to form a precursor to TiAs using this arsine. In contrast to the synthesis of **1–4**, reaction of one equivalent of TiCl$_4$ with As(NMe$_2$)$_3$, resulted in the immediate formation of a dark-green solution. After work-up a dark-green solid (**5**) was isolated in high yield (98%), the analytical data for which suggested the formation of a 1 : 1 adduct, [TiCl$_4${As(NMe$_2$)$_3$}]. However, the ^{1}H NMR of **5** showed two peaks at 2.7 and 3.7 ppm, in a 2 : 1 ratio, suggesting the presence of both bridging and terminal NMe$_2$ groups. In order to fully investigate the nature of **5** the crystal structure was determined by single crystal X-ray diffraction, which showed the formation of the novel complex [TiCl$_3$(NMe$_2$)(μ-NMe$_2$)$_2$AsCl] rather than the simple 1 : 1 adduct, [TiCl$_4${As(NMe$_2$)$_3$}]. The results are shown in Fig. 3; selected bond lengths and angles are given in Table 1. Compound **5** crystallised into the monoclinic space group $P2_1/n$. The structure of **5** (Fig. 3), shows it is monomeric with a 6-coordinate titanium centre which possesses three terminal Cl ligands and one terminal and two bridging NMe$_2$ groups in a distorted octahedral geometry. Thus, two of the NMe$_2$ groups are bridging to the arsenic atom, which also has a chlorine atom attached. Upon comparing the Ti–N bond lengths of **5** with that of a similar complex, the terminal and bridging NMe$_2$ Ti–N bond lengths (1.864(2) Å and approximately 2.3 Å respectively) are found to be consistent with the Ti–N bond lengths observed for the complex [TiCl$_2$(NMe$_2$)$_2$(HNMe$_2$)] (approximately 1.85 Å (C$_2$H$_6$N) and 2.25 Å (C$_2$H$_7$N)).[30] The formation of **5** is the result of an interesting substituent exchange between one of the dimethylamido groups on As(NMe$_2$)$_3$, and a chlorine atom from TiCl$_4$ to form the adduct [TiCl$_3$(NMe$_2$)(μ-NMe$_2$)$_2$AsCl], in which the nitrogen atoms of two NMe$_2$ groups coordinate to the titanium centre in preference to coordination *via* the arsenic atom. This is the first time that this type of exchange reaction has been observed for As. The reason behind the exchange is not clear, however similar observations have been reported during solvolysis reactions between TiCl$_4$ and aliphatic primary and secondary amines.[31]

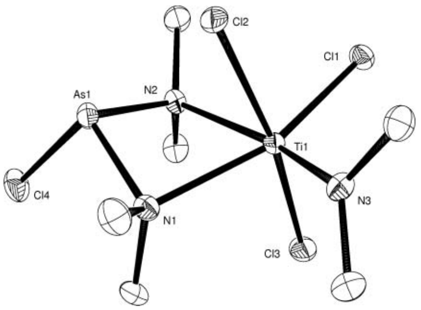


Fig. 3 ORTEP representation of [TiCl$_3$(NMe$_2$)(μ-NMe$_2$)$_2$AsCl] (**5**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

TGA of compounds (1)–(5)

In order to study the decomposition pathway of compounds **1–5** and to assess their suitability as CVD precursors, thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) was carried out (Fig. 4). The TGA/DSC of **1** resulted in a two-step weight loss profile, with losses occurring at approximately 120 and 220 °C. Weight loss completion had occurred by 320 °C, where a residual mass of 11% was reported. The determined residual mass was not in agreement with that expected for TiAs (25%), however, it should be noted that sublimation of the precursor could occur which would result in a higher weight loss than expected. Similarly, TGA of **2** resulted in a two-step weight loss profile, with losses occurring at approximately 130 and 360 °C (residual mass for **2** 6%). Overall the TGA of **1** and **2** indicates that weight loss is complete by 320 and 240 °C respectively, starting at around the melting point (120 °C). These characteristics indicate the potential of **1** and **2** as CVD precursors, in LPCVD or AACVD. However, it is possible that the weight loss could correspond to the dissociation of the arsine ligand before decomposition due to the weak Ti–As bonds present in the complexes.

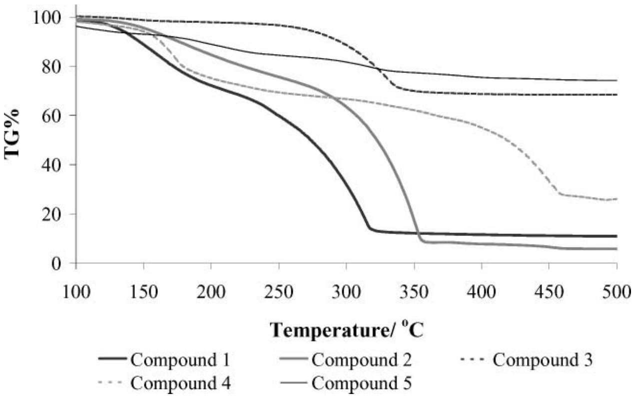


Fig. 4 TGA plots for compounds **1–5**.

TGA of **3** resulted in a two-step decomposition profile, with weight losses occurring at approximately 80 and 200 °C. A high residual mass of 69% was observed which may be attributed to the formation of titanium carbide or an oligomer as indicated by the low solubility of **3**. Compound **3** was not therefore suitable for use in CVD.

TGA of **4** resulted in a three step weight loss profile, with weight losses at approximately 80, 290 and 460 °C. A residual mass of 25% was observed, which is lower than that expected for TiAs remaining after decomposition (38%), which could be due to difficulties in the isolation and manipulation of the compound.

Although the formation of **5** is interesting due to the novel exchange, the compound is thought to be unsuitable as a precursor to TiAs due to the lack of a pre-formed Ti–As bond. However, the decomposition of this compound was of interest to investigate whether a titanium nitride material could be isolated. TGA of **5** resulted in a five-step weight loss profile, with weight losses occurring at approximately 20, 150, 250, 350 and 420 °C. A residual mass of 74% was reported, suggesting that this complex is suitable for use in CVD.

AACVD of compounds

Single-source precursors **1**, **2**, **4** and **5** were used in AACVD in an attempt to deposit TiAs thin films. Compound **3** was not investigated due to its poor solubility in a range of solvents.

Compound **1** was generated *in situ* from the reaction of $TiCl_4$ with one equivalent of $AsPh_3$ in dichloromethane or toluene. A dark red solution formed immediately and the reaction was allowed to mix for 2 min before the AACVD reaction was started. AACVD of **1** was conducted using both toluene and dichloromethane, at substrate temperatures of 200, 400 and 600 °C. In all instances a strongly adherent rainbow film was deposited, which was typically accompanied by a white non-adhesive powder, indicative of homogeneous gas phase reactions. X-ray powder diffraction of the rainbow films resulted in diffractograms consistent with that of TiO_2 anatase, demonstrating peaks at approximately 25.3, 36.9, 37.8, 38.6, 48.1, 53.9, 55.1, 62.1 and 63.8 $2\theta/°$ (Fig. 5). The deposition of TiO_2 was confirmed in all instances by WDX analysis, with approximate 1 : 2 ratios of titanium to oxygen being obtained. WDX analysis also indicated that there was no arsenic present within the deposited films. The WDX results are in agreement with the TGA results and that previously reported for $[SnCl_4(AsPh_3)_2]$ where films of SnO_2 were formed rather than tin arsenide.[20]

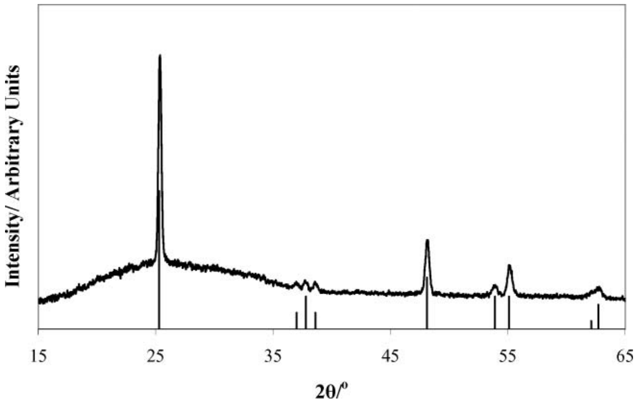


Fig. 5 Typical TiO_2 anatase powder X-ray diffractogram deposited *via* the AACVD of compounds **1**, **2** and **4**.

In contrast to the *in situ* formation of **1** for the AACVD reaction, compound **2** was synthesised (Experimental section) and isolated prior to use in AACVD. Thus, **2** (0.5 g) was dissolved in toluene (40 cm^3), and AACVD was conducted using a substrate temperature of 550 °C. Similarly to **1**, a rainbow film was deposited, which again upon conduction of powder X-ray diffraction, produced a diffractogram consistent with TiO_2 anatase. WDX analysis was conducted on the resultant rainbow film, which confirmed TiO_2 deposition again with zero arsenic content.

The AACVD results for both **1** and **2** are consistent with what was predicted by TGA, with apparent dissociation of arsine during decomposition, and subsequent oxidation of titanium, resulting in the deposition of TiO_2 anatase. Consequently, precursors **1** and **2** were unsuccessful in depositing TiAs *via* AACVD.

For precursors **4** and **5**, *in situ* AACVD was conducted using two different methods; simultaneous and sequential. The simultaneous method refers to that previously described for **1** (where the arsine and $TiCl_4$ are added into the reaction flask simultaneously, prior to the conduction of AACVD), whilst the sequential method involves briefly passing the arsine through the rig for approximately five minutes, prior to the addition of $TiCl_4$. The AACVD was conducted from the *in situ* reaction of $TiCl_4$ and $^tBuAsH_2$ in toluene, using substrate temperatures of 400 and 600 °C. Strongly adherent rainbow films were deposited in all instances. X-ray powder diffraction of the resultant films indicated diffractograms consistent with TiO_2 anatase when deposited *via* the simultaneous method, with sequential AACVD resulting in amorphous film deposition. Scanning electron microscopy (SEM) was conducted on the TiO_2 films deposited at 400 °C using the simultaneous method, with island growth agglomerates of TiO_2 anatase demonstrated (Fig. 6). Upon comparing the elemental compositions of the films deposited using the two methods, whilst no arsenic content was detected *via* simultaneous AACVD, an approximate 3 : 1 ratio of Ti : As was observed *via* the sequential method. These results suggest some incorporation of arsenic into the film, which could be the result of the formation of titanium arsenide, or the deposition of arsenic; however, oxidation largely results in the formation of TiO_2.

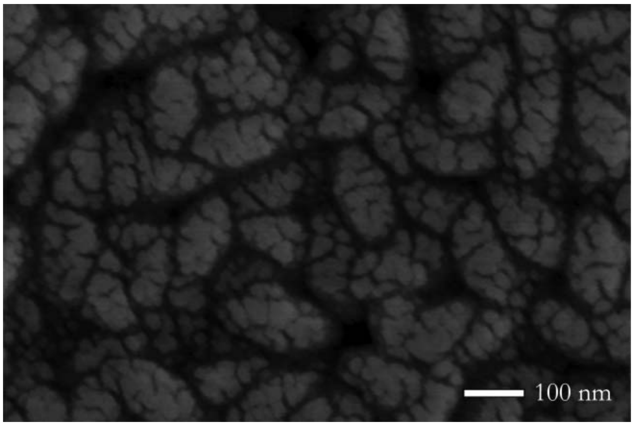


Fig. 6 SEM image of TiO_2 anatase deposited by the simultaneous AACVD of $TiCl_4$ and $^tBuAsH_2$ at 400 °C, at x100,000 magnification.

As previously mentioned **5** is not considered to be an appropriate single-source precursor to TiAs due to lack of pre-formed Ti–As bonds. The sequential AACVD of **5** resulted in the deposition of an amorphous film, however due to the minimal thickness of the deposited film, analysis *via* WDX was not possible.

LPCVD of compounds

From the AACVD results it was evident that the weak Ti–As bonds (in **1**, **2** and **4**) were not being maintained during decomposition, which in addition to the oxophilic nature of titanium, typically resulted in TiO_2 anatase being deposited. As such, LPCVD was conducted in an attempt to minimise oxygen incorporation into the system thus eliminating the potential for TiO_2 deposition. LPCVD was conducted on compounds **1**, **3** and **5** with typically amorphous films being deposited. In general, a rainbow/grey and an orange deposit were observed in all cases, with at least one of these demonstrating arsenic incorporation (for compounds **1** and **3**) and nitrogen incorporation for compound **5**, as detected by WDX. Overall the results of the LPCVD experiments suggest that either TiO_2 or arsenic containing films are formed, with no evidence for the deposition of TiAs *via* LPCVD.

Conclusions

A range of $TiCl_4$ arsine adducts have been synthesised and characterised. The expected five and six-coordination complexes were obtained for $[TiCl_4(AsPh_3)_n]$ $n = 1, 2$, $[TiCl_4Ph_2AsCH_2AsPh_2]$, and $[TiCl_4{}^tBuAsH_2]$. However, reaction of $TiCl_4$ and $As(NMe_2)_3$ resulted in substituent exchange and formation of the novel compound $[TiCl_3(NMe_2)(\mu\text{-}NMe_2)_2AsCl]$. The single-source route to TiAs was investigated as it uses inexpensive and considerably less complicated apparatus as well as less toxic precursors (than for example arsine employed in conventional dual-source CVD routes). However, the prior synthesis and isolation of very air sensitive precursors have notable problems with the single-source route. In addition, the relatively weak Ti–As bonds in these complexes resulted in oxidation and the formation of titanium oxide films.

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