

Novel ion pairs obtained from the reaction of titanium(IV) halides with simple arsane ligands

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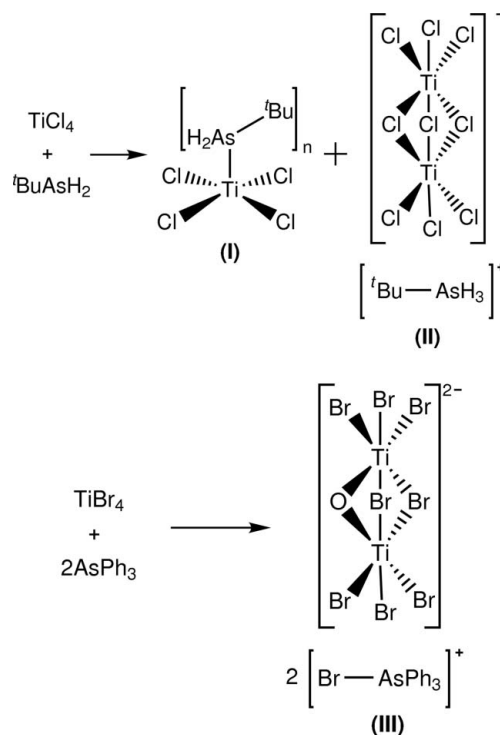
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The compounds *tert*-butylarsenium(III) tri- μ -chlorido-bis[trichloridotitanium(IV)], (C₄H₁₂As)[Ti₂Cl₉] or [^tBuAsH₃]-[Ti₂(μ -Cl)₃Cl₆]⁻ (II), and bis[bromidotriphenylarsenium(V)] di- μ -bromido- μ -oxido-bis[tribromidotitanium(IV)], (C₁₈H₁₅-AsBr)₂[Ti₂Br₈O] or [Ph₃AsBr]₂[Ti₂(μ -O)(μ -Br)₂Br₆]²⁻ (III), were obtained unexpectedly from the reaction of simple arsane ligands with Ti^{IV} halides, with (II) lying on a mirror plane in the unit cell of the space group *Pbcm*. Both compounds contain a completely novel ion, with [^tBuAsH₃]⁺ constituting the first structurally characterized example of a primary arsenium cation. The oxide-bridged titanium-containing [Ti₂(μ -O)(μ -Br)₂Br₆]²⁻ dianion in (III) is also novel, while the bromidotriphenylarsenium(V) cation is structurally characterized for only the second time.

Comment

The deposition of transition metal pnictide thin films is a growing area of research, owing mainly to the useful properties of these films, examples being TiN (Carmalt *et al.*, 2002; Newport *et al.*, 2002), ZrN (Potts *et al.*, 2009), TiP (Blackman *et al.*, 2004), TiAs (Thomas, Blackman *et al.*, 2010), CoAs (Senzaki & Gladfelter, 1994; Klingan *et al.*, 1995) and MnAs (Lane *et al.*, 1994). Such films are often grown by chemical vapour deposition (CVD). This process combines a volatile metal compound with a volatile pnictogen compound in a gas-phase reaction before deposition onto a substrate occurs, but these volatile starting materials can be toxic, flammable and hazardous to work with. To circumvent this problem, 'single-source' precursors have been developed (Cowley & Jones, 1994; Carmalt & Basharat, 2007). These are molecules which contain a preformed M–Pn bond (Pn = pnictogen) and they are, in general, far less toxic and hazardous to work with. In an attempt to obtain single-source precursors to thin films of TiAs, we recently reported a series of novel titanium arsane coordination compounds. These were mostly adducts of TiCl₄

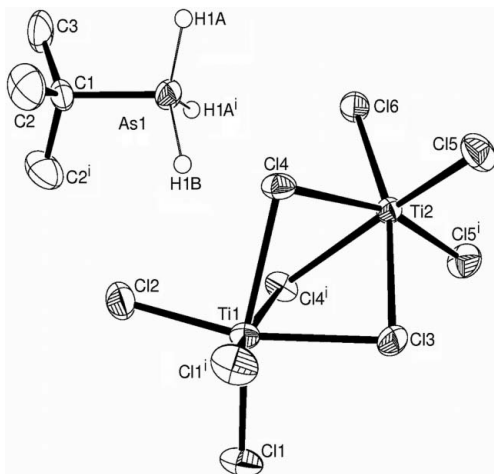
with simple tertiary arsanes, *e.g.* [TiCl₄(AsPh₃)_{*n*}] (*n* = 1, 2), although the reaction product of TiCl₄ with ^tBuAsH₂, *viz.* (I), was also reported (Thomas, Pugh *et al.*, 2010).



It was possible to determine that an adduct had formed by comparing the chemical shift of the coordinated ^tBuAsH₂ ligand with that of the free ^tBuAsH₂ in the ¹H NMR spectrum of (I), although the exact stoichiometry of the product could not be determined. Owing to the exceptionally high volatility of (I), it was not possible at the time to grow crystals of the product. However, upon standing for several weeks at 255 K, orange rods were deposited from a concentrated hexane solution. The resulting product was not the expected adduct; instead, an ion pair had formed to give compound (II), the structure of which is reported here (Fig. 1).

Compound (II) crystallizes in the orthorhombic space group *Pbcm* and consists of a *tert*-butylarsenium cation with a [Ti₂(μ -Cl)₃Cl₆]⁻ anion. It constitutes the first structurally characterized example of a primary arsenium cation. This type of primary alkyl cation is ubiquitous for nitrogen, the lightest member of group 15, but primary alkyl phosphonium cations are extremely rare: only six examples exist in the Cambridge Structural Database (CSD, update of August 2010; Allen, 2002).

As is expected upon descending group 15, the length of the Pn–H bonds increases: the N–H bonds in ammonium cations are significantly shorter than the P–H bonds in phosphonium cations, which range from 1.212 to 1.405 Å (Fluck *et al.*, 1986; Karnop *et al.*, 1997). In (II), the H atoms were located in a Fourier difference map *ca* 1.5 Å from the As centre, continuing the trend and consistent with the larger atomic radius of As compared with P and N. However, it was necessary to use As1–H and C1···H distance restraints

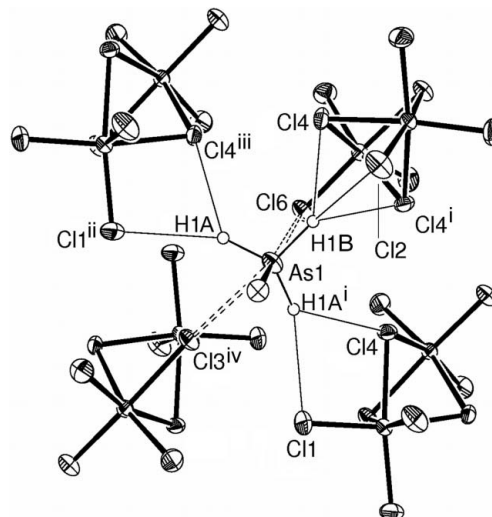
**Figure 1**

A view of the $[\text{BuAsH}_3]^+$ cation and $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anion of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms of the *tert*-butyl group have been omitted for clarity. [Symmetry code: (i) $x, y, -z + \frac{1}{2}$]

during the refinement to obtain a sensible tetrahedral geometry at the As atom.

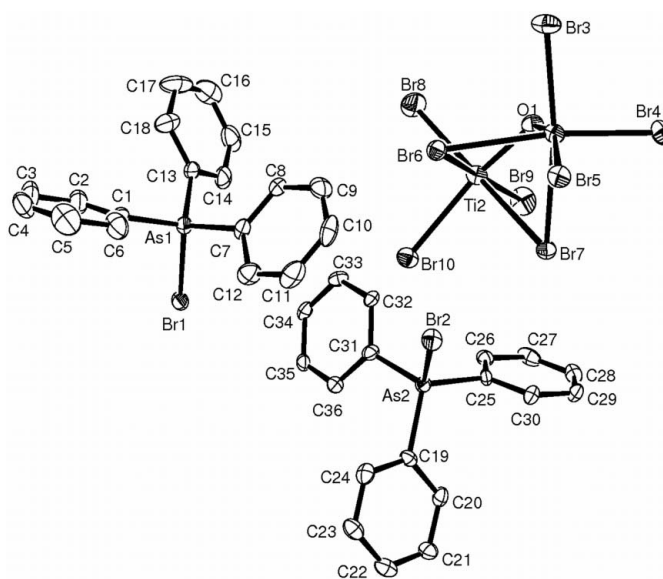
The $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anion of (II) consists of two octahedral Ti^{IV} centres with three bridging chloride anions and six terminal chloride anions. As is expected for anions which bridge two metal centres, the range of bridging Ti—Cl distances is significantly wider than the range of Ti—Cl distances for the terminal chloride anions (Table 1). The angles around the bridging chloride anions are close to the expected value of 90° for an octahedral compound. There are 15 examples of this anion in the CSD and the molecular geometry in (II) is consistent with that of the structures reported previously (e.g. Hollman *et al.*, 2005).

Compound (II) lies on a mirror plane within the unit cell and the asymmetric unit consists of one half of each of the arsenium cation and the $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anion, with an overall Z value of 4. The intermolecular interactions are mostly limited to As—H \cdots Cl interactions between the arsenium H atoms and neighbouring $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anions. The two symmetry-related arsenium H atoms each interact with two chloride anions: atom H1A interacts with a Cl1 and a Cl4 from the same adjacent anion [$\text{H1A}\cdots\text{Cl1}(x, -y + \frac{1}{2}, z - \frac{1}{2}) = 2.94(3) \text{ \AA}$ and $\text{H1A}\cdots\text{Cl4}(x, -y + \frac{1}{2}, -z) = 2.79(2) \text{ \AA}$], whereas atom H1B interacts with three chloride anions from another $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anion, namely Cl2, Cl4 and $\text{Cl4}(x, y, -z + \frac{1}{2})$, with H \cdots Cl distances of 2.868(13), 2.786(12) and 2.786(12) \AA , respectively (Fig. 2). Also present are two short contacts between the As centre and two different $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anions, *viz.* $\text{As1}\cdots\text{Cl3}(-x + 1, y - \frac{1}{2}, z) = 3.4679(13) \text{ \AA}$ and $\text{As1}\cdots\text{Cl6} = 3.4028(14) \text{ \AA}$, which are significantly shorter than the sum of the van der Waals radii of the two atoms (*ca* 3.60 \AA ; Bondi, 1964). The direction of the $\text{As1}\cdots\text{Cl3}(-x + 1, y - \frac{1}{2}, z)$ interaction is diametrically opposite to the direction of the As1—H1B bond (Fig. 2), and the direction of the $\text{As1}\cdots\text{Cl6}$ interaction is diametrically opposite to the direction of the As1—C1 bond.

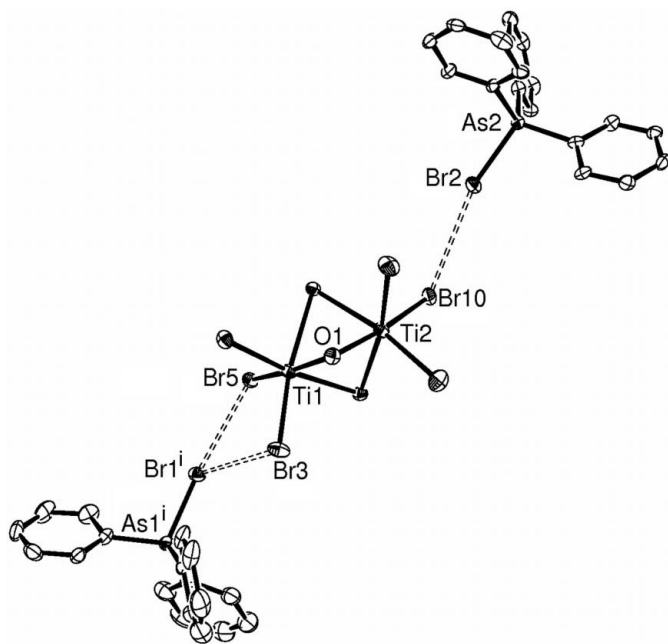
**Figure 2**

A view of the hydrogen bonding (thin solid lines) and As \cdots Cl interactions (dashed lines) between the cation and anion in (II). Displacement ellipsoids are drawn at the 50% probability level and the methyl groups of the arsenium cation have been omitted for clarity. [Symmetry codes: (i) $x, y, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, -z$; (iv) $-x, y - \frac{1}{2}, z$.]

As mentioned above, we have previously reported the synthesis of adducts of TiCl_4 with simple tertiary arsanes such as AsPh_3 (Thomas, Pugh *et al.*, 2010). However, it was found that these adducts were unsuitable precursors because the weak Ti—As bond decomposed too readily and films of TiAs were not formed. In an attempt to synthesize compounds with stronger Ti—As bonds, AsPh_3 was reacted with the softer and less Lewis acidic TiBr_4 . Upon crystallization of the product, instead of the expected 1:1 adduct, an ion pair was isolated, *viz.* (III), which resulted from oxidation of the AsPh_3 ligand by water (Fig. 3).

**Figure 3**

A view of the two unique $[\text{Ph}_3\text{AsBr}]^+$ cations and $[\text{Ti}_2(\mu\text{-O})(\mu\text{-Br})_2\text{Br}_6]^{2-}$ anion of (III), showing the atom-numbering scheme for the heteroatoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.


Figure 4

A view of the Br...Br interactions (dashed lines) between the cations and anion of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $x - 1$, $y - 1$, z .]

Compound (III) crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains two bromoditriphenylarsenium(V) cations and a $[\text{Ti}_2(\mu\text{-O})(\mu\text{-Br})_2\text{Br}_6]^{2-}$ dianion. It is the first structurally characterized example of this dianion. Structurally, it is similar to the $[\text{Ti}_2(\mu\text{-Cl})_3\text{Cl}_6]^-$ anion observed in (II), with two octahedrally coordinated Ti^{IV} centres, six terminal halide anions and two bridging halide anions, but in (III) a bridging oxide dianion is present instead of one of the bridging halide anions. The presence of an oxide dianion significantly affects the geometry at the Ti centres, with the deviation from an ideal octahedron evidenced in the O—Ti—Br (*trans*) angles, which are a long way from the ideal value of 180° (Table 2). The Ti—O—Ti bond angle and the bridging Ti—Br—Ti angles also show evidence of significant deviation away from the ideal value of 90° as a result of the oxide dianion.

The bromoditriphenylarsenium cation in (III) has been structurally characterized only once before (Chitsaz *et al.*, 1999). This was isolated with a $[\text{TeBr}_6]^{2-}$ counter-ion from the reaction of Ph_3AsBr_2 and TeBr_4 . Structurally, the two cations are almost identical, with the previously reported As—Br distances [2.276 (3) and 2.283 (3) Å] consistent with those found in (III) (Table 2). Similarly, the As—C distances of 1.89 (2)–1.90 (2) Å are also consistent with those found in (III).

The cations and dianion of (III) interact mainly through the Br atom attached to the arsenium centre (Fig. 4). Atom Br1 exhibits halogen–halogen interactions with both Br3 [3.6644 (10) Å] and Br5 [3.2844 (10) Å] of the dianion [both atoms Br3 and Br5 are located at the symmetry position ($1 + x$, $1 + y$, z)], which are significantly shorter than the sum of the

van der Waals radii for two Br atoms (*ca* 3.70 Å; Bondi, 1964). There is only one interaction involving atom Br2; the Br2...Br10 distance of 3.6758 (10) Å is also shorter than the sum of the van der Waals radii for two Br atoms.

Experimental

Compound (II) was prepared according to the published procedure of Thomas, Pugh *et al.* (2010). A solution of the reaction product dissolved in hexane (20 ml) was cooled to 255 K. After *ca* eight weeks, orange crystals of (II) had formed. For the preparation of compound (III), a solution of AsPh_3 (0.8 g, 2.6 mmol) in toluene (20 ml) was added to a solution of TiBr_4 (0.49 g, 1.33 mmol) in toluene (10 ml). The resulting solution turned deep red immediately on addition of the AsPh_3 . The reaction was stirred for 1 h and then refluxed for 24 h. After this time, volatiles were removed *in vacuo*, affording a black–brown solid (yield 67%). Orange crystals of (III) were obtained upon cooling a saturated hexane solution to 255 K for one week. $^1\text{H NMR}$ (C_6D_6): δ 7.40 (*m*, 12H, *m*-Ph), 7.03 (*m*, 18H, *o*-Ph and *p*-Ph).

Compound (II)

Crystal data

$(\text{C}_4\text{H}_{12}\text{As})[\text{Ti}_2\text{Cl}_9]$	$V = 1812.0$ (5) Å ³
$M_r = 549.91$	$Z = 4$
Orthorhombic, $Pbcm$	Mo $K\alpha$ radiation
$a = 9.7061$ (15) Å	$\mu = 4.00$ mm ⁻¹
$b = 17.855$ (3) Å	$T = 150$ K
$c = 10.4555$ (16) Å	$0.25 \times 0.10 \times 0.01$ mm

Data collection

Bruker SMART APEX diffractometer	14917 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2006)	2329 independent reflections
$T_{\min} = 0.435$, $T_{\max} = 0.961$	1767 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 1.06$	$\Delta\rho_{\max} = 0.52$ e Å ⁻³
2329 reflections	$\Delta\rho_{\min} = -0.52$ e Å ⁻³
94 parameters	
4 restraints	

Compound (III)

Crystal data

$(\text{C}_{18}\text{H}_{15}\text{AsBr})_2[\text{Ti}_2\text{Br}_8\text{O}]$	$\gamma = 67.448$ (1)°
$M_r = 1523.34$	$V = 2228.12$ (10) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.4991$ (2) Å	Mo $K\alpha$ radiation
$b = 10.7921$ (3) Å	$\mu = 10.83$ mm ⁻¹
$c = 21.5971$ (6) Å	$T = 120$ K
$\alpha = 81.210$ (1)°	$0.20 \times 0.20 \times 0.08$ mm
$\beta = 83.017$ (2)°	

Data collection

Bruker–Nonius APEXII CCD camera on a κ -goniostat diffractometer	33234 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	10149 independent reflections
$T_{\min} = 0.221$, $T_{\max} = 0.478$	7721 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

Table 1
Selected geometric parameters (Å, °) for (II).

C11—Ti1	2.2085 (10)	C14—Ti2	2.5189 (11)
C12—Ti1	2.2206 (15)	C15—Ti2	2.1844 (10)
C13—Ti1	2.4668 (15)	C16—Ti2	2.2192 (14)
C13—Ti2	2.4908 (14)	As1—H1A	1.504 (10)
C14—Ti1	2.4909 (10)	As1—H1B	1.518 (10)
Ti1—C13—Ti2	88.23 (4)	Ti1—C14—Ti2	87.07 (3)

Table 2
Selected geometric parameters (Å, °) for (III).

C1—As1	1.899 (7)	C25—As2	1.905 (6)
C7—As1	1.893 (7)	C31—As2	1.893 (7)
C13—As1	1.909 (7)	As1—Br1	2.2689 (10)
C19—As2	1.904 (6)	As2—Br2	2.2753 (9)
O1—Ti1—Br5	160.37 (15)	Ti1—Br7—Ti2	68.67 (4)
O1—Ti2—Br10	160.49 (15)	Ti1—O1—Ti2	115.0 (2)
Ti1—Br6—Ti2	69.79 (4)		

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	460 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.14$	$\Delta\rho_{\max} = 1.06 \text{ e } \text{Å}^{-3}$
10149 reflections	$\Delta\rho_{\min} = -1.07 \text{ e } \text{Å}^{-3}$

H atoms bonded to As in (II) were located in a Fourier difference map *ca* 1.5 Å from the As centre. Initial attempts at refining the model with unrestrained H atoms were unsuccessful. The C1...H1A/H1B and As—H distances were then restrained to 2.70 (1) and 1.52 (1) Å, respectively, in order to obtain a sensible geometry at the As atom. H atoms bonded to C atoms were placed in geometrically assigned positions, with C—H = 0.95 (CH) or 0.98 Å (CH₃), and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH})$ or $1.5U_{\text{eq}}(\text{CH}_3)$. The H atoms on atom C3 in (II) exhibited positional disorder; this was modelled by fixing the occupancy of each H atom at 0.50.

Data collection: *SMART* (Bruker, 2006) for (II); *COLLECT* (Nonius, 1998) for (III). Cell refinement: *SAINT* (Bruker, 2006) for (II); *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* for (III). Data reduction: *SAINT* for (II); *DENZO* and *COLLECT* for (III). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3254). Services for accessing these data are described at the back of the journal.

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