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Arsenic(III) halide complexes with phosphine and arsine co-ligands: synthesis, spectroscopic and structural properties

Nicholas J. Hill, William Levason and Gillian Reid

Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ

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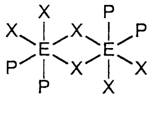
AsX_3 (X = Cl, Br or I) reacts with one molar equivalent of L [L = o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$ or $MeC(CH_2AsMe_2)_3$] in rigorously anhydrous CH_2Cl_2 or thf solution to give colourless or yellow solids of composition [AsX_3L]. Using two molar equivalents of PMe_3 with AsX_3 affords solids of empirical formula [$AsX_3(PMe_3)_2$], whereas one molar equivalent of PMe_3 with $AsCl_3$ gives the 1 : 1 complex [$AsCl_3(PMe_3)$]. Reaction of AsX_3 with $AsMe_3$ gives only the 1 : 1 product [$AsX_3(AsMe_3)$], whether using a 1 : 1 or 1 : 2 $AsCl_3$: $AsMe_3$ ratio. The products have been characterised by microanalysis, and IR, ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopies, where appropriate. The crystal structures of three species, [$AsCl_3(PMe_3)$], [$AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] and [$AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] have been determined. [$AsCl_3(PMe_3)$] adopts a dimeric structure formed through μ-dichloro-bridged edge-shared square pyramidal moieties with *anti* PMe_3 ligands in the axial sites. Interestingly, in the lattice, there are two crystallographically independent dimers which are arranged orthogonally with long range As ··· Cl contacts between between them, giving rise to infinite chains. Thus, in one dimer the As centres are formally 5-coordinate, while in the adjacent dimer the coordination is [5 + 1]. The complexes [$AsX_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] (X = Br or I) are both dimeric through μ-dihalo-bridged bioctahedra in the isomer (A) form. Trends in bond length and angle distributions are considered and the stereochemical activity of the lone pair on the As(III) acceptor discussed.

Introduction

We have shown recently that the heavy p-block ions of group 15, bismuth(III) and antimony(III), readily form complexes with polydentate and macrocyclic thio- and selenoether ligands to give a diverse range of unusual, and often polymeric, structural motifs. These are based on a combination of primary M–X (X = Cl, Br or I) interactions and a series of secondary M ··· E (E = S or Se) and, in some cases, M ··· X interactions.[1–5] In the course of this work, we also prepared a series of Sb(III) and Bi(III) halo complexes involving phosphine and arsine ligands, of which three examples were structurally characterised.[6] Both [$Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2$] and [$Sb_2Br_6\{o\text{-}C_6H_4(PPh_2)_2\}_2$] are dimeric in the isomer (A) arrangement identified previously by Norman *et al.*[7] for a range of phosphine complexes of Bi(III) and Sb(III), and we saw no evidence for coordination numbers greater than six. Interestingly, [$(SbCl_3)_2\{o\text{-}C_6H_4(AsMe_2)_2\}$] adopts a quite different arrangement. In this case, the $SbCl_2$-$\{o\text{-}C_6H_4(AsMe_2)_2\}$ and $SbCl_4$ units are linked through weak, asymmetric chlorine bridges and further long Sb ··· Cl contacts to give a polymeric sheet.[6] We have now extended our studies to include the coordination chemistry of arsenic trihalides with phosphine and arsine ligands. Studies involving AsX_3 acting as a Lewis acid are *extremely* rare and, prior to our work, the only isolated examples included [$AsCl_3(PMe_3)_2$], [$AsCl_3(AsMe_3)$] and [$AsI_3(AsMe_3)$] from the early work of Summers and Sisler,[8] and a more recent report from Baum *et al.* concerning [$AsCl_3(AsEt_3)]_2$.[9] Only the latter has been crystallographically authenticated, revealing a dimeric μ-dichloro edge-bridged square pyramidal geometry. The preparations of [$AsX_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] (X = Cl, Br or I) were also reported in the late 1950's by Sutton, and these were assigned (in fact incorrectly—see below) as 5-coordinate monomers on the basis of the limited range of techniques (conductivity and molecular weight determinations) available at this time.[10]† In this paper, we report the synthesis and spectroscopic characterisation of a series of complexes formed between AsX_3 (X = Cl, Br or I) and L (L = PMe_3, $AsMe_3$, o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$ and $MeC(CH_2AsMe_2)_3$, including the crystal structures of [$AsCl_3(PMe_3)$], [$AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] and [$AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}$].



isomer (A)

Results and discussion

Reaction of AsX_3 (X = Cl, Br or I) with one molar equivalent of L [L = o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$ or $MeC(CH_2AsMe_2)_3$] in rigorously anhydrous CH_2Cl_2 (or thf for the iodo systems) solution affords colourless or yellow solids of composition [AsX_3L], which were isolated in moderate to good yield by filtration *in vacuo*. Using two molar equivalents of PMe_3 with AsX_3 affords solids of empirical formula [AsX_3-$(PMe_3)_2$], whereas one molar equivalent of PMe_3 with $AsCl_3$ gives the 1 : 1 complex [$AsCl_3(PMe_3)$]. In contrast, reaction of AsX_3 with $AsMe_3$ using either a 1 : 1 or 1 : 2 $AsCl_3$: $AsMe_3$ ratio gives only the 1 : 1 product [$AsX_3(AsMe_3)$]. Due to the moisture sensitivity of the As(III) halides, all reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and the complexes were stored in a dinitrogen-purged dry box. Infrared spectroscopy on the chloro and bromo complexes reveals two broad features in each case in the ranges 380–420 (As–Cl) and 260–270 cm^{-1} (As–Br) which are assigned to As–X stretching modes. The products are poorly soluble in

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† *Note added at proof*: since this manuscript was submitted a paper dealing with the synthesis of [$PBr_3(PMe_3)$] has been published: G. Müller, H.-J. Matheus and M. Winkler, *Z. Naturforsch., Teil B*, 2001, **56**, 1155.

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non-donor solvents and $^{31}P\{^1H\}$ NMR spectroscopy shows that solutions of $[AsX_3\{o\text{-}C_6H_4(PPh_2)_2\}]$ decompose readily in $CDCl_3$ and CD_2Cl_2, giving a complex mixture of products in each case, including halogenated $o\text{-}C_6H_4(PPh_2)_2$. The $^{31}P\{^1H\}$ NMR spectra of the $AsCl_3/PMe_3$ systems each reveal a broad singlet at 27 ppm. On addition of excess PMe_3, this resonance is lost and a broad resonance appears at much lower frequency, indicative of fast exchange with PMe_3 (−62 ppm). The $^{31}P\{^1H\}$ NMR spectrum of $[AsBr_3(PMe_3)_2]$ shows a singlet at +16 ppm. The ^1H NMR spectra of $[AsCl_3(PMe_3)]$ and $[AsCl_3(PMe_3)_2]$ show two overlapping doublets, consistent with both the 1 : 1 and 1 : 2 $AsCl_3$: PMe_3 species being present in each case. In contrast, only one doublet is seen for $[AsBr_3(PMe_3)_2]$ (J_{PH} = 12 Hz). The ^1H NMR spectra of $[AsX_3\{MeC(CH_2AsMe_2)_3\}]$ (X = Br or I) are broad, indicative of an exchanging system. For the other arsine complexes, ^1H NMR spectroscopy shows the resonances expected for the coordinated arsine ligands, but is not very informative otherwise.

Since, prior to this work, there were no crystallographic reports on As(III) phosphine coordination complexes and only one As(III) arsine complex, $[AsCl_3(AsEt_3)]_2$, has been structurally characterised, we sought crystallographic authentication for three of the complexes; $[AsCl_3(PMe_3)]$, $[AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ and $[AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. The structure of the PMe_3 complex (Fig. 1, Table 1) reveals two crystallographically independent $AsCl_3(PMe_3)$ moieties in the asymmetric unit, each of which forms a μ-dichloro-bridged dimer by symmetry expansion across a crystallographic inversion centre. Both molecules adopt edge-shared square pyramidal geometries with planar $Cl_2As(\mu\text{-}Cl)_2AsCl_2$ cores and one PMe_3 ligand coordinated to each As centre, occupying mutually *anti* positions. The As–P distances of 2.380(5) and 2.388(5) Å are very similar in the two dimers and, in the case of the dimer involving As2, further examination of the bond length distribution reveals a nearly symmetrical $As_2(\mu\text{-}Cl)_2$ core [2.795(5), 2.908(5) Å] and two terminal As–Cl distances of 2.298(5) and 2.270(5) Å. The angles subtended at As2 are close to the 90 and 180° expected and the remaining coordination site is probably occupied by the lone pair. In contrast, the bond length distribution at As1 is very significantly distorted, with an asymmetric $As_2(\mu\text{-}Cl)_2$ core [2.625(6), 2.907(6) Å]. The terminal As1–Cl distances are *ca.* 0.1 Å different [2.333(6), 2.242(5) Å]. Furthermore, examination of the packing of these dimeric units within the crystal lattice reveals that the alternating As1 and As2 dimers are arranged almost orthogonally and that there is a further long range intermolecular As1 ··· Cl5 interaction at *ca* 3.43 Å. These interactions give infinite chains of weakly associated dimer units in a staircase arrangement [Fig. 1(b)]. The long As ··· Cl distance is within the formal sum of the van der Waal's radii for As and Cl (3.60 Å), suggesting a weak, secondary interaction which occupies the sixth coordination site at As1. The distorted geometry in the As1 dimer may arise from some stereochemical activity of the As1-based lone pair, which cannot occupy an open vertex. There is no corresponding long range As2 ··· Cl interaction and, therefore, the chains are not cross-linked. The presence of the two different dimeric forms (5-coordinate and [5 + 1]-coordinate arsenic) gives rise to a new structural motif for group 15 halide complexes with phosphine or arsine co-ligands.

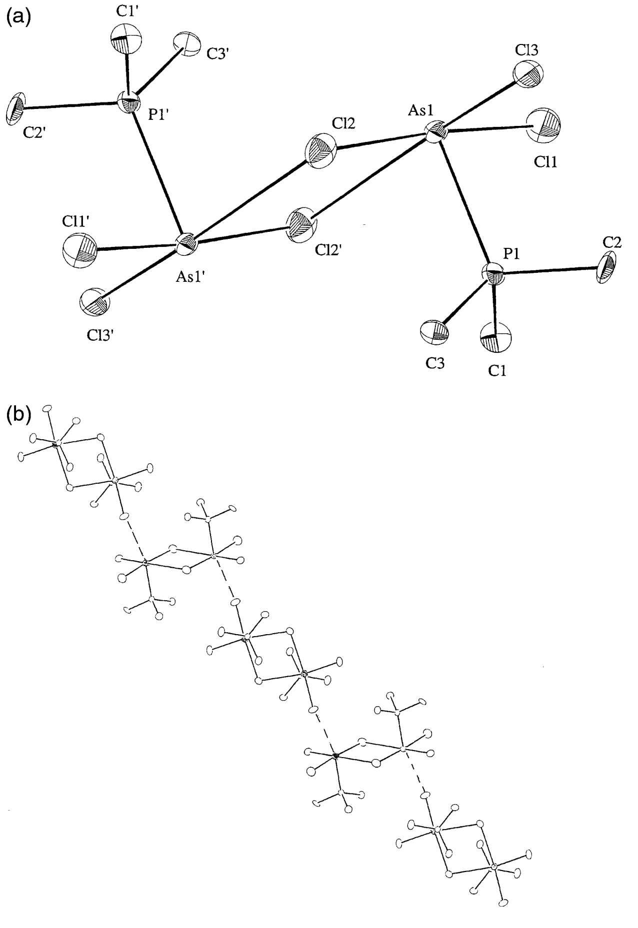

Fig. 1 (a) View of the structure of one of the crystallographically independent dimeric units in $[AsCl_3(PMe_3)]$ with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. (b) View of the packing showing the long range As1 ··· Cl5 intermolecular interactions (dashed line) giving a weakly associated chain. As atoms are shaded.

Table 1 Selected bond lengths (Å) and angles (°) for $[AsCl_3(PMe_3)]$

As1–P1	2.380(5)	Cl2–As1–P1	91.1(2)
As1–Cl1	2.333(6)	Cl2′–As1–Cl3	167.5(2)
As1–Cl2	2.625(6)	Cl2′–As1–P1	82.9(2)
As1–Cl2′	2.907(6)	Cl3–As1–P1	91.9(2)
As1–Cl3	2.242(5)	Cl4–As2–Cl5	174.7(2)
As2–P2	2.388(5)	Cl4–As2–Cl5′	94.3(2)
As2–Cl4	2.298(5)	Cl4–As2–Cl6	95.6(2)
As2–Cl5	2.795(5)	Cl4–As2–P2	86.1(2)
As2–Cl5′	2.809(5)	Cl5–As2–Cl5′	81.2(2)
As2–Cl6	2.270(5)	Cl5–As2–Cl6	88.7(2)
		Cl5–As2–P2	90.8(2)
Cl1–As1–Cl2	175.6(2)	Cl5′–As2–Cl6	169.4(2)
Cl1–As1–Cl2′	98.0(2)	Cl5′–As2–P2	85.7(2)
Cl1–As1–Cl3	92.8(2)	Cl6–As2–P2	91.2(2)
Cl1–As1–P1	84.4(2)	As1–Cl2–As1′	98.6(2)
Cl2–As1–Cl2′	81.4(2)	As2–Cl5–As2′	98.8(2)
Cl2–As1–Cl3	87.4(2)		

The structure of the individual $Cl_2(PMe_3)As(\mu\text{-}Cl)_2As(PMe_3)Cl_2$ molecules in $[AsCl_3(PMe_3)]$ can be compared with that observed for $[AsCl_3(AsEt_3)]_2$, which is also a $(\mu\text{-}Cl)_2$ edge-bridged square pyramidal species with *anti* $AsEt_3$ ligands occupying the apical sites and four Cl's in the basal plane.[9] However, this species does not show any intermolecular interactions and, in fact, the $AsEt_3$ ligands are tilted slightly towards the vacant coordination site on the other arsenic centre, partially blocking this site.

Probably the closest related species is $[Sb_2I_6(PMe_3)_2]\cdot thf$, which does show secondary intermolecular Sb ··· I interactions between adjacent dimers, however, as the dimers are crystallographically identical in this species, the intermolecular interactions result in them aligning in a parallel fashion.[7]

$[AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (Fig. 2, Table 2) and $[AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (Fig. 3, Table 3), although not formally isostructural with one another, adopt very similar structures. Both are μ-dihalo dimers, based upon edge-shared bioctahedra in the isomer (A) form. Each central As(III) is coordinated to two bridging halides, two *cis* terminal halides and the two As centres from a chelating diarsine ligand. These structures are similar to that reported for $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$,[6] which

Table 2 Selected bond lengths (Å) and angles (°) for $[AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$

As1–Br1	2.463(2)	Br2–As1–Br3	98.85(6)
As1–Br2	2.886(2)	Br2–As1–Br3′	118.56(6)
As1–Br3	2.830(2)	Br2–As1–As2	78.37(6)
As1–Br3′	3.345(2)	Br2–As1–As3	163.85(8)
As1–As2	2.448(2)	Br3–As1–Br3′	83.16(6)
As1–As3	2.537(2)	Br3–As1–As2	83.62(7)
		Br3–As1–As3	81.93(6)
Br1–As1–Br2	90.56(6)	Br3′–As1–As2	159.97(7)
Br1–As1–Br3	167.30(7)	Br3′–As1–As3	77.58(5)
Br1–As1–Br3′	99.87(7)	As2–As1–As3	85.72(6)
Br1–As1–As2	90.00(7)	As1–Br3–As1′	96.84(6)
Br1–As1–As3	86.67(6)		

Table 3 Selected bond lengths (Å) and angles (°) for $[AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$

As1–I1	2.8456(11)	I2–As1–I1′	94.19(3)
As1–I1′	3.434(1)	I2–As1–I3	98.91(3)
As1–I2	2.8376(11)	I2–As1–As2	84.23(4)
As1–I3	3.0202(11)	I2–As1–As3	86.27(4)
As1–As2	2.6067(12)	I3–As1–I1′	114.36(3)
As1–As3	2.4785(12)	I3–As1–As2	164.40(4)
		I3–As1–As3	80.79(3)
I1–As1–I1′	84.52(3)	As2–As1–I1′	80.44(3)
I1–As1–I2	171.52(4)	As2–As1–As3	84.19(4)
I1–As1–I3	89.24(3)	As3–As1–I1′	164.49(4)
I1–As1–As2	87.29(4)	As1–I1–As1′	95.48(3)
I1–As1–As3	92.74(4)		

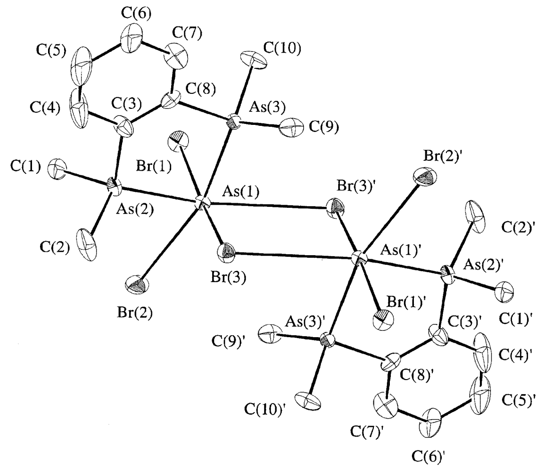

Fig. 2 View of the structure of $[AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

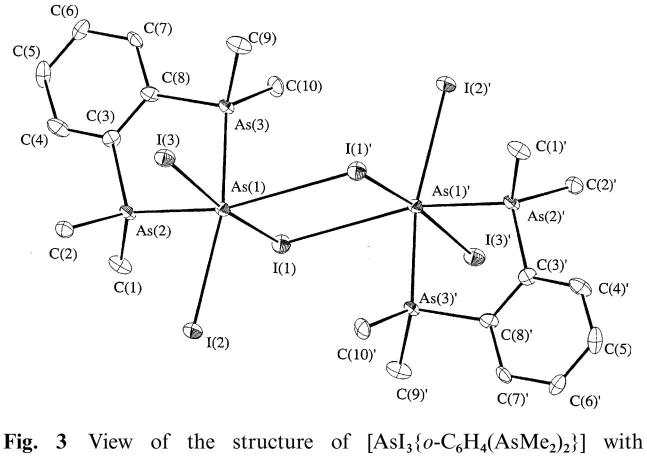

Fig. 3 View of the structure of $[AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

showed d(Bi–As) = 2.801(2), 2.974(2) Å and d(Bi–I) = 2.992(2)–3.328(1) Å, involving a rather more symmetric iodo-bridged Bi_2I_2 core and the bond length distribution parallels that seen $[Bi_2I_6\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$, $[Sb_2Br_6(dmpe)_2]$ and $[Bi_2Br_6(dmpe)_2]$[7] (dmpe = $Me_2P(CH_2)_2PMe_2$, *i.e.* within each of the three types of bond, M–X(μ-bridging), M–X(terminal) and M–E (M = Bi, Sb or As Lewis acid; X = halide; E = P or As donor atom), there is one long and one short bond. This pattern is consistent with the asymmetry being mainly a consequence of the greater *trans* influence of the phosphine or arsine ligand relative to the halide, together with the fact that the dimers are formed essentially through weak association (*via* halide bridging) of two square pyramidal units. Clearly the lone pair on As1 (and its symmetry equivalent) does not occupy a vacant vertex, but there may be some stereochemical activity contributing to the distortions in bond lengths and angles around As1 (and As1′). Consideration of the bond angles at As1 suggests that the lone pair may be directed within one triangular face of the octahedron in each case, defined by Br1, Br2, Br3′ in $[AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$ and I1′, I2, I3 in $[AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$.

The As1–As2 and As1–As3 distances involving the chelating $o\text{-}C_6H_4(AsMe_2)_2$ ligand are also somewhat asymmetric, differing by *ca* 0.1 Å—see above. The As–As distances for the complexes lie in the range 2.448(2)–2.607(1) Å, compared with 2.469(3) Å in the only other structurally characterised example, $[AsCl_3(AsEt_3)]_2$, although the latter species involves a 5-coordinate central As(III).[9] It is notable that these As–As distances are in accord with those seen for various tetra-alkyl or tetra-aryl diarsines [*e.g.* $Me_2AsAsMe_2$, 2.429(1);[11] $Mes_2AsAsMes_2$, 2.472(3) Å (Mes = mesityl)[12]], suggesting that they are essentially 'normal' sigma bonds.

Conclusions

The syntheses of a series of phosphine and arsine complexes with arsenic trihalides are described, together with the first crystallographic data on an arsenic(III) phosphine complex and only the second and third examples of arsenic(III) arsines. These results demonstrate that the non-metallic AsX_3 fragments are reasonable Lewis acids, giving good yields of the products. The structures obtained have been compared with related systems involving antimony(III) and bismuth(III) halides. While the $o\text{-}C_6H_4(AsMe_2)_2$ complexes belong to the familiar isomer (A) type, the structure of $[AsCl_3(PMe_3)]$ represents a new structural motif in these systems.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 1710 spectrometer over the range 220–4000 cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 using a Bruker AC300 spectrometer, while $^{31}P\{^1H\}$ NMR spectra used a Bruker DPX400 spectrometer operating at 162.0 MHz and are referenced to external 85% H_3PO_4. Microanalyses were obtained from the University of Strathclyde Microanalytical Laboratory. Arsenic trihalides (Aldrich or Alfa) were obtained commercially and used as received. The phosphine and arsine ligands were prepared by the literature methods,[13–15] except for PMe_3 and $AsMe_3$, which were obtained from Aldrich and Strem, respectively. Standard Schlenk techniques and anhydrous solvents were used for all preparations.

Preparations

$[AsCl_3\{o\text{-}C_6H_4(AsMe_2)_2\}]$. Dropwise addition of a CH_2Cl_2 solution (10 cm^3) of $o\text{-}C_6H_4(AsMe_2)_2$ (0.071 g, 0.25 mmol) to a CH_2Cl_2 solution (10 cm^3) of $AsCl_3$ (0.045 g, 0.25 mmol) immediately produced a white solid, which was isolated by filtration, washed with CH_2Cl_2 and dried *in vacuo*. Yield 77 mg, 67%. Calculated for $C_{10}H_{16}As_3Cl_3$: C, 25.7; H, 3.5; found: C,

Table 4 Crystallographic data

	[$AsCl_3(PMe_3)$]	[$AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}$]	[$AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}$]
Formula	$C_3H_9AsCl_3P$	$C_{10}H_{16}As_3Br_3$	$C_{10}H_{16}As_3I_3$
MW	257.36	600.71	741.71
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$	$P2_1/n$
a/Å	12.002(6)	9.8794(3)	8.7874(2)
b/Å	12.297(6)	16.0455(6)	12.0405(3)
c/Å	12.328(4)	11.3094(4)	16.7508(5)
β/°	91.97(4)	110.973(1)	90.9090(7)
U/Å^3	1819(1)	1673.99(9)	1772.09(7)
Z	8	4	4
μ(Mo-Kα)/cm^{-1}	47.09	153.43	108.33
Unique obs. reflections	3377	3929	3757
Obs. reflections [$I > 2\sigma(I)$]	1706	2324	2525
R	0.073	0.073	0.037
R_w	0.089	0.078	0.046

25.4; H, 3.6%. ^{1}H NMR: δ 1.55 (br, AsMe, 12H), 7.3–7.6 (br m, o-C_6H_4, 4H). IR ν/cm^{-1}: 419, 386 (As–Cl).

[$AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}$]. Procedure as above. White powder. Yield 82%. Calculated for $C_{10}H_{16}As_3Br_3$: C, 20.0; H, 2.7; found: C, 20.2; H, 3.0%. ^{1}H NMR: δ 1.25 (s, AsMe, 12H), 7.2–7.6 (m, o-C_6H_4, 4H). IR ν/cm^{-1}: 263 br (As–Br).

[$AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}$]. Procedure as above, using anhydrous THF solutions of AsI_3 and o-$C_6H_4(AsMe_2)_2$. Yellow solid. Yield 81%. Calculated for $C_{10}H_{16}As_3I_3$: C, 16.2; H, 2.2; found: C, 16.6; H, 2.5%. ^{1}H NMR: δ 1.22 (s, AsMe, 12H), 7.2–7.6 (m, o-C_6H_4, 4H).

[$AsBr_3\{MeC(CH_2AsMe_2)_3\}$]. Procedure as above. Yellow solid. Yield 0.11 g, 53%. Calculated for $C_{11}H_{27}As_4Br_3$: C, 18.9; H, 3.9; found: C, 18.9; H, 3.8%. ^{1}H NMR: δ 1.12 (s, CMe, 3H), 1.62 (br, AsMe, 9H), 2.15 (br, CH_2, 6H).

[$AsI_3\{MeC(CH_2AsMe_2)_3\}$]. Addition of an equimolar CH_2Cl_2 solution (10 cm^3) of $MeC(CH_2AsMe_2)_3$ to a thf solution (10 cm^3) of AsI_3 gave a yellow solution. The solution was slowly concentrated *in vacuo* to afford a yellow precipitate, which was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Yield 82%. Calculated for $C_{11}H_{27}As_4I_3$: C, 15.7; H, 3.2; found: C, 16.2; H, 3.5%. ^{1}H NMR: δ 1.10 (s, CMe, 3H), 1.30 (br, AsMe, 9H), 1.95 (br, CH_2, 6H).

[$AsCl_3\{o\text{-}C_6H_4(PMe_2)_2\}$]. Addition of a chilled (*ca.* −30 °C) diethyl ether solution (10 cm^3) of $AsCl_3$ (0.036 g, 0.20 mmol) to a cold (−30 °C) diethyl ether solution (10 cm^3) of o-$C_6H_4(PMe_2)_2$ (0.039 g, 0.20 mmol) immediately produced a white solid, which was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 58%. Calculated for $C_{10}H_{14}AsCl_3P_2\cdot 1/4Et_2O$: C, 33.2; H, 4.7; found: C, 33.1; H, 4.8%. ^{1}H NMR: δ 2.0 (m, Me, 12H), 7.6–8.1 (m, o-C_6H_4, 4H). ^{31}P{^{1}H} NMR: δ 32. IR ν/cm^{-1}: 414, 380 (As–Cl).

[$AsCl_3\{o\text{-}C_6H_4(PPh_2)_2\}$]. Addition of a CH_2Cl_2 solution (10 cm^3) of o-$C_6H_4(PPh_2)_2$ to an equimolar CH_2Cl_2 solution (10 cm^3) of $AsCl_3$ produced a very pale green solution. Removal of solvent *in vacuo* gave a yellow–green waxy solid, which was triturated in hexane to obtain a light yellow powder. Yield 0.165 g, 74%. Calculated for $C_{30}H_{24}AsCl_3P_2$: C, 57.4; H, 3.9; found: C, 57.0; H, 3.6%. IR ν/cm^{-1}: 412, 388 (As–Cl).

[$AsBr_3\{o\text{-}C_6H_4(PPh_2)_2\}$]. Procedure as above. Yellow powder. Yield 64%. Calculated for $C_{30}H_{24}AsBr_3P_2$: C, 47.3; H, 3.2; found: C, 48.0; H, 3.3%. IR ν/cm^{-1}: 268 (As–Br).

[$AsI_3\{o\text{-}C_6H_4(PPh_2)_2\}$]. Procedure as above. Yellow powder. Yield 78%. Calculated for $C_{30}H_{24}AsI_3P_2$: C, 39.9; H, 2.7; found: C, 40.2; H, 2.7%.

[$AsCl_3(PMe_3)$]. Addition of a chilled (*ca.* −30 °C) diethyl ether solution (10 cm^3) of $AsCl_3$ (0.09 g, 0.50 mmol) to a cold (*ca.* −30 °C) toluene solution of PMe_3 (0.50 mmol, 0.50 cm^3 of a 1.0 mol dm^{-3} solution of PMe_3 in toluene) immediately produced a white solid, which was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 40%. Calculated for $C_3H_9AsCl_3P$: C, 14.0; H, 3.5; found: C, 13.0; H, 3.5%. ^{1}H NMR: δ 2.20 (d, 12 Hz), 2.15 (d, 12 Hz). ^{31}P{^{1}H} NMR: δ 27. IR ν/cm^{-1}: 409, 380 (As–Cl).

[$AsCl_3(PMe_3)_2$]. Procedure as above, using two molar equivalents of PMe_3. Yield 65%. Calculated for $C_6H_{12}AsCl_3P_2$: C, 21.6; H, 5.4; found: C, 21.8; H, 5.3%. ^{1}H NMR: δ 2.20 (d, 12 Hz), 2.15 (d, 12 Hz). ^{31}P{^{1}H} NMR: δ 28. IR ν/cm^{-1}: 413, 382 (As–Cl).

[$AsBr_3(PMe_3)_2$]. Procedure as above. White solid. Yield 61%. Calculated for $C_6H_{18}AsBr_3P_2$: C, 15.4; H, 3.9; found: C, 15.5; H, 3.6%. ^{1}H NMR: δ 2.20 (d, 12 Hz). ^{31}P{^{1}H} NMR: δ 16. IR ν/cm^{-1}: 268 (As–Br).

[$AsCl_3(AsMe_3)$]. Procedure as for [$AsCl_3(PMe_3)$], giving the 1 : 1 $AsCl_3$: $AsMe_3$ product irrespective of the reaction stoichiometry. White powder. Yield 67%. Calculated for $C_3H_9As_2Cl_3$: C, 11.9; H, 3.0; found: C, 11.6; H, 2.7%. IR ν/cm^{-1}: 419, 382 (As–Cl).

[$AsI_3(AsMe_3)$]. Procedure as for [$AsI_3(PMe_3)_2$], using two molar equivalents of $AsMe_3$. Yellow powder. Yield 47%. Calculated for $C_3H_9As_2I_3$: C, 6.3; H, 1.6; found: C, 5.9; H, 1.8%. ^{1}H NMR: δ 1.20 (s, Me).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 4. Modest quality crystals of [$AsCl_3(PMe_3)$] were obtained by layering a solution of $AsCl_3$ in diethyl ether onto a solution of PMe_3 in toluene in an N_2-purged glove box, while small crystals of [$AsBr_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] and [$AsI_3\{o\text{-}C_6H_4(AsMe_2)_2\}$] were obtained by slow evaporation from a solution of the appropriate complex in CH_2Cl_2 in an N_2-purged dry box. Data collection used a Rigaku AFC7S four-circle diffractometer [$AsCl_3(PMe_3)$] or an Enraf Nonius Kappa CCD diffractometer (others) (T = 150 K) with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[16–18] Selected bond lengths and angles are presented in Tables 1–3.

CCDC reference numbers 170403–170405.

See http://www.rsc.org/suppdata/dt/b1/b107926n/ for crystallographic data in CIF or other electronic format.

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