Preparation and Characterization of a Material of Composition BiP (Bismuth Phosphide) and Other Intergroup 15 Element Phases

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The reaction between equimolar quantities of $BiCl_3$ and the silylphosphine $P(SiMe_3)_3$ in toluene or THF (tetrahydrofuran) solution affords a black precipitate with the composition of bismuth phosphide, BiP, which has been examined by EDXA, SEM, XPS, powder XRD, solid-state ^{31}P NMR spectroscopy, and elemental analysis. Alternative possible routes to BiP involving the reactions between Na_3P and $BiCl_3$ and between $Bi(NMe_2)_3$ and $P(SiMe_3)_3$ have also been investigated, both of which afford black powders of composition close to BiP, although in the latter case there is some contamination with bismuth metal. Analogous reactions with either $SbCl_3$ or $AsCl_3$ and $P(SiMe_3)_3$ afford black and dark brown precipitates, respectively, which are formulated as the materials antimony phosphide, SbP, and arsenic phosphide, AsP, on the basis of similar analyses. Preliminary experiments have also shown that the related arsenides, BiAs and SbAs, can be prepared from reactions between either $BiCl_3$ or $SbCl_3$ and the silylarsine $As(SiMe_3)_3$, and that a ternary phase with the composition $BiSbP_2$ is formed in the reaction between $BiCl_3$, $SbCl_3$, and $P(SiMe_3)_3$ in a 1:1:2 mole ratio. A material of composition close to elemental phosphorus is obtained from the reaction between PCl_3 and $P(SiMe_3)_3$.

Introduction

Element phosphides, E_xP_y, constitute an important and structurally diverse class of compound, examples of which are known for almost all elements. There are, however, some conspicuous absences particularly in the case of the heavier group 15 elements. Thus, as noted in the text *Chemistry of the Elements* by Greenwood and Earnshaw,[1] “phosphorus forms binary compounds with all elements except Sb, Bi and the inert gases” and, in a recent and comprehensive review on element phosphides by von Schnering and Hönle,[2] it is stated that “Bi, Hg and Pb form no binary phosphides at all”. In fact, with the recent exception of phosphorus(V) nitride, P_3N_5, reported by Schnick,[3] there is very little definitive characterization data for solid-state compounds that involve only the group 15 elements.

A survey of the early literature reveals that attempts to prepare binary phosphides of arsenic, antimony, and bismuth have resulted in only poorly characterized materials.[4] Arsenic monophosphide is reportedly formed by the action of dry arsine on phosphorus trichloride below 20 °C or via a similar reaction involving phosphine and arsenic trichloride,[5] while more recent reports describe phosphorus−arsenic alloys of the type $P_{1-x}As_x$ ($x = 0.05, 0.1-0.5$) which adopt an orthorhombic layered structure similar to that of orthorhombic black phosphorus. These alloys were transformed from the orthorhombic phase to one of rhombohedral symmetry and finally to a simple cubic form by increasing the pressure at room temperature (a similar transformation is known for elemental phosphorus); the cubic phase exhibits superconductivity at low temperature.[6]

Early reports of the existence of an antimony phosphide phase are inconclusive. Antimony monophosphide was reportedly prepared by the action of phosphorus on a solution of antimony tribromide in carbon disulfide, although attempts to repeat this claim were unsuccessful.[7] In the case of bismuth monophosphide, only poorly characterized black powders have been obtained, the properties of which resemble those of a

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phosphiferous bismuth. Neither by direct or indirect methods has a bismuth phosphide been prepared with any certainty.[7]

One of the most general preparative routes to element phosphides is to heat the element in question with an appropriate amount of elemental phosphorus at high temperature either in an inert atmosphere or in an evacuated sealed tube. However, any potential synthesis of bismuth phosphide directly from the elements is thwarted both by the apparent limited solubility of phosphorus in molten bismuth[7] and by the fact that these elements are known to crystallize separately from molten mixtures; crystalline orthorhombic black phosphorus has, in fact, been obtained by recrystallization of phosphorus from molten bismuth.[8] This problem of restricted mutual solubility in the molten state was also encountered in attempted preparations of antimony phosphide.[9] It should be noted, however, that most of the heteronuclear diatomic molecules, such as BiP, SbP, and AsP, have been studied spectroscopically in the gas phase (see, for example, refs 10 and 11).

The related element arsenides, E_xAs_y, are also an important and structurally diverse class of materials, examples of which are likewise known for most elements, and many have important electronic properties, such as the group 13 (Al, Ga, In) arsenides. In contrast, the group 15 arsenides, like the phosphides, do not constitute a well-characterized group of compounds, although there are a number of reports of the existence of an alloy of arsenic and antimony (see ref 4 and literature cited therein), and one phase of the mineral allemonite has a composition corresponding to the formula AsSb.[4] Early reports of an arsenic–bismuth alloy indicate that two layers form as a result of these elements having only limited mutual solubility in the liquid state, although subsequent investigations revealed that this formation of layers was due to insufficient mixing of the melts. Nevertheless, the solubility of arsenic in bismuth is only slight (see ref 4 and literature cited therein).

Our interest in preparing bismuth phosphide, BiP, in particular stemmed from the realization that it is isoelectronic with lead(II) sulfide, PbS,[12] which is an intrinsic semiconductor with a bandgap of 0.37 eV. This material has a wide range of applications including use in photoconductive cells and transistors, as an infrared detector, and as a mirror coating. Herein we describe the preparation and characterization of a material of empirical composition BiP, together with the related binary phosphides of antimony and arsenic. Preliminary results on the preparation of the ternary compound, $BiSbP_2$, are also presented together with details on some related arsenides, namely, BiAs and SbAs. A communication of part of this work relating to the preparation of BiP has appeared.[13]

Preparation and Properties of Bismuth Phosphide

Solution precipitation routes, using a variety of solvents, to III–V (or 13–15) materials involving the elimination of a silyl halide Me_3SiX (X = Cl, Br, I) have previously been described by the groups of Wells,[14] Barron,[15] Buhro,[16] Alivisatos,[17] Nozik,[18] and Fitzmaurice[19] according to eq 1. This method relies on the

$$EX_3 + E'(SiMe_3)_3 \rightarrow EE' + 3Me_3SiX \qquad (1)$$

$$E = \mathrm{Al, Ga, In;\ X = Cl, Br, I;\ E' = P, As, Sb}$$

formation of a strong Si–X bond and has been used in the preparation of solid AlAs,[14e] GaP,[14b,c] GaAs,[14a,d,17a,19] GaSb,[14f] InAs[14a] and InP.[15,17b,18]

In general, initial reactions occur rapidly at or below room temperature via intermediate species such as the phosphine, arsine, or stibine adducts $[X_3E \leftarrow E'(SiMe_3)_3]$ and the dimeric, four-membered ring compounds $[\{EX_2E'(SiMe_3)_2\}_2]$, examples of which have been isolated and crystallographically characterized in many cases.[14b–d] Heating of solid samples of these primary products to temperatures of about 300 °C subsequently results in complete elimination of all remaining Me_3SiX with formation of the EE′ phase.

In contrast to the group 13–15 chemistry, treatment of a stirred solution of $BiCl_3$ in toluene or THF (tetrahydrofuran) with 1 equiv of $P(SiMe_3)_3$ at room temperature led to the immediate formation of an insoluble black precipitate (**1a**), full elemental analytical data for which were in accord with a material of composition close to BiP with only minor amounts of carbon, hydrogen, silicon, and chlorine present. The observation that the elimination of Me_3SiCl is much more facile here than in the case of the analogous 13–15 reactions shown in eq 1 is presumably a consequence of the relative weakness of the Bi–Cl bond. A number of further analyses, described below, were carried out in order to characterize **1a** more fully and, more specifically, to determine whether this material was a genuine bismuth phosphide compound or merely an intimate mixture of elemental bismuth and phosphorus.

Energy-dispersive X-ray analysis (EDXA) of **1a** confirmed the presence of bismuth and phosphorus with only minimal levels of impurities (Figure 1) consistent with the elemental analytical data. No appreciable

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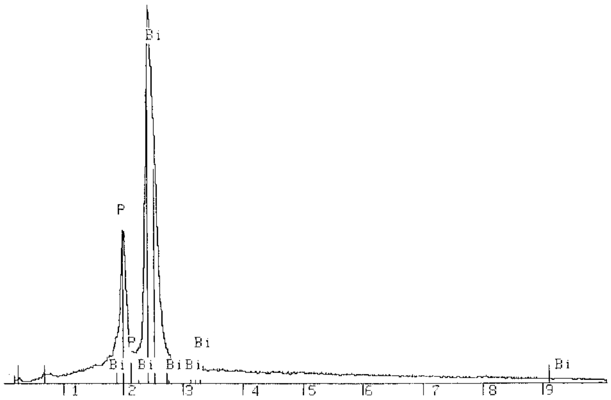

Figure 1. EDXA spectrum (in keV) for **1a**.

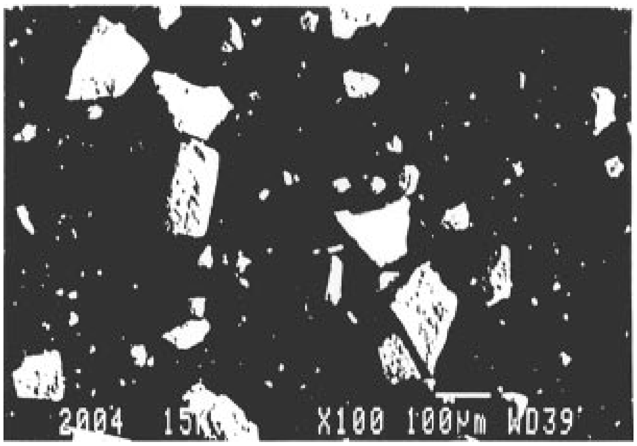

Figure 2. SEM of **1a**.

quantities of carbon, silicon, or oxygen were observed over a number of surface sites, indicating that any amounts present were less than 1%. Chlorine contamination was more difficult to gauge by this technique since the primary chlorine and bismuth peak energies are nearly coincident, although elemental analytical data showed that <1% chlorine was present. These EDXA data also indicated that the surface composition of **1a** over several sites, with detection areas typically 1 μm in diameter, was uniform. Although this technique cannot provide direct information as to the chemical nature of the bismuth and phosphorus present, if **1a** were an intermixed precipitate of Bi and P, the Bi:P ratios might be expected to vary somewhat from site to site and the scale of mixing would have to be on the order of tens of nanometers. A more quantitative EDXA analysis, obtained over two sites, revealed a ratio of Bi:P of 1:0.86 in reasonable agreement with the expected ratio of 1:1 although indicating that a slight excess of bismuth was present.

The apparently homogeneous nature of **1a** was also evident from scanning electron microscopy (SEM, Figure 2) which revealed surfaces of uniform appearance. However, the SEM data also revealed the absence of any crystallites, thereby indicating that the material was possibly amorphous, but to probe the structural properties and crystallinity of **1a** in more detail, an X-ray diffraction (XRD) study on powdered samples was carried out. The results of the powder XRD study revealed that **1a**, as prepared, is probably amorphous since the powder pattern obtained was essentially featureless although a few broad peaks consistent with the presence of metallic bismuth were present. Whether or not any metallic bismuth is present as a major or minor component of solid **1a**, however, is unclear from these data.

To further investigate the chemical composition of **1a**, X-ray photoelectron spectroscopic (XPS) studies were carried out. All binding energies were corrected for specimen charging by referencing the carbon 1s signal to 284.8 eV. Initial analysis of the surface of **1a** indicated that probably three bismuth containing species were present with Bi($4f_{7/2}$) binding energies of 156.8, 158.8, and 160.4 eV.[20] The lowest energy peak corresponds to **1a** (see below) while the two higher energy peaks are most likely due to bismuth oxo species (the binding energy of Bi_2O_3 is reported as 159.3 eV[21]). Etching the sample surface with argon atoms resulted in reduced surface charging and an XPS spectrum which exhibited only one peak in the Bi($4f_{7/2}$) binding region (Figure 3). The observed binding energy of 157.1 eV is almost identical with that reported for Bi metal (157.0 eV[21]) which could imply that the bismuth in **1a** is present as bismuth metal. However, in view of the fact that the Bi($4f_{7/2}$) binding energy of bismuth sulfide (Bi_2S_3) is 158.9 eV,[21,22] it is likely that the bismuth binding energies for bismuth and bismuth phosphide are quite close and within the errors associated with the XPS experiment (±0.5 eV). It is also possible that surface reduction occurs on sputtering and that the observed binding energies do correspond to bismuth metal, although it should be noted that the width of the Bi($4f_{7/2}$) peak observed for BiP is different from that expected for Bi metal.

Examination of the phosphorus 2p region of the XPS spectrum of unetched **1a** revealed the presence of peaks at 130.1 and 133.8 eV.[23] On etching, a slight loss of surface phosphorus was observed together with minor changes in the P(2p) binding energies (130.0 and 133.9 eV). Since the P(2p) binding energies for BP (130.3 eV), GaP (128.8 eV), and InP (129.5 eV)[21] are very close to 130.0 eV, we propose that the 130.0 eV peak is due to **1a** while the other, at 139.9 eV, is due to a phosphorus oxo species. We note, however, that red phosphorus exhibits a peak at 130.0 eV in the XPS.[21]

Compound **1a** was also investigated by solid-state MAS ^{31}P NMR spectroscopy (observing phosphorus directly). The principal feature in the spectrum (obtained using a 60 s delay) was a broad signal at ca. δ -2 (reference H_3PO_4), although this is not easy to interpret because of the paucity of published ^{31}P NMR data for element phosphides from which comparisons can be made. Moreover, there is also very little published ^{31}P NMR data concerning the allotropes of phosphorus itself, a detailed study of which would afford valuable information. It is clear that the observed signal for **1a** is not due to the presence of white phosphorus, which resonates at δ -462,[24] and a chemical shift of -2 ppm is also quite different from a value of δ $+50$ which has previously been obtained for red

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[20] For any Bi 4f signal, two peaks are always observed due to spin−orbit coupling effects ($4f_{7/2}$ and $4f_{5/2}$). These two peaks are always separated by 5.3 eV, so only the position of the lower binding energy $4f_{7/2}$ peak is quoted.

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[22] Briggs, D.; Seah, M. P. *Practical Surface Analysis*, 2nd ed.; Wiley: Chichester, 1990.

[23] Phosphorus 2p XPS peaks are also split into doublets ($2p_{3/2}$ and $2p_{1/2}$) but the small separation of 0.8 eV is such that this splitting is often not resolved.

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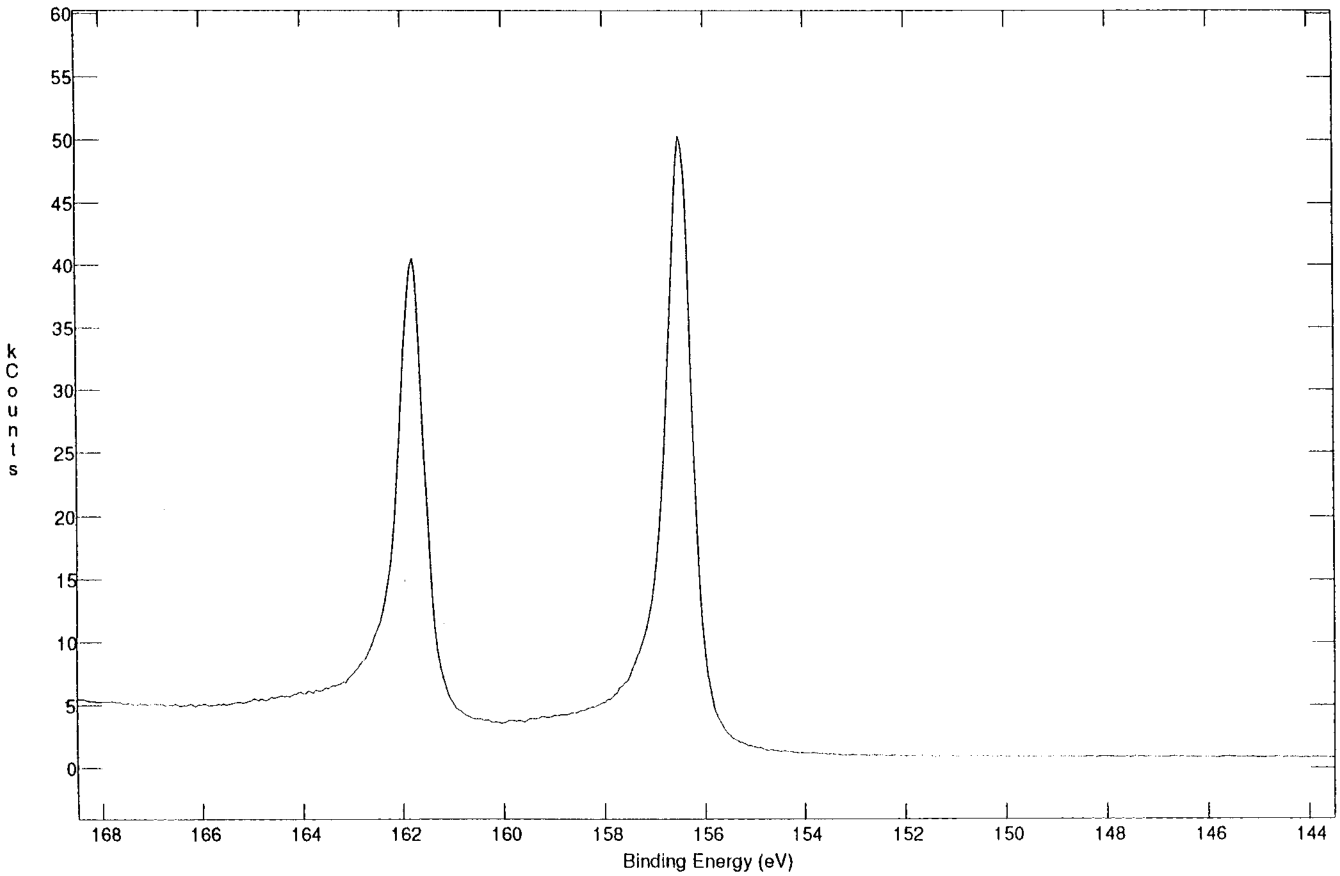

Figure 3. XPS spectrum of an etched surface of **1a** showing the Bi 4f binding energies.

phosphorus.[25] Red phosphorus, however, is a somewhat structurally ill-defined material. We have also sought to obtain ^{31}P NMR data for samples of red phosphorus since any elemental phosphorus present in **1a** could be in an amorphous form akin to this allotrope. For one sample, we observed a signal at ca. δ +5 using a 0.5 s delay, although when a 60 s delay was used, the spectrum became more complicated with broad resonances appearing at δ +54 and +7; for a second sample, obtained with a 60 s delay, broad signals were observed at ca. δ +92 and +4. Any detailed discussion of the various spectra obtained for red phosphorus samples is not warranted here (although the fact that different spectra are observed when different delay times are used indicates that the samples probably contain both crystalline and amorphous components, the former having a faster relaxation rate such that they are effectively saturated when measurements are made with a short delay) but while it is evident that none of the spectra correspond exactly to what is observed for **1a**, in the absence of more data for elemental phosphorus, it is not possible to decide whether the phosphorus present in **1a** exists in compound or elementary form.

As mentioned in the Introduction, the isoelectronic relationship between PbS and BiP were reason to expect that the electronic properties of **1a** might be interesting. Preliminary conductivity studies[26] on a pressed thin disk of **1a** indicate that this material is a semiconductor, with an activation energy (bandgap) of similar magnitude to that of PbS (0.37 eV). As anticipated on the basis of electronegativity differences, the bandgaps of the group 13 phosphides GaP (2.24 eV)[27] and InP (1.27 eV)[27] are significantly larger than that of BiP. It is important to point out, however, that our value for the BiP bandgap should be regarded as preliminary because of the sensitivity of the conductivity measurements to the degree of crystallinity of the sample and the nature of any grain boundaries present. Ultraviolet photoelectron spectroscopy (UPS) is a method by which the bandgap may be measured directly and we have carried out a UPS analysis of **1a**, but since the resolution of the spectrometer is only about 0.5 eV, it has not been possible to obtain a direct measurement of the bandgap in this way. We note, however, that the UPS spectra for **1a** and bismuth metal appear quite different.

Preliminary thermolysis experiments were carried out by heating samples of **1a** in an evacuated ampule which was connected to a vacuum line by means of a liquid nitrogen cooled trap. Initial heating of **1a** to 300 °C resulted in the condensation of traces of Me_3SiCl in the trap (identified by ^{1}H NMR spectroscopy) while further heating of the sample at this temperature, followed by a temperature increase to 500 °C, resulted in the sublimation of some white phosphorus and examination of the dark gray residue by EDXA revealed that it comprised 95% bismuth and 5% phosphorus. Thermogravimetric analysis (TGA) of **1a** confirmed that no weight loss occurred before 500 °C (in fact there was some weight gain possibly due to sample oxidation), whereas a similar experiment carried out on a mixed, ground sample of elemental bismuth and red phosphorus showed a sharp weight loss of about 20% at 400 °C most likely corresponding to the loss of phosphorus as

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P_4. Moreover, differential scanning calorimetry (DSC) studies of the latter sample showed a substantial endotherm at about 250 °C corresponding to the melting of the elemental bismuth, and, although this feature was also present in a DSC profile of **1a**, it was much less marked. Both these TGA and DSC data are therefore consistent with **1a** being a compound as opposed to a mixture of the elements although possibly containing traces of metallic bismuth consistent with the powder XRD data.

Alternative Routes to Bismuth Phosphide

Two alternative routes to bismuth phosphide have been explored. One such route was based on a method which has been used for the preparation of nanocrystalline 13−15 semiconductors such as GaP.[28] This approach involved the in situ preparation of Na_3P from sodium metal and white phosphorus in refluxing toluene, followed by reaction of the resulting suspension with one equivalent of $BiCl_3$ at 0 °C as shown in eq 2.

$$Na_3P + BiCl_3 \rightarrow BiP + 3NaCl \qquad (2)$$

After 24 h, a black precipitate (**1b**) was obtained which was subsequently washed with aqueous ethanol to remove the NaCl. As in the case of the silyl halide elimination reactions (eq 1), the reaction conditions are much milder for $BiCl_3$ than for the group 13 trihalides which require refluxing in toluene for 2 days.

An EDXA spectrum of **1b** revealed a uniform surface composition of bismuth and phosphorus with minimal impurities due to sodium and oxygen. A more quantitative EDXA analysis of **1b** over a number of sites showed a Bi:P atom ratio of 1:1.05 in good agreement with the expected ratio of 1:1. The uniformity of the material was confirmed by SEM, but as in the case of **1a**, no crystallites were observed in these experiments.

The second alternative synthesis of bismuth phosphide involved the elimination of a silylamine as shown in eq 3 and was based on a similar method which has

$$Bi(NMe_2)_3 + P(SiMe_3)_3 \rightarrow BiP + 3Me_3Si(NMe_2) \qquad (3)$$

been employed in the preparation of polycrystalline powders of Sb_2Te_3 and Bi_2Te_3 from the reactions between $Sb(NMe_2)_3$ or $Bi(NMe_2)_3$ and $Te(SiMe_3)_2$ at low temperature.[29] The reaction of equimolar quantities of $Bi(NMe_2)_3$ and $P(SiMe_3)_3$ in toluene solution at room temperature resulted initially in the formation of a black precipitate **1c**, followed by the deposition of a silver mirror onto the glass wall of the reaction flask. An EDXA analysis of **1c** after removal of all volatiles showed the presence of bismuth and phosphorus, but there was clearly less phosphorus than that required for a 1:1 Bi:P stoichiometry. Furthermore, a more quantitative EDXA analysis showed the presence of both BiP and metallic Bi and an overall Bi:P atom ratio of 1:0.52. Clearly, at this stage, this method of preparation of bismuth phosphide is less satisfactory than either of the routes shown in eqs 1 and 2. Nevertheless, it will be worthwhile to explore other reaction conditions and the use of alternative bismuth sources such as bismuth alkoxides and a variety of other bismuth amides, the focal point of these ongoing studies being the preparation of thin films of BiP by CVD methods since both $Bi(NMe_2)_3$ and $P(SiMe_3)_3$ have appreciable volatility.

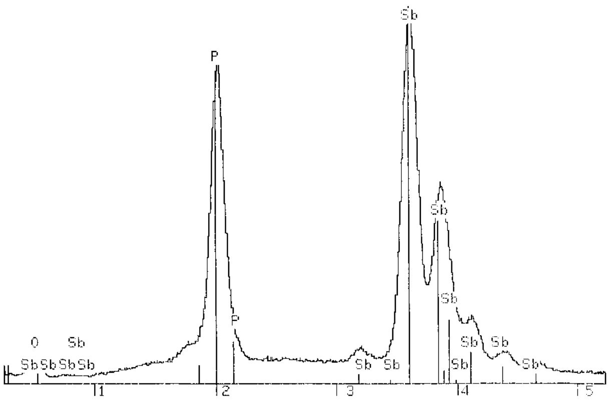

Figure 4. EDXA spectrum (in keV) for **2**.

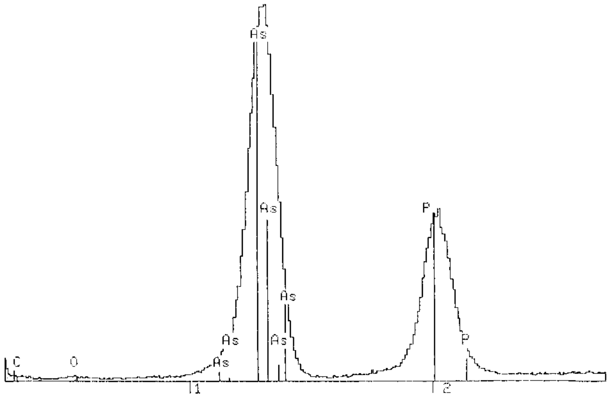

Figure 5. EDXA spectrum (in keV) for **3**.

Preparation and Properties of Antimony and Arsenic Phosphides

Given the success of the silyl chloride elimination route in the preparation of bismuth phosphide, it was decided to employ the same methodology as shown in eq 1 for the preparation of antimony and arsenic phosphides. The reactions of either $SbCl_3$ or $AsCl_3$ with $P(SiMe_3)_3$ in toluene solution occurred readily at room temperature and resulted in black and brown precipitates of materials formulated as SbP (**2**) and AsP (**3**), respectively. Empirical elemental compositions for **2** and **3** were established on the basis of elemental analytical data which also revealed the presence of only trace quantities of carbon, hydrogen, silicon, and chlorine. From EDXA analyses it was established that the surfaces of **2** (Figure 4) and **3** (Figure 5) were of uniform composition comprising either antimony or arsenic and phosphorus. Contamination due to carbon, oxygen, silicon, and chlorine was minimal (<1−2%), and more quantitative EDXA analyses showed that the ratio of either Sb or As to P over a number of sites (seven sites for **2** and two sites for **3**) was close to 1:1 in both cases with a variation of about ±2%.

Examination of the surfaces of **2** and **3** by SEM revealed that both possessed a uniform appearance but, while the surface of **2** resembled that of **1a**, a micrograph of **3** (Figure 6) was indicative of a layer type material.

Solid-state MAS ^{31}P NMR spectra, observing phosphorus directly, were obtained for both **2** and **3**. In the

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[29] Groshens, T. J.; Gedridge Jr., R. W.; Lowe-Ma, C. K. *Chem. Mater.* **1994**, *6*, 727.

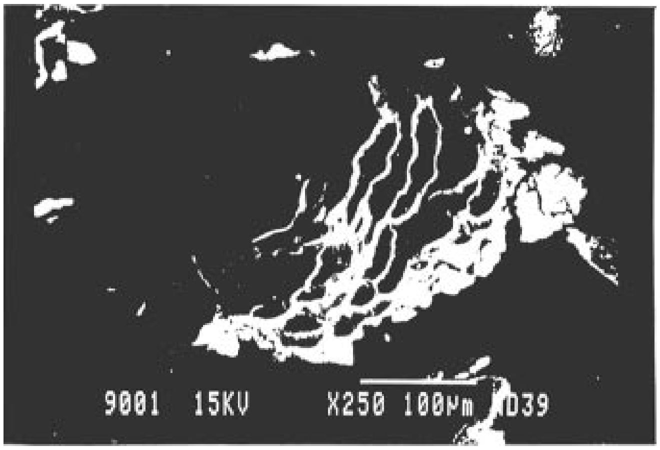

Figure 6. SEM of **3**.

case of **2**, a broad signal was observed at ca. δ −13 using a delay of 0.5 s, whereas with a delay of 60 s, a broad resonance was seen at ca. −6 ppm, these spectra being similar to that observed for **1a**. In the case of **3**, however, the spectra obtained were rather different from either **1a**/**2** or red phosphorus. Thus with a 0.5 s delay, three sharp signals of roughly equal intensity were observed at δ +10, +5, and 0, while with a delay of 60 s, two signals were observed at δ +7 and 0, the former being the more intense. Clearly, the phosphorus present in **1a** and **2** would seem to be in a similar environment, whereas for **3** a significantly different environment is indicated. However, as for the discussion for the solid-state ^{31}P NMR data for **1a**, in the absence of much definitive data for element phosphides or elemental phosphorus, it is not possible to be more specific as to the nature of the phosphorus present.

Further insights into the chemical composition of **2** and **3** were obtained from XPS studies. As in the case of **1a**, the unetched surface of **2** was somewhat heterogeneous as evidenced by the appearance of two peaks in the Sb($3d_{5/2}$) binding region (528.6 and 530.3 eV).[30] Since the Sb($3d_{5/2}$) peak at 530.3 eV disappeared on etching, it is attributed to an antimony oxide species (the binding energy of Sb_2O_3 is 530.0 eV[21]). The peak at 528.4 eV (postetch value) is therefore assigned to SbP. Although this Sb($3d_{5/2}$) binding energy is close to that reported for metallic antimony (528.1 eV[21]), it should be noted that there is very little change of binding energy on proceeding to the antimonides InSb (528.0 eV) and AlSb (526.6 eV).[21] The observations made in the P(2p) region of the spectra of **2** and **3** are similar to that discussed for **1a**. Thus, prior to etching, two peaks were evident (129.1 and 133.0 eV). Since the peak at higher binding energy disappeared on etching it was evidently due to a phosphorus oxo species and the peak at 129.6 eV (postetch value) is therefore assigned to SbP. As with **1a**, surface charging was much reduced after etching so that the binding energy values for the etched surface are likely to be more accurate although the possibility of surface reduction should not be ignored as in the case of **1a**.

For **3**, XPS analysis of an etched sample revealed an As(3d)[31] peak at 41.7 eV (cf. elemental As, 41.6 eV[21]) and a P(2p) peak at 129.7 eV (cf. red P, 130.0 eV[21]). As in the case of **1a** and **2**, the As(3d) binding energy is virtually identical with that of the free element.

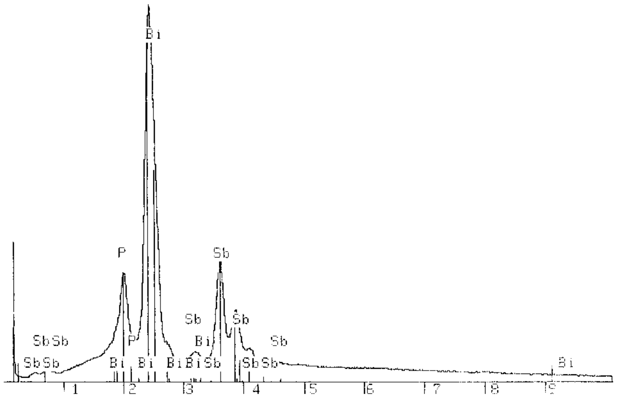

Figure 7. EDXA spectrum (in keV) for **4**.

Both **2** and **3** were examined by powder XRD but in both cases, the patterns obtained were entirely featureless, consistent with materials of an amorphous nature.

In addition to the binary phases **1**−**3** described above, preliminary experiments indicate that the silyl chloride elimination route (eq 1, X = Cl) is also viable for the preparation of ternary phases, and in this regard, we note the preparation of the 13−15 ternary phases Ga_xIn_yP and $InAs_xP_y$ by similar means as described by Wells and co-workers.[32] For example, a black material of composition $BiSbP_2$ (**4**) was prepared via the reaction between $SbCl_3$, $BiCl_3$, and 2 equiv of $P(SiMe_3)_3$ in toluene solution at room temperature as shown in eq 4.

$$BiCl_3 + SbCl_3 + 2P(SiMe_3)_3 \rightarrow BiSbP_2 + 6Me_3SiCl \quad (4)$$

Evidence for **4** being the ternary phase, $BiSbP_2$, was obtained from an EDXA analysis (Figure 7), which showed minimal levels of impurities. A more quantitative analysis over a number of sites revealed an atom ratio of Sb:Bi:P of 1:0.9:1.7 with a variation of about ±2%, in reasonable agreement with the expected 1:1:2 ratio.

Initial experiments also indicate that the analogous arsenides, BiAs (**5**) and SbAs (**6**), can be prepared by a similar method to that employed for the synthesis of the binary phosphides **1a**, **2** and **3** but using $As(SiMe_3)_3$ instead of $P(SiMe_3)_3$, as shown in eq 5. Thus, the

$$ECl_3 + As(SiMe_3)_3 \rightarrow EAs + 3Me_3SiCl \quad (5)$$

$$E = Sb, Bi$$

reaction of either $BiCl_3$ or $SbCl_3$ with 1 equiv of $As(SiMe_3)_3$ in toluene solution at room temperature resulted in the immediate formation of black precipitates of **5** and **6**, respectively. EDXA analysis of **5** (Figure 8) and **6** (Figure 9) showed primarily Bi or Sb and As and more quantitative analyses revealed that the atom ratio of either Bi or Sb to As was close to 1:1 in each case. The XPS of an etched surface of **5** revealed peaks with Bi($4f_{7/2}$) binding energies of 157.2 and 159.7

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[30] For any Sb 3d signal, two peaks are always observed due to spin−orbit coupling effects ($3d_{5/2}$ and $3d_{3/2}$). These two peaks are always separated by 9.4 eV, so only the position of the lower binding energy $3d_{5/2}$ peak is quoted.

[31] As 3d peaks are separated by a splitting of 0.7 eV which is usually not resolved, so the value quoted is an average.

[32] Halaoui, L. I.; Kher, S. S.; Lube, M. S.; Aubuchon, S. R.; Hagan, C. R. S.; Wells, R. L.; Coury, L. A. *ACS Symposium Ser., Nanotechnology: Molecularly Designed Materials*; Chow, G.-M., Gonsalves, K. E., Eds.; American Chemical Society: Washington, DC, 1996; Chapter 12, p 622.

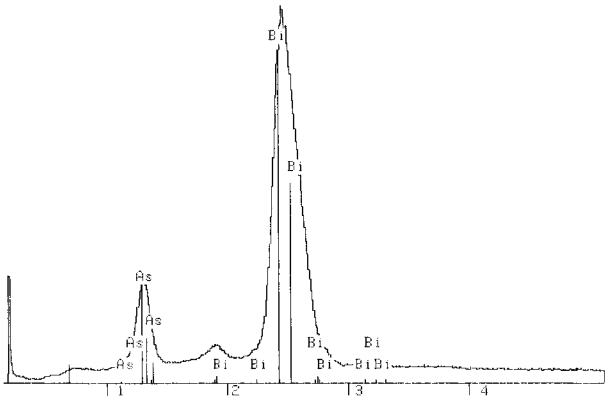

Figure 8. EDXA spectrum (in keV) for **5**.

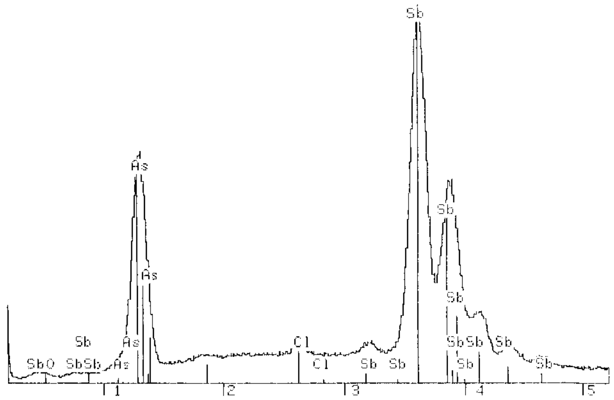

Figure 9. EDXA spectrum (in keV) for **6**.

eV, the latter of which is assigned to a bismuth oxide phase and the former to **5** (cf. 157.0 eV for **1a**). Similarly, of the two As(3d) peaks with binding energies of 41.9 and 44.8 eV, the former is assigned to **5** and the latter to an oxo species, some of which thus clearly remains after etching in this case.

As a final experiment, we treated PCl_3 with $P(SiMe_3)_3$ with the expectation of preparing a form of elemental phosphorus. On addition of the two reagents in toluene, an orange precipitate **7** formed, an EDXA spectrum for which showed the presence of phosphorus with only traces of chlorine and residual silicon.

Conclusions

In summary, elemental analytical, EDXA, XPS, powder XRD, solid-state ^{31}P NMR spectroscopy, preliminary conductivity, UPS, TGA, and DSC data for the product of the reaction between $BiCl_3$ and $P(SiMe_3)_3$ (**1a**) are consistent with the formation of a material of composition BiP although the data do not allow us to completely rule out the possibility that the predominant species present are elemental bismuth and phosphorus. In the case of the XPS data, this is not of particular concern because the Bi(4f) and P(2p) binding energies for BiP are not expected to differ greatly from those of the elements themselves in view of the relatively small electronegativity difference between these elements. Moreover, the EDXA analyses reveal that the atom ratios are consistently close to 1:1 and consonant with a compound of formulation BiP; in the event that the material formed were simply an intermixed precipitate of the two elements, more variation in the observed atom ratios might be expected. Similar analyses are also consistent with the formation of the materials SbP, AsP, $BiSbP_2$, BiAs, and SbAs, albeit with the proviso that as in the case of BiP, XPS data do not allow a clear distinction to be made between the elements themselves and the presumed compounds. Alternative routes to BiP have also been examined although at this stage, the silyl chloride elimination method is preferable.

Further studies are in progress in an effort to prepare better quality samples, preferably of a crystalline nature, whereby some indication of the structure can be gained from either X-ray or electron diffraction techniques.

Experimental Section

General Procedures. All preparations were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen or argon. All solvents were distilled from appropriate drying agents immediately prior to use (sodium for toluene, sodium/benzophenone for THF). The halides $BiCl_3$ (99%+), $SbCl_3$ (99%+), $AsCl_3$, and PCl_3 were procured commercially and either used without further purification in the case of $BiCl_3$ and $SbCl_3$ (if some insoluble residue was present on dissolution of either $BiCl_3$ or $SbCl_3$, this was first removed by filtration) or purified by distillation in the case of $AsCl_3$ and PCl_3. The compounds $Bi(NMe_2)_3$,[33] $P(SiMe_3)_3$,[34] and $As(SiMe_3)_3$[35] were prepared according to literature methods.

SEM data were obtained on a Hitachi S2300 instrument with a Link beryllium window/thin window/windowless detector and the images were downloaded in PC format for processing and on a JEOL JSM 820 instrument equipped with a Kevex quantum detector delta 4 and Kevex Quantex 6.2 software. Quantitative EDXA data were also obtained on the latter instrument, whereas standard EDXA analyses were carried out on the same instrument using Thompson WinEDS PC-based acquisition and processing software. XPS analyses were carried out on a Vacuum Generators ESCAscope imaging XPS instrument using Mg Kα radiation and the associated Vacuum Generators processing software. UPS data were also obtained on this instrument using a helium discharge lamp radiation source operating at 21.2 eV. Samples for EDXA, SEM, and XPS were mounted on either copper tape or silicon wafers. Powder XRD data were obtained on a Siemens D5000 transmission powder diffractometer using germanium monochromated copper Kα radiation (1.504 Å). Solid-state ^{31}P NMR measurements were made on a Bruker MSL 300 spectrometer using single pulse excitation with either 60 or 0.5 s pulse delays at a resonance frequency of 121.496 MHz. Chemical shifts were measured relative to 85% H_3PO_4 and spectral widths were of the order of 125 kHz with samples being spun at 10−12 kHz; all samples were handled and packed under a dinitrogen atmosphere.

Preparations. *BiP (1)*: BiP was prepared by one of three methods: (a) Preparation of **1a**: In a typical experiment, a sample of $P(SiMe_3)_3$ (0.5 mL, 1.72 mmol) was added dropwise to a stirred solution of $BiCl_3$ (0.542 g, 1.72 mmol) in toluene (15 mL) at room temperature resulting in the immediate formation of a black precipitate. The reaction mixture was allowed to stir for a further 1 h after which time the black solid was allowed to settle and the solvent was removed by syringe. The black solid was then washed three times with fresh toluene and then pumped to dryness (0.350 g, 85% yield assuming a composition of BiP). Complete elemental analysis on one such sample gave the following percentage composition (calculated values in parentheses): Bi, 78.80 (87.10); P, 12.30 (12.90); C, 1.45 (0.00); H, 0.20 (0.00); Cl, 0.50 (0.00); Si, 1.60 (0.00), ratio Bi:P = 1:1.05, total 94.85%.

THF can also be used as a solvent for this reaction but regardless of whether this solvent or toluene is used, the resulting powders are often rather pyrophoric probably due

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(33) Carmalt, C. J.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Moenandar, I.; Norman, N. C. *Inorg. Synth.* **1996**, *31*, 98.

(34) Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. *Inorg. Synth.* **1990**, *27*, 243.

(35) Wells, R. L.; Self, M. F.; Johansen, J. D.; Laske, J. A.; Aubuchon, S. R.; Jones III, L. J. *Inorg. Synth.* **1996**, *31*, 150.

to the presence of residual surface P−$SiMe_3$ functions. Washing the product with EtOH afforded materials that were much more easily handled.

Quantitative EDXA data obtained for a sample of **1a** for two different surface sites gave the following relative atom percentages: Bi:P 54:46, 54:46, av 54:46; Bi:P ratio 1:0.86.

(b) Preparation of **1b**: White phosphorus (0.085 g, 2.74 mmol) was placed in a three-necked 100 mL round-bottom flask and washed with THF (10 mL) to remove any traces of water. Toluene (40 mL) and sodium (0.144 g, 6.25 mmol) were then added, and the mixture was refluxed for 2 days. A black suspension resulted which was allowed to cool slowly to room temperature. A solution of $BiCl_3$ (0.657 g, 2.083 mmol) in THF (20 mL) was then added to the black suspension at 0 °C and the mixture was stirred at room temperature for 24 h resulting in a black precipitate. The black solid was allowed to settle, and the solvent was removed by syringe and ethanol (10 mL) was added to remove any residual Na_3P followed by the addition of distilled, degassed water (15 mL) to remove any NaCl. This procedure was repeated three times and followed by a final addition of ethanol (10 mL) to aid in the drying of the black precipitate, which was then pumped to dryness (0.466 g, 93% yield assuming the composition BiP).

Quantitative EDXA data obtained for a sample of **1b** for three different surface sites gave the following relative atom percentages: Bi:P 50:50, 51:49, 45:55; av 49:51; Bi:P ratio 1:1.05.

(c) Preparation of **1c**: A sample of $P(SiMe_3)_3$ (0.41 mL, 1.38 mmol) was added dropwise to a freshly prepared, stirred solution of $Bi(NMe_2)_3$ (0.400 g, 1.17 mmol) in toluene (10 mL) at room temperature, which resulted in the immediate formation of a black precipitate. However, after a few minutes, a silvery mirror was observed on the inside of the flask. The reaction mixture was allowed to stir overnight, after which time the black solid was allowed to settle and the solvent was removed by syringe. The solid was then washed three times with fresh toluene and then pumped to dryness (0.262 g, 93% yield assuming a composition of BiP).

Quantitative EDXA data obtained for a sample of **1c** for three different surface sites gave the following relative atom percentages: Bi:P 53:47, 68:32, 76:24, av 66:34; Bi:P ratio 1:0.52, showing that this material is far from homogeneous.

Thermolysis of 1a: A sample of **1a** was placed in an ampule and heated under vacuum to 550 °C using a furnace. Any volatiles given off were collected in a liquid nitrogen trap. A dark gray solid residue remained and a small amount of condensable liquid was collected in the nitrogen trap which was identified as Me_3SiCl by ^1H NMR (δ +1.2).

Quantitative EDXA data for two different surface sites of the remaining gray solid gave the following relative atom percentages: Bi:P 95:6, 93:7, av 94:6; Bi:P ratio 1:0.06.

SbP (**2**): A sample of $P(SiMe_3)_3$ (1.0 mL, 3.34 mmol) was added dropwise to a stirred solution of $SbCl_3$ (0.761 g, 3.44 mmol) in toluene (20 mL) at room temperature, which resulted in the immediate formation of a black precipitate. The reaction mixture was allowed to stir for a further 2 h, after which time the black solid was allowed to settle overnight. The solvent was then removed by syringe and the residue was washed three times with fresh toluene and then pumped to dryness (0.381 g, 75% yield assuming the composition SbP). Complete elemental analysis on one such sample gave the following atom percentages (calculated values in parentheses): Sb, 73.90 (79.70); P, 16.50 (20.30); C, 2.00 (0.00); H, 0.55 (0.00); Cl, 0.65 (0.00); Si, 1.50 (0.00), ratio Sb:P = 1:0.88, total 95.13%.

Quantitative EDXA data obtained for a sample of **2** for seven different surface sites gave the following relative atom percentages: Sb:P 53:47, 51:49, 54:46, 53:47, 51:49, 50:50, 51:49, av 52:48; Sb:P ratio 1:0.93.

AsP (3): A sample of $P(SiMe_3)_3$ (1.5 mL, 5.17 mmol) was added dropwise to a stirred solution of $AsCl_3$ (0.43 mL, 5.17 mmol) in toluene (15 mL) at room temperature which resulted in the immediate formation of a brown precipitate. The reaction mixture was allowed to stir for a further 2 h, after which time the brown solid was allowed to settle overnight. The solvent was then removed by syringe and the residue was washed three times with fresh toluene and then pumped to dryness.

Quantitative EDXA data obtained for a sample of **3** for two different surface sites gave the following relative atom percentages: As:P 52:48, 51:49, av 51:49; As:P ratio 1:0.94.

$BiSbP_2$ (4): A sample of $P(SiMe_3)_3$ (1.0 mL, 3.34 mmol) was added dropwise to a stirred solution of $SbCl_3$ (0.393 g, 1.72 mmol) and $BiCl_3$ (0.543 g, 1.72 mmol) in toluene (40 mL) at room temperature which resulted in the immediate formation of a black precipitate. The reaction mixture was allowed to stir for a further 3 h, after which time the black solid was allowed to settle overnight. The solvent was then removed by syringe, and the residue was washed three times with fresh toluene and then pumped to dryness (0.608 g, 90% yield assuming the composition $BiSbP_2$).

Quantitative EDXA data obtained for a sample of **4** for two different surface sites gave the following relative atom percentages: Sb:Bi:P 27:24:49, 28:24:48, av 28:24:48; Sb:Bi:P ratio 1:0.86:1.74.

BiAs (5): A sample of $As(SiMe_3)_3$ (1.54 g, 5.23 mmol) was added dropwise to a stirred solution of $BiCl_3$ (1.58 g, 5.00 mmol) in toluene (40 mL) at room temperature which resulted in the immediate formation of a black precipitate. The reaction mixture was allowed to stir for a further 2 h, after which time the black solid was allowed to settle and the solvent was removed by syringe. The residue was then washed three times with fresh toluene and then pumped to dryness (1.38 g, 97% yield assuming the composition BiAs).

Quantitative EDXA data obtained for a sample of **5** for two different surface sites gave the following relative atom percentages: Bi:As 58:42, 58:42, av 58:42; Bi:As ratio 1:0.73.

SbAs (6): A sample of $As(SiMe_3)_3$ (1.48 g, 5.23 mmol) was added dropwise to a stirred solution of $SbCl_3$ (1.12 g, 4.90 mmol) in toluene (40 mL) at room temperature which resulted in the immediate formation of a black precipitate. The reaction mixture was allowed to stir for a further 2 h, after which time the black solid was allowed to settle and the solvent was removed by syringe. The solid was then washed three times with fresh toluene and then pumped to dryness (0.959 g, 99% yield assuming the composition SbAs).

Quantitative EDXA data obtained for a sample of **6** for two different surface sites gave the following relative atom percentages: Sb:As 40:60, 58:42, 44:56; av 47:52; Sb:As ratio 1:0.90.

P_x (7): A sample of PCl_3 (0.09 mL, 1.03 mmol) was added dropwise to a stirred solution of $P(SiMe_3)_3$ (0.3 mL, 1.03 mmol) in toluene (10 mL) at room temperature, resulting in the formation of a yellow solution, which rapidly darkened to orange, together with the formation of an orange precipitate. The reaction mixture was allowed to stir at room temperature for 2 h after which time the orange solid was allowed to settle overnight. The solvent was then removed by syringe, and the remaining solid washed three times with toluene (3 × 10 mL) and then dried by vacuum pumping (0.068 g, 107% assuming a composition of phosphorus only).

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