A Synthesis of Bismuth(III) Phosphide: the First Binary Phosphide of Bismuth

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The synthesis and preliminary characterisation of bismuth(III) phosphide, BiP, is described from the reaction between equimolar quantities of $BiCl_3$ and $P(SiMe_3)_3$.

Element phosphides, E_xP_y, are an important and structurally diverse class of compound, examples of which are known for most elements, although there are a few for which binary phosphides have not been characterised. Thus, in a recent and comprehensive review by von Schnering and Hönle,[1] it is reported that 'Bi, Hg and Pb form no binary phosphides at all' whilst Greenwood and Earnshaw[2] state that 'phosphorus forms binary compounds with all elements except Sb, Bi and the inert gases'. Indeed, solid-state binary compounds involving only elements of group 15 are in general quite poorly characterised, with the recent exception of phosphorus(V) nitride, P_3N_5, reported by Schnick,[3] although most of the heteronuclear diatomic molecules have been studied spectroscopically in the gas phase.

With particular reference to bismuth and phosphorus, molecular BiP has been studied spectroscopically,[4] but a survey of the early literature[5] reveals that a number of attempts to make a solid binary material incorporating these two elements resulted only in poorly characterised black powders. Any potential synthesis directly from the elements themselves is thwarted by the apparent insolubility of phosphorus in molten bismuth.[6] As part of our interest in the chemistry of bismuth, particularly the recent structural characterisation of the first Bi–P bonds in a range of bismuth(III) halide phosphine complexes,[7] we sought a synthetic route to bismuth(III) phosphide, $\{BiP\}_x$, and describe herein some preliminary results.

We were guided in our attempts to synthesise bismuth phosphide by the recent work of Wells *et al.*[8] and also of Barron *et al.*[9] and Buhro[10] concerning a synthesis of GaAs and related group 13–15 materials according to eqn. (1).

$$ECl_3 + E'(SiMe_3)_3 \rightarrow EE' + 3Me_3SiCl \qquad (1)$$

($E = Ga, In$; $E' = P, As$).

This method, which relies on the elimination of volatile Me_3SiCl and is driven by the strength of the Si–Cl bond, has been used in the preparation of solid GaP,[8b,c] GaAs,[8a,d] InAs[8a] and InP.[9] An initial reaction occurs rapidly in solution at room temperature or below to form a colourless species with the empirical formula $\{ECl_2E'(SiMe_3)_2\}$, which has been isolated and crystallographically characterised as a dimer in some cases. Heating of solid samples of this primary product to about 300 °C (650 °C for InP[9]) then results in elimination of the remaining 2 equiv. of Me_3SiCl and formation of the EE′ phase.

In contrast to the group 13–15 chemistry, treatment of a stirred solution of $BiCl_3$ in toluene with $P(SiMe_3)_3$ (1 equiv.) at room temperature led to the immediate formation of a black precipitate **1**.† Full elemental analytical data† for **1** was in accord with the formation of a material of composition close to BiP indicating that elimination of Me_3SiCl is much more facile here than in the analogous 13–15 reaction shown in eqn. (1), probably in part due to the relative weakness of the Bi–Cl bond. In an attempt to characterise **1** more fully, particularly with a view to determining whether this material was a genuine bismuth phosphide compound or merely an intimate admixture of elemental bismuth and phosphorus, a number of further analyses were carried out.

A solid-state MAS ^{31}P NMR spectrum of **1**, observing phosphorus directly, showed a broad signal centred at δ *ca.* +70 (ref. H_3PO_4) with three sharper but much less intense signals present as shoulders at δ −1.75, −11.40 and −21.70. These data are not easy to interpret fully although a chemical shift at δ +70 (which we presume is representative of the bulk material) is very unlikely to be to due to elemental P_4, for example, which resonates at δ −462.[11] There appears to be very little data available on the ^{31}P NMR chemical shifts for solid element phosphides from which more meaningful comparisons might be drawn.

An X-ray powder data set obtained for powdered **1** showed it to be essentially amorphous. Heating a sample of **1** to about 300 °C led initially to a very small amount of a condensible liquid (identified as Me_3SiCl by ^1H NMR) and subsequently to decomposition resulting in the sublimation of phosphorus (as P_4) and leaving metallic bismuth identified from its X-ray powder pattern.

Good evidence for **1** being BiP was obtained by energy dispersive X-ray analysis (EDXA)‡ which revealed a uniform surface composition of BiP (Fig. 1) with minimal impurities (<0.5–1%). No carbon, silicon or oxygen was observed over a number of surface sites indicating that any oxygen present is less than 1%. The data also indicated that the surface composition of **1** was uniform on seven or more spots, with detection areas of typically 1 μm, and therefore that **1** is very unlikely to be an intermixed precipitate of Bi and P.§ Moreover, scanning electron microscopy (SEM) (Fig. 2) revealed surfaces of uniform appearance, but no crystallites were observed which is consistent with the previously ascertained amorphous nature of the material (see above). Preliminary Bi XPS data are also consistent with the presence of a BiP compound rather than metallic bismuth.

In conclusion, the data we have obtained so far are consistent with the formation of a material which is primarily bismuth(III) phosphide from the reaction between $BiCl_3$ and $P(SiMe_3)_3$. Preliminary experiments indicate that SbP and AsP can be made in a similar manner using $SbCl_3$ and $AsCl_3$ respectively, and also that ternary phases with compositions such as $BiSbP_2$ and phosphorus rich phases such as BiP_3 can be made from reactions between $BiCl_3$–$SbCl_3$ or $BiCl_3$–PCl_3 mixtures and $P(SiMe_3)_3$ respectively. We are currently investi-

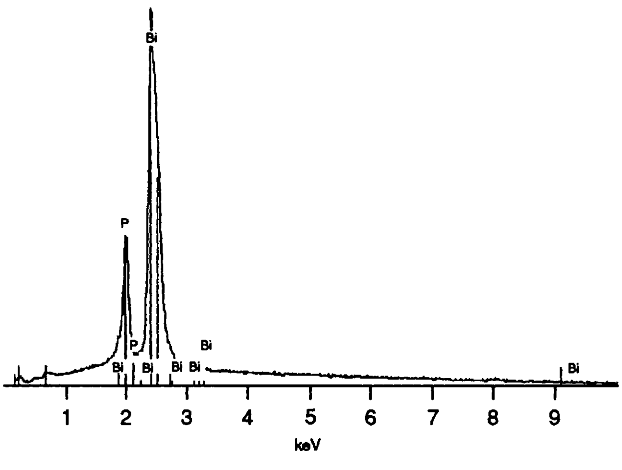

Fig. 1 An EDXA spectrum of **1** showing the presence of bismuth and phosphorus and indicating very low levels of impurities

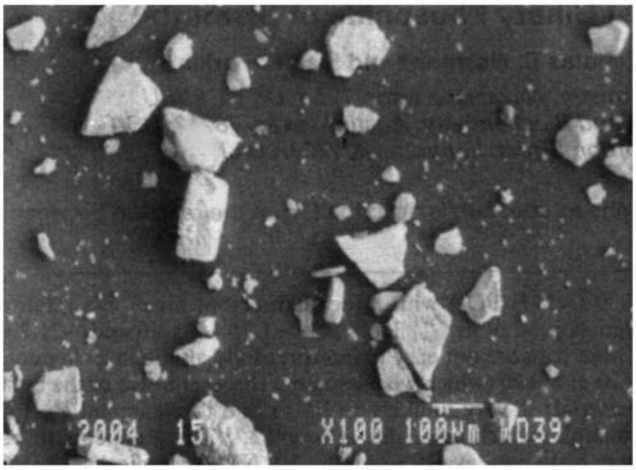

Fig. 2 A scanning electron micrograph (SEM) of **1** showing its homogeneous but non-crystalline nature

gating the electronic properties of **1** which should be interesting in view of its isoelectronic relationship with lead(II) sulfide, PbS.

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Footnotes

† A sample of $P(SiMe_3)_3$ (0.5 cm^3, 1.72 mmol) was added dropwise to a stirred solution of $BiCl_3$ (0.54 g, 1.72 mmol) in toluene (15 cm^3) at room temp. which resulted 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 solid was then washed three times with fresh toluene and then pumped to dryness (0.35 g, 85% assuming a composition of BiP). BiP requires Bi, 87.10; P, 12.90; C, 0.00; H, 0.00; Cl, 0.00; Si, 0.00. Found Bi, 78.80; P, 12.30; C, 1.45; H, 0.19; Cl, 0.50; Si, 1.62; Bi : P, 1 : 1.05, total 94.85%. Some of the remainder may be oxygen, although this is not evident in the EDXA data.

A sample prepared in an identical manner but using a slight excess of $BiCl_3$ afforded a black powder for which the analytical results were Bi, 76.85; P, 9.05; C, 1.35; H, 0.25; Cl, 10.40; Si, 0.15; total 98.05%. This gives a Bi : P ratio of 1 : 0.80. Assuming all the phosphorus is present as BiP (due to the very low amounts of C, H and Si) and that the remainder of the bismuth is present as $BiCl_3$, this gives an experimental Bi : Cl ratio of 1 : 3.85 which is close to the expected 1 : 3 ratio. In both experiments, removal of the $SiMe_3$ groups from the phosphorus is essentially complete.

‡ SEM and EDXA data were obtained on a JEOL JSM 820 instrument equipped with a Kevex quantum detector delta 4 and Kevex Quantex 6.2 software.

§ While the EDXA results do not demonstrate conclusively that **1** is not an intermixed precipitate, they do limit the scale of such a process to less than 1 µm. Moreover, the similarity of the EDXA spectra for many observed sites is suggestive of a compound rather than a mixture.

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