

Imino-bis(diisopropylphosphine chalcogenide) complexes of arsenic, antimony and bismuth. Synthesis, CVD studies and X-ray structure of $M[N(EP'Pr_2)_2]_n$ (E = Se, S; M = As, Sb, Bi)†

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Bismuth, and antimony complexes of imino-bis(diisopropylphosphine chalcogenide) ligands, $M[N(EP'Pr_2)_2]_n$ (E = S or Se; M = Bi and Sb) have been prepared by the reaction of the sodium salt of $NH(EP'Pr_2)_2$ (E = S or Se) with the appropriate group 15 metal salt in methanol. The complexes are monomeric in the solid state and air stable. The crystal structures of $Bi[(Pr_2PS)_2N]_3$ and $Sb[(Pr_2PS)_2N]_3$ have been determined by X-ray diffraction. The compounds are isostructural, with distorted octahedral coordination geometries and extended P–Se bonds. The bismuth compounds have been used in both AA-MOCVD and LP-MOCVD to deposit thin films of bismuth chalcogenide.

Introduction

Group 15 chalcogenides are at present of considerable interest owing to their potential use in a range of applications including as: semiconductors, optical data storage media, electro-active materials, thermoelectric coolers and photodiode arrays.^{1–3} In an expansion of our studies on group 12 and other transition-metal^{4–6} chalcogenide complexes as molecular single-source precursors for the fabrication of solid-state chalcogenide materials we report the synthesis and X-ray characterisation of a series of imino-bis(diisopropylphosphine chalcogenide) complexes of bismuth, antimony and arsenic.

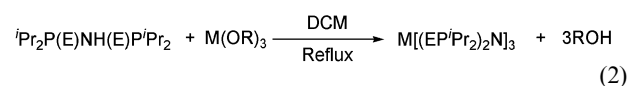
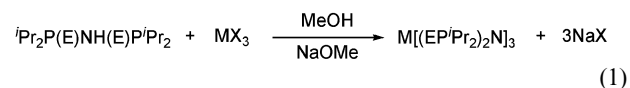
Narrow band gap semiconductor materials such as Bi_2S_3 , had until recently received scant attention as compared to other semiconducting metal chalcogenides such as CdS .⁶ For example whilst various bismuth- and antimony-based sulfur complexes have been studied,⁷ the selenium analogues are poorly represented with only handful of examples documented. Trindade and co-workers⁸ recently reported one of the first examples of the chemical vapour deposition (CVD) of Bi_2S_3 from the air-stable bismuth(III) dithiocarbamate complexes, $Bi(S_2CNRR')_3$ using LP-MOCVD. Bochmann *et al.*⁹ have demonstrated similar results using bulky thiolate and selenolate complexes of the type $M(EC_6H_2R'_3-2,4,6)_3$. However the latter method led to a final product contaminated with elemental bismuth/antimony. The present investigation was undertaken in order to test the suitability of dichalcogenoimidodiphosphanto compounds as molecular single source precursors for the preparation of group 15 chalcogenide solid-state materials.

Results and discussion

Dichalcogenoimidodiphosphanto anions $[R_2P(E)N-P(E)R_2]^-$ (where E = O, S and Se) are versatile ligands, with a strong tendency to form inorganic (carbon free) chelate rings.¹⁰ Transition metal complexes incorporating such ligands have demonstrated improved thermal and chemical stability over traditional organic based ligands such as β -diketonate complexes, which are susceptible to oxidation, polymerisation and

hydration,¹¹ they are hence excellent candidates as single source precursors for CVD⁶ and quantum dot synthesis.¹²

Dichalcogenoimidodiphosphanto compounds of bismuth and antimony are generally accessible *via* two alternative methods [eqns. (1) and (2); E = S or Se].



The interaction of metal halides (or nitrates) with the corresponding ligand [eqn. (1)] under basic methanolic conditions ($NaOCH_3/CH_3OH$) has the advantage of yielding compounds free of ionic impurities under very mild conditions.^{6,10} The dichalcogenoimidodiphosphanto ligands employed in this study are $NH(SeP'Pr_2)_2$ **1** and $NH(SP'Pr_2)_2$ **2**. The generation of **1** or **2**, in a one-pot synthesis from chlorodiisopropyl phosphine, is relatively straightforward and has been documented elsewhere.¹⁰

We have studied the reactions of **1** and **2** and their salts with group 15 metal salts.¹³ Improved complex formation was observed by reaction of **1** (or **2**) with sodium methoxide in anhydrous methanol yielding the sodium salt $NaN(PE'Pr_2)_2$. As *in-situ* treatment of $NaN(PE'Pr_2)_2$, with the appropriate group 15 metal salt yields compounds **3–6** in good-to-excellent yields. For example, the reaction of bismuth(III) nitrate pentahydrate with $NaN(PSe'Pr_2)_2$ directly produces $Bi[(Pr_2PSe)_2N]_3$ **3** as a deep-orange powder in 95% yield. The analogous reaction of **1** with antimony(III) chloride gave **4** as a brilliant orange powder in 29% yield. The analogous sulfur $Bi[(Pr_2PS)_2N]_3$ **5** and $Sb[(Pr_2PS)_2N]_3$ **6** compounds were prepared in a similar manner to the selenium precursors using **2**. Yields, typically, were similar to those obtained for **2** and **3**, respectively. Attempts to obtain arsenic sulfide- and selenide-precursors using the above method were generally unsuccessful. In some cases brown powders were obtained, however the material isolated decomposed readily at room temperature and gave inconsistent analyses.

† Dedicated to the memory of Professor Noel McAuliffe.

Complexes **3–6** all show good solubility in common organic solvents and are air-stable in the solid state for prolonged periods. The volatility characteristics of the precursors were determined by thermogravimetric analysis (TGA), showing clean sublimation without any residues, which is a desirable characteristic for compounds to be used as precursors for MOCVD.

AA-MOCVD and LP-MOCVD Studies

Bismuth chalcogenides are extensively used as laser-sensitive optical data storage media, especially selenides.^{1–3} We have investigated the suitability of compounds **3** and **5** for use as precursors for deposition of bismuth chalcogenide thin films on glass substrates by aerosol assisted- (AA) and low-pressure- (LP) MOCVD. Film deposition was achieved from compound **3** by AA-MOCVD at 475 °C with an argon gas flow rate of 140 sccm, yielding films of Bi₂Se₃ composed of polygonal grains in a dense base layer (Fig. 1). Study by XRD indicated that LP-MOCVD yielded films of rhombohedral Bi₂Se₃ (JCPDS: 33–214) at precursor temperatures of 225–275 °C, with substrate temperatures of 375–450 °C (Fig. 2). These films comprised dense layers of irregular grains. Some of the films grown at 400 °C, with a precursor temperature of 225 °C were shown by XRD to be a mixture of rhombohedral Bi₂Se₃ and hexagonal BiSe phases. However EDAX analysis on random sites of the film showed that Bi : Se ratio was close to 2 : 3. The variation of growth temperature can lead to changes in the phase of as deposited material¹⁴ as in a study of indium sulfide deposited from mixed alkyl dithiocarbamate indium precursors. However, changes in phase were not reproducible in this case in later experiments ($T_{\text{prec}} = 225$ °C, $T_{\text{subs}} = 400$ °C) predominantly resulted in single-phase Bi₂Se₃.

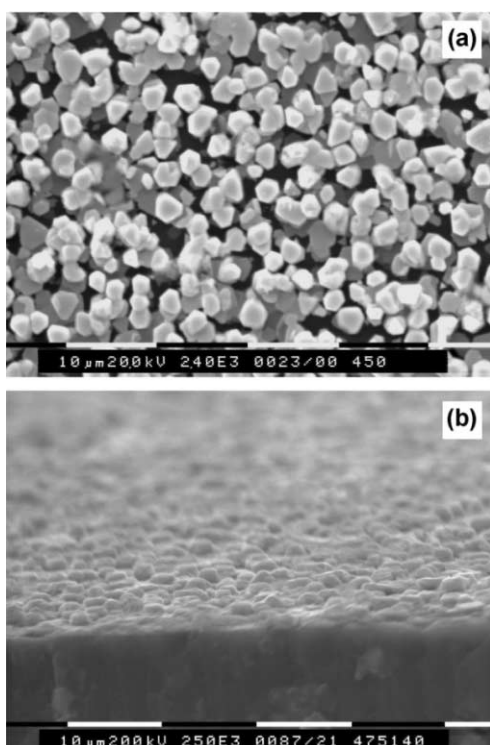


Fig. 1 SEM images of Bi₂Se₃ films grown on glass from compound **3** by AA-MOCVD at 475 °C.

AA-MOCVD of compound **5** led to deposition of grey films of orthorhombic Bi₂S₃ (JCPDS 43–1471), at 450–475 °C, with a carrier gas (Ar) flow rate of 140 sccm. Grey films of Bi₂S₃ were also produced by LP-MOCVD of compound **5** at a precursor temperature of 250 °C and substrate temperatures of 350–425 °C. EDAX analysis of these films confirmed the presence of

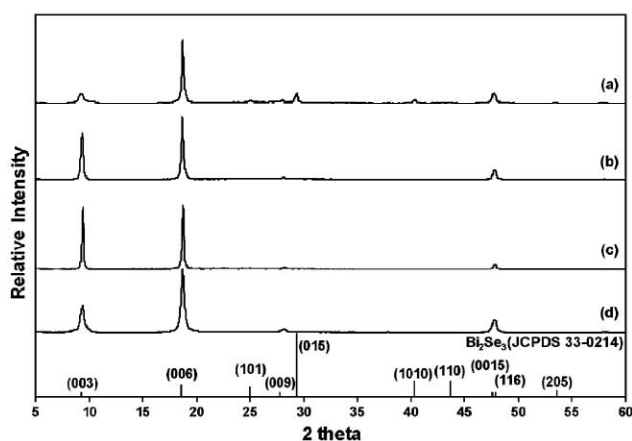


Fig. 2 XRD patterns of Bi₂Se₃ films grown on glass by LP-MOCVD of Bi[(SePPr₂)₂N]₃ at (a) $T_{\text{prec}} = 275$ °C, $T_{\text{subs}} = 425$ °C, (b) $T_{\text{prec}} = 225$ °C, $T_{\text{subs}} = 425$ °C, (c) $T_{\text{prec}} = 225$ °C, $T_{\text{subs}} = 400$ °C and (d) $T_{\text{prec}} = 225$ °C, $T_{\text{subs}} = 375$ °C.

bismuth and sulfur but those deposited by AA-MOCVD were sulfur deficient, whereas the films deposited by LP-MOCVD contained *ca.* 60% sulfur, in good agreement with the phase predicted by XRD. SEM studies showed the films deposited from AA-MOCVD to be composed of ribbons, whereas the films deposited by LP-MOCVD were seen to have a granular morphology.

Solid state structures

The monomeric nature of these materials in the solid state has been confirmed by single crystal X-ray analyses. These studies also showed the two compounds, Bi[(Pr₂PSe)₂N]₃ **3** and Sb[(Pr₂PSe)₂N]₃ **4** to be isomorphous (Table 1). Both structures have crystallographic C₂ symmetry about an axis passing through the metal centre and the nitrogen atom N(2) of one of the chelating ligands (Fig. 3). The coordination geometry around the metal centres is distorted octahedral,¹⁵ with *cis* angles in the range 79.39(4) to 103.50(4)° for **3** and 79.793(12) to 104.390(14)° for **4**, the most acute angles being inter-ligand (Table 2). In both structures the unique M–Se bond lengths differ significantly, ranging between 2.928(10) to 2.974(13) Å in **3** and between 2.869(3) and 2.927(4) Å in **4**. These differences are, however, not exceptional and even larger ranges of Bi–Se

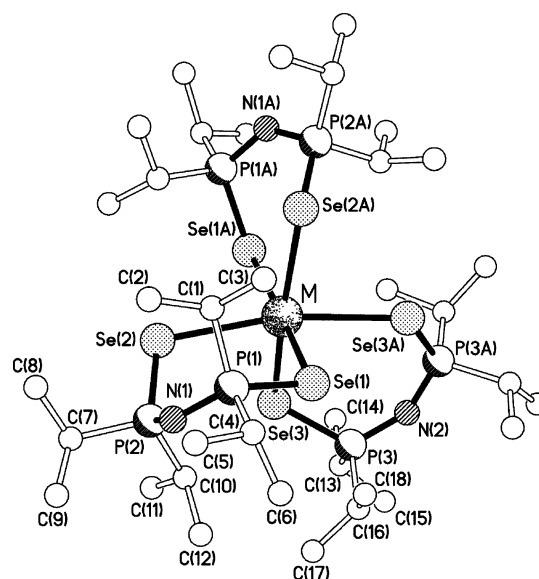


Fig. 3 X-Ray single crystal structure of isomorphous M[(Pr₂PSe)₂N]₃ frameworks (M = Bi or Sb) with symmetry operation $-x, y, 0.5-z$ for atoms A.

Table 1 Selected parameters for compounds (3) and (4)

Compound	(3)	(4)
Chemical formula	C ₃₆ H ₈₄ N ₃ P ₆ Se ₆ Bi	C ₃₆ H ₈₄ N ₃ P ₆ Se ₆ Sb
<i>M_r</i>	1427.62	1340.39
<i>T</i> /K	293(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i> (no. 15)	<i>C2/c</i> (no. 15)
Unit cell dimensions		
<i>a</i> /Å	25.300(3)	24.959(4)
<i>b</i> /Å	13.0081(14)	12.9416(17)
<i>c</i> /Å	19.672(3)	19.316(3)
β /°	120.203(10)	119.819(4)
<i>V</i> , Z	5595.1(11), 4	5413.1(14), 4
<i>D_c</i> /Mg m ⁻³	1.695	1.645
Radiation type	Mo-K α	Mo-K α
λ /Å	0.71073	0.71073
No of reflections for cell determination	28	248
θ range for cell determination/°	4.80–12.48	1.83–26.42
Crystal size/mm	0.43 × 0.33 × 0.33	0.25 × 0.25 × 0.20
Crystal colour	Red	Orange
Diffractometer	Siemens P4	Bruker APEX
μ /mm ⁻¹	7.252	4.749
<i>F</i> (000)	2792	2664
θ range for data collection/°	1.82–25.00	1.83–26.42
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 ≤ <i>h</i> ≤ 30 0 ≤ <i>k</i> ≤ 15 –23 ≤ <i>l</i> ≤ 20	–31 ≤ <i>h</i> ≤ 30 –15 ≤ <i>k</i> ≤ 16 –24 ≤ <i>l</i> ≤ 23
Reflections collected	4997	21220
Independent reflections (<i>R_{int}</i>)	4880 (0.0447)	5566 (0.0233)
Refinement method	Full matrix least squares	on <i>F</i> ²
Data/restraints/parameters	4385/0/237	5566/0/ 248
Goodness of fit on <i>F</i> ²	0.992	1.042
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0517 <i>wR</i> 2 = 0.0790	<i>R</i> 1 = 0.0181 <i>wR</i> 2 = 0.0418
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1059 <i>wR</i> 2 = 0.1107	<i>R</i> 1 = 0.0203 <i>wR</i> 2 = 0.0424
Extinction coefficient	0.00000(2)	–
Largest diff. peak and hole/e Å ⁻³	0.855 and –0.560	0.430 and –0.297
Structure solution	SHELXTL 5.03	SHELXS97
Structure refinement	SHELXTL 5.03	SHELXL97

Table 2 Selected bond distances (Å) and angles (°) for compounds (3) and (4)

	(3)	(4)
M–Se(1)	2.928(10)	2.873(4)
M–Se(2)	2.974(13)	2.927(4)
M–Se(3)	2.945(14)	2.869(3)
P(1)–N(1)	1.616(8)	1.604(15)
P(2)–N(1)	1.560(9)	1.595(15)
P(3)–N(2)	1.574(5)	1.585(9)
P(1)–Se(1)	2.185(3)	2.198(5)
P(2)–Se(2)	2.200(3)	2.200(6)
P(3)–Se(3)	2.184(3)	2.192(6)
Se(1)–M–Se(1A)	175.97(7)	175.562(10)
Se(1)–M–Se(2)	90.71(3)	91.226(12)
Se(1)–M–Se(2A)	86.77(4)	86.051(12)
Se(1)–M–Se(3)	103.50(5)	103.379(12)
Se(1)–M–Se(3A)	79.39(4)	79.793(12)
Se(2)–M–Se(3)	84.22(4)	83.099(12)
Se(2)–M–Se(2A)	102.78(6)	104.390(14)
Se(2)–M–Se(3A)	167.62(3)	167.986(6)
Se(3)–M–Se(3A)	90.82(5)	91.176(14)
N–P–Se	117.3(3)–119.5(5)	117.28(6)–120.55(7)
P–Se–M	106.55(9)–115.61(8)	106.502(18)–116.517(17)

and Sb–Se distances are observed in the solid state structures of the closely related Bi[(Ph₂PSe)₂N]₃ and Sb[(Ph₂PSe)₂N]₃ analogues.¹⁶ The chelate ring geometries in **3** and **4** are essentially identical, but within each structure distinct differences are observed. In **3** for example, the chelate ring containing Se(1) and Se(2) has Bi, Se(1), Se(2) and N(1) coplanar to within 0.01 Å with P(1) and P(2) lying, respectively, 0.81 Å above and below this plane, whereas in the ring containing Se(3) and Se(3A), Bi,

Se(3), Se(3A) and N(2) are coplanar and P(3) and P(3A) lie only 0.47 Å above and below, respectively. The P–Se bond lengths in the two structures, which lie in the range 2.184–2.200 Å, are appreciably increased compared to those (2.096–2.103 Å) seen in the structure of the free ligand **1**,¹⁰ whilst the P–N bond lengths are shortened (1.560–1.616 Å compared to 1.686–1.693 Å¹⁰) as a consequence of deprotonation and coordination. There are no intermolecular packing interactions of note.

Experimental

Unless otherwise stated all reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All glassware was flamed dried under vacuum prior to use. All solvents and reagents were purchased from Sigma–Aldrich chemical company and used as received. ¹Pr₂P–(Se)NHP(Se)¹Pr₂ **1** and ¹Pr₂P(S)NHP(S)¹Pr₂ **2** were synthesised from 1,1,1,3,3,3-hexamethyldisilazane according to literature methods.¹⁰ ¹H and ³¹P NMR studies were carried out using a Bruker AC300 FTNMR instrument. Mass spectra were recorded on a Kratos concept 1S instrument. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm⁻¹, resolution 4 cm⁻¹). Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

Bi[(¹Pr₂PSe)₂N]₃ (**3**)

Sodium methoxide (0.56 g, 9.82 mmol) was added to a stirred solution of **1** (4.00 g, 9.82 mmol) in anhydrous methanol (100 cm³). The resulting pink solution was stirred at room temperature for 10 min. Bismuth(III) nitrate pentahydrate (1.58 g, 3.27

mmol) was added and the reaction mixture stirred at room temperature for 2 h. The resulting suspension was filtered and the recovered solid washed with methanol (100 cm³) before drying under vacuum. Recrystallisation from chloroform–methanol yielded 4.41 g (95%) of deep orange powder (mp 251–254 °C); FT-IR (KBr): 1226, 761 (ν(P–N–P)), 429 (ν(P–Se)) cm⁻¹; ¹H NMR (CDCl₃): δ 1.32 (m, 72H, 24CH₃), 2.40 (m, 12H, 12CH); ³¹P{¹H} NMR (CDCl₃): δ 58.9 [m, 6SeP, ¹J(³¹P–⁷⁷Se) 571 Hz]; MS (MALDI-TOF): *m/z* 1428 (100%, M + H) (Found: C, 30.36; H, 6.14; N, 2.82; P, 12.83. C₃₆H₈₄N₃P₆Se₆Bi requires: C, 30.28; H, 5.93; N, 2.94; P, 13.01%).

Sb[(ⁱPr₂PSe)₂N]₃ (4)

Sodium methoxide (0.56 g, 9.82 mmol) was added to a stirred solution of **1** (4.00 g, 9.82 mmol) in anhydrous methanol (100 cm³). The resulting pink solution was stirred at room temperature for 10 min. Antimony(III) chloride (0.75 g, 3.27 mmol) was added and the reaction mixture stirred at room temperature for 3 h. The resulting suspension was filtered and the recovered solid washed with methanol (100 cm³) before drying under vacuum. Recrystallisation from chloroform–methanol yielded 1.40 g (29%) of orange powder (mp 197–200 °C); FT-IR (KBr): 1221, 763 (ν(P–N–P)), 425 (ν(P–Se)) cm⁻¹; ¹H NMR (CDCl₃): δ 1.23 (m, 72H, 24CH₃), 2.43 (m, 12H, 12CH); ³¹P{¹H} NMR (CDCl₃): δ 58.7 [m, 6SeP, ¹J(³¹P–⁷⁷Se) 562 Hz]; MS (MALDI-TOF): *m/z* 935 (25%, M – L), 858 (11%, M – L – Se), 408 (100%, L + H) (Found: C, 32.13; H, 6.18; N, 2.99; P, 13.90. C₃₆H₈₄N₃P₆Se₆Sb requires: C, 32.29; H, 6.32; N, 3.13; P, 13.86%).

Bi[(ⁱPr₂PS)₂N]₃ (5)

Sodium methoxide (0.56 g, 9.82 mmol) was added to a stirred solution of **2** (3.07 g, 9.82 mmol) in anhydrous methanol (100 cm³). The resulting pink solution was stirred at room temperature for 10 min. Bismuth(III) nitrate pentahydrate (1.58 g, 3.27 mmol) was added and the reaction mixture stirred at room temperature for 2 h. The resulting suspension was filtered and the recovered solid washed with methanol (100 cm³) before drying under vacuum. Recrystallisation from chloroform–methanol yielded 3.52 g (93%) of bright yellow powder (mp 171–174 °C); FT-IR (KBr): 1226, 761 (ν(P–N–P)), 538 (ν(P–S)) cm⁻¹; ¹H NMR (CDCl₃): δ 1.23 (m, 72H, 24CH₃), 2.45 (m, 12H, 12CH); ³¹P{¹H} NMR (CDCl₃): δ 59.9 (s, 6SP); MS (MALDI-TOF): *m/z* 1147 (20%, M + H), 834 (100% M – L) (Found: C, 37.82; H, 7.39; N, 3.59; P, 16.27; S, 16.92. C₃₆H₈₄N₃P₆S₆Bi requires C, 37.71; H, 7.38; N, 3.67; P, 16.21; S, 16.78%).

Sb[(ⁱPr₂PS)₂N]₃ (6)

Sodium methoxide (0.56 g, 9.82 mmol) was added to a stirred solution of **2** (3.07 g, 9.82 mmol) in anhydrous methanol (100 cm³). The resulting pink solution was stirred at room temperature for 10 min. Antimony(III) chloride (0.75 g, 3.27 mmol) was added and the reaction mixture stirred at room temperature for 2 h. The resulting suspension was filtered and the recovered solid washed with methanol (100 cm³) before drying under vacuum. Recrystallisation from chloroform–methanol yielded 1.07 g (31%) of pale cream powder (mp 282–285 °C); FT-IR (KBr): 1229, 764 (ν(P–N–P)), 536 (ν(P–S)) cm⁻¹; ¹H NMR (CDCl₃): δ 1.28 (m, 72H, 24CH₃), 2.41 (m, 12H, 12CH); ³¹P{¹H} NMR (CDCl₃): δ 59.8 (s, 6SP); MS (MALDI-TOF): *m/z* 747 (31%, M – L), 714 (22%, M – L – S), 408 (100%, L + H) (Found: C, 40.66; H, 7.71; N, 3.99; P, 17.39; S, 18.47. C₃₆H₈₄N₃P₆S₆Sb requires C, 40.83; H, 7.99; N, 3.97; P, 17.55; S, 18.17%).

X-Ray crystallography

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into dichloromethane solutions of the

appropriate compound. Single crystal structure determinations of **3** and **4** were carried out from data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Siemens P4 diffractometer for **3** and a Bruker APEX diffractometer for **4**. The structures were solved by Direct Methods^{17,18} and refined by full-matrix least squares on *F*².^{19,20} All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. The crystal data, data collection and refinement parameters are summarised in Table 1.

CCDC reference numbers 199591 and 199592.

See <http://www.rsc.org/suppdata/dt/b2/b212151d/> for crystallographic data in CIF or other electronic format.

CVD Experimental

Preparation of thin films by LP-MOCVD. A cold wall, horizontal reactor was used. The glass substrates were heated by a tungsten halogen lamp and precursor by a Carbolite tube furnace with the system under a dynamic vacuum at ≈10⁻² Torr. The precursors, as above (~200 mg) were used in each experiment, over growth periods of 60 min.

Preparation of thin films by AACVD. The precursor, (~200 mg) was dissolved in THF (30 cm³). The glass substrates were heated by a Carbolite tube-furnace. Aerosol droplets of the precursor solution were generated by the piezoelectric modulator of a humidifier. A Platon flow gauge controlled the flow of the argon carrier gas at constant flow rates of 140 and 200 sccm, carrying the aerosol droplets into the deposition chamber.

Characterisation of thin films. X-Ray powder diffraction studies were done on a Bruker AXS D8 diffractometer using monochromated Cu-Kα radiation. The samples were mounted flat and scanned from 5 to 90° in a step size of 0.01 or 0.02° with a count rate of 2 or 5 s. Films were carbon coated using an Edward's E306A coating system before SEM and EDAX analyses. SEM was carried out on a Philips XL30 FEG and EDAX was preformed using a DX4. Each AACVD experiment was carried out for 90 min.

Conclusion

This paper describes the synthesis and characterisation of imino-bis(diisopropylphosphine chalcogenide) complexes of bismuth, antimony and arsenic. These air stable complexes have been shown to be monomeric in the solid state by X-ray single crystal diffraction, possessing isostructurally distorted octahedral configurations, with extended P–Se bonds. Thermolytic decomposition of the bismuth precursors has been carried in the solid state using both AA-MOCVD and LP-MOCVD affording Bi₂E₃ thus illustrating that such dichalcogenoimido-diphosphato compounds are excellent candidates as molecular single source precursors for the preparation of group 15 chalcogenide solid-state materials

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