

BISMUTH(III) COMPLEXES
OF TETRAORGANODICALCOGENOIMIDODIPHOSPHINIC ACIDS.
CRYSTAL AND MOLECULAR STRUCTURE OF $\text{Bi}[(\text{SPMe}_2)(\text{SPPPh}_2)\text{N}]_3$
AND $\text{Bi}[(\text{OPPh}_2)_2\text{N}]_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}]$

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New 1:1 adducts of the type $\text{BiCl}_3[(\text{XPR}_2)(\text{YPR}'_2)\text{NH}]$ ($\text{R} = \text{R}' = \text{Ph}$, $\text{X} = \text{Y} = \text{O}$ (**1**), **S** (**2**); $\text{R} = \text{R}' = \text{Me}$, $\text{X} = \text{Y} = \text{S}$ (**3**); $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, $\text{X} = \text{Y} = \text{S}$ (**4**)) were prepared from anhydrous BiCl_3 and $(\text{XPR}_2)(\text{YPR}'_2)\text{NH}$. Reactions of anhydrous BiCl_3 and $\text{K}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]$ afforded isolation of the first bismuth(III) complexes of the type $\text{Bi}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_3$ [$\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, $\text{X} = \text{Y} = \text{S}$ (**5**); $\text{R} = \text{R}' = \text{Ph}$, $\text{X} = \text{O}$, $\text{Y} = \text{S}$ (**6**)] which contain asymmetric tetraorganodichalcogenoimidodiphosphinato ligands. The compounds were characterized by means of IR and multinuclear NMR spectroscopy. Attempts to grow single crystals of **6** resulted in isolation of the unexpected, partially oxidized derivative $\text{Bi}[(\text{OPPh}_2)_2\text{N}]_2[(\text{OPPh}_2)(\text{SPPPh}_2)\text{N}]$ (**7**). The crystal and molecular structure of **5** and **7** was determined by single-crystal X-ray diffraction. In both cases the crystals contain discrete molecules. For compound **5** two independent molecules are present in the unit cell and the main difference is the isobidentate [$\text{Bi-S } 2.8040(14) / 2.7959(14) \text{ \AA}$] and anisobidentate [$\text{Bi-S } 2.7234(16) / 2.8768(16) \text{ \AA}$] behavior of the SPNPS ligand in molecule **5a** vs. **5b**, respectively. As result of the monometallic biconnective (bidentate) pattern of the organophosphorus ligand moieties distorted octahedral BiO_6 and BiSO_5 cores are formed in compounds **5** and **7**, respectively.

INTRODUCTION

The coordination chemistry of tetraorganodichalcogenoimidodiphosphinato ligands, $[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]$ (**a**), raised considerable interest in last years due to (i) the high flexibility of the XPNPY skeleton which allows easy accommodation of the ligand unit to different coordination requirements related to a particular metal atom,¹ and (ii) potential applications of the corresponding metal complexes, e.g. NMR shift reagents,^{2,3} selective metal extractants,⁴ industrial uses as catalytic systems,⁵⁻⁷ or optical devices.⁸⁻¹¹ Several metal complexes of the type $\text{M}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_n$ (Ga ,¹² In ,^{12,13} Zn ,^{14,15} Cd ,^{14,16} Hg ¹⁷), including bismuth(III) derivatives,^{18,19} were

investigated as single-source precursors for metal chalcogenide materials.

So far, few $\text{Bi}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_3$ complexes were reported (Table 1), most of them containing symmetric phosphorus ligands, *i.e.* same chalcogen and organic groups attached to the phosphorus atoms in a ligand unit. The first functionalized organobismuth(III) derivatives of the type $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiCl}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]$ (X , $\text{Y} = \text{O}$, S , Se ; R , $\text{R}' = \text{Me}$, Ph) were recently reported.²⁸ Only very few adducts in which a tetraorganodichalcogenoimidodiphosphinic acid moiety is coordinated to a metal center [Al , Sn(II)] are known,¹ but no adducts between Bi(III) trihalides and $(\text{XPR}_2)(\text{YPR}'_2)\text{NH}$ were prepared and characterized so far.

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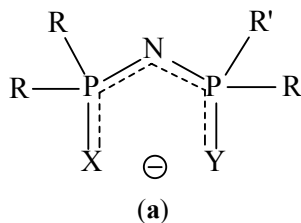


Table 1

Bismuth(III) complexes of dichalcogenoimidodiphosphinic acids.

Compound	Spectroscopic studies	Ref.
Bi[(OPPh ₂) ₂ N] ₃	³¹ P, MS, single-crystal X-ray	[20,21]
Bi[(SPMe ₂) ₂ N] ₃	¹ H	[22]
Bi[(SPPr ¹) ₂ N] ₃	IR, ¹ H, ³¹ P, MS, single-crystal X-ray	[19,23]
Bi[(SPPPh ₂) ₂ N] ₃ ·Me ₂ CO	³¹ P, single-crystal X-ray	[20,24]
Bi[(SePPr ¹) ₂ N] ₃	IR, ¹ H, ³¹ P, MS, single-crystal X-ray	[18,23]
Bi[(SePPPh ₂) ₂ N] ₃	IR, ³¹ P, MS, single-crystal X-ray	[25]
Bi[(SPPPh ₂)(SePPPh ₂)N] ₃ ·CH ₂ Cl ₂	³¹ P, ⁷⁷ Se, MS, single-crystal X-ray	[26]
Bi[(TePPr ¹) ₂ N] ₃	single-crystal X-ray	[27]

We report here on the synthesis and characterization of some new BiCl₃[(XPR₂)(YPR'₂)NH] and Bi[(XPR₂)(YPR'₂)N]₃ complexes as well as the crystal and molecular structure of Bi[(SPMe₂)(SPPPh₂)N]₃ and Bi[(OPPh₂)₂N]₂[(OPPh₂)(SPPPh₂)N].

anhydrous bismuth(III) trichloride with a dichalcogenoimidodiphosphinic acid in a 1:1 molar ratio, while metathesis reactions between the alkali salt of the appropriate imidodiphosphinic acid with anhydrous BiCl₃ in a 3:1 molar ratio, resulted in isolation of Bi[(XPR₂)(YPR'₂)N]₃ complexes, according to equation (2):

RESULTS

The 1:1 adducts BiCl₃[(XPR₂)(YPR'₂)NH] were obtained, according to equation (1), by reacting



	R	R'	X	Y
(1)	Ph	Ph	O	O
(2)	Ph	Ph	S	S
(3)	Me	Me	S	S
(4)	Me	Ph	S	S



	R	R'	X	Y
(5)	Me	Ph	S	S
(6)	Ph	Ph	O	S

Due to the oxygen and moisture sensitivity of the compounds, the preparation and the manipulation of the compounds were performed in argon atmosphere, using dried solvents distilled prior to use. Details of the preparations are given in the Experimental section. The 1:1 adducts were isolated as colorless (1) or yellow (2-4) solids, which exhibit a low solubility in common organic solvents. The complexes 5 and 6 were isolated as bright-yellow and white-yellow solids, respectively.

They are highly soluble in THF, but exhibit quite low solubility in CDCl₃.

The new compounds were characterized using IR and multinuclear (¹H, ¹³C, ³¹P) NMR spectroscopies. The infrared spectra of the adducts 1-4 exhibit strong absorption bands in the range 960-900 cm⁻¹ which were assigned to ν_{as}(P₂NH) and are indicative for the presence of the phosphorus ligand in the protonated form.

The solution NMR spectra of the isolated products are consistent with the formation of the title complexes. The ^1H and ^{13}C NMR spectra, recorded in CDCl_3 , DMSO-d_6 or $\text{CDCl}_3\text{-DMSO-d}_6$, showed the resonances for the organic groups attached to phosphorus atoms, with the expected splitting due to phosphorus-proton and phosphorus-carbon couplings, respectively. The ^{31}P NMR spectra exhibit one resonance for the adducts **1-3** and two resonances for compounds **4-6**, consistent with equivalent and non equivalent phosphorus atoms in a ligand unit, respectively. The signals were assigned by comparison with the spectra of the free acids or the alkali salts used as starting materials. No resonances indicative of hydrolysis products, *i.e.* free $(\text{XPR}_2)(\text{YPR}'_2)\text{NH}$ pro-ligands, were observed for compounds **5** and **6**.

Attempts to grow single crystals suitable X-ray diffraction studies failed in the case of the adducts

1-4. Single crystals of $\text{Bi}[(\text{SPMe}_2)(\text{SPPH}_2)\text{N}]_3$ (**5**) were grown from a $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ mixture using the slow diffusion technique. Attempts to grow crystals of the monothioderivative $\text{Bi}[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]_3$ (**6**) from a $\text{CHCl}_3/\text{n-hexane}$ mixture resulted in isolation of the unexpected mixed-ligand complex $\text{Bi}[(\text{OPPh}_2)_2\text{N}]_2[(\text{OPPh}_2)(\text{SPPH}_2)\text{N}]$ (**7**), due to partial oxidation of the parent compound. The molecular structures of compounds **5** and **7** were established by X-ray diffraction studies which revealed their monomeric nature, *i.e.* the lack of intermolecular Bi-chalcogen interactions. Selected bond distances and angles are listed in Tables 2 and 3. Figures 1 and 2 show the ORTEP-like view of the molecular structure of **5** and **7**, respectively, with the atom numbering scheme.

Table 2

Selected interatomic distances (Å) and angles (deg) in $\text{Bi}[(\text{SPMe}_2)(\text{SPPH}_2)\text{N}]_3$ (**5**).

5a^a		5b^b	
Bi(1)-S(1)	2.8040(14)	Bi(2)-S(3)	2.7234(16)
Bi(1)-S(2)	2.7959(14)	Bi(2)-S(4)	2.8768(16)
P(1)-S(1)	2.010(2)	P(3)-S(3)	2.012(2)
P(2)-S(2)	2.015(2)	P(4)-S(4)	2.001(2)
P(1)-N(1a)	1.591(5)	P(3)-N(2a)	1.586(5)
P(2)-N(1)	1.578(5)	P(4)-N(2)	1.592(5)
S(1)···S(2a) ^c	3.950(2)	S(3)···S(4c) ^c	4.141(2)
S(1)-Bi(1)-S(2b)	171.12(5)	S(3)-Bi(2)-S(4d)	176.98(5)
S(1)-Bi(1)-S(1a)	81.41(5)	S(3)-Bi(2)-S(3c)	83.35(5)
S(1)-Bi(1)-S(1b)	81.41(5)	S(3)-Bi(2)-S(3d)	83.35(5)
S(1)-Bi(1)-S(2)	97.32(5)	S(3)-Bi(2)-S(4)	99.21(5)
S(1)-Bi(1)-S(2a)	89.71(4)	S(3)-Bi(2)-S(4c)	95.32(5)
S(1a)-Bi(1)-S(1b)	81.41(5)	S(3c)-Bi(2)-S(3d)	83.35(5)
S(1b)-Bi(1)-S(2)	89.71(4)	S(3d)-Bi(2)-S(4)	95.32(5)
S(2)-Bi(1)-S(2a)	91.45(5)	S(4)-Bi(2)-S(4c)	82.20(5)
S(2a)-Bi(1)-S(1a)	97.32(5)	S(4c)-Bi(2)-S(3d)	99.21(5)
Bi(1)-S(1)-P(1)	112.55(7)	Bi(2)-S(3)-P(3)	106.45(7)
Bi(1)-S(2a)-P(2a)	110.36(7)	Bi(1)-S(4c)-P(4c)	106.80(7)
S(1)-P(1)-N(1a)	118.1(2)	S(3)-P(3)-N(2c)	117.33(19)
P(1)-N(1)-P(2a)	132.7(3)	P(3)-N(2c)-P(4c)	129.4(3)
S(2a)-P(2a)-N(1a)	119.0(2)	S(4c)-P(4c)-N(2c)	118.10(19)

^a Symmetry equivalent position ($I-x+y$, $2-x$, z) and ($2-y$, $I+x-y$, z) are denoted by "a" and "b";

^b Symmetry equivalent position ($-x+y$, $-x$, z) and ($-y$, $x-y$, z) are denoted by "c" and "d";

^c Non-bonding distances.

Table 3

Selected interatomic distances (Å) and angles (deg) in Bi[(OPPh₂)₂N]₂[(OPPh₂)(SPPPh₂)N] (7).

Bi(1)-O(1)	2.304(6)	Bi(1)-S(1)	2.941(3)
Bi(1)-O(2)	2.348(6)	Bi(1)-O(3)	2.334(6)
Bi(1)-O(4)	2.378(7)	Bi(1)-O(5)	2.355(6)
P(1)-O(1)	1.527(6)	P(2)-S(1)	2.013(3)
P(1)-N(1)	1.573(8)	P(2)-N(1)	1.582(7)
P(3)-O(2)	1.570(7)	P(4)-O(3)	1.548(6)
P(3)-N(2)	1.588(7)	P(4)-N(2)	1.575(7)
P(5)-O(4)	1.582(6)	P(6)-O(5)	1.527(6)
P(5)-N(3)	1.573(7)	P(6)-N(3)	1.579(7)
O(1)···S(1) ^a	3.623(8)	O(4)···O(5) ^a	3.226(11)
O(2)···O(3) ^a	3.165(10)		
S(1)-Bi(1)-O(4)	165.41(17)	O(2)-Bi(1)-O(5)	164.1(2)
O(1)-Bi(1)-O(3)	171.1(2)		
S(1)-Bi(1)-O(1)	86.48(15)	O(4)-Bi(1)-O(1)	81.5(2)
S(1)-Bi(1)-O(2)	104.70(18)	O(4)-Bi(1)-O(2)	84.5(2)
S(1)-Bi(1)-O(3)	102.27(17)	O(4)-Bi(1)-O(3)	89.6(2)
S(1)-Bi(1)-O(5)	87.33(16)	O(4)-Bi(1)-O(5)	86.0(2)
O(1)-Bi(1)-O(2)	94.1(2)	O(3)-Bi(1)-O(5)	82.1(2)
O(2)-Bi(1)-O(3)	85.1(2)	O(5)-Bi(1)-O(1)	97.1(2)
Bi(1)-O(1)-P(1)	130.7(4)	Bi(1)-S(1)-P(2)	100.18(12)
Bi(1)-O(2)-P(3)	127.4(4)	Bi(1)-O(3)-P(4)	129.3(4)
Bi(1)-O(4)-P(5)	122.7(4)	Bi(1)-O(5)-P(6)	128.9(3)
O(1)-P(1)-N(1)	117.6(4)	S(1)-P(2)-N(1)	120.2(3)
P(1)-N(1)-P(2)	139.3(5)		
O(2)-P(3)-N(2)	118.7(4)	O(3)-P(4)-N(2)	117.8(4)
P(3)-N(2)-P(4)	133.2(5)		
O(4)-P(5)-N(3)	120.3(4)	O(5)-P(6)-N(3)	118.1(4)
P(5)-N(3)-P(6)	133.5(5)		

^a Non-bonding distances.

DISCUSSION

Regardless the protonated or deprotonated nature of the phosphorus ligand attached to the metal center, the ¹H and ¹³C NMR spectra suggest the organic groups attached to the same type of phosphorus atom are equivalent, consistent with a fast exchange process of the conformation of the six-membered BiXYP₂N rings in solution, at room temperature. Moreover, for compounds **5** and **6** the three ligands in a molecular unit are equivalent since only one set of resonances appears in the NMR spectra. The magnitude of the ³¹P chemical shifts is consistent with the presence of a free (XPR₂)(YPR'₂)NH pro-ligand in compounds **1-4** and deprotonated phosphorus ligands in compounds **5** and **6**, respectively, as well as with the coordination through both chalcogen atoms of a ligand moiety to the metal center.

As established by single-crystal X-ray diffraction studies, the crystal of compound Bi[(SPMe₂)(SPPPh₂)N]₃ (**5**) contains two discrete independent molecules (**5a** and **5b**) in the unit cell. The main difference between these molecules resides in the coordination pattern of the dithioimidodiphosphinato ligands, *i.e.* isobidentate in **5a**, with equal metal sulfur bonds [Bi(1)-S(1) 2.8040(14) Å, Bi(1)-S(2a) 2.7959(14) Å], and anisobidentate in **5b**, with different metal sulfur bonds [Bi(2)-S(3) 2.7234(16) Å, Bi(2)-S(4a) 2.8768(16) Å]. The magnitude of the metal-sulfur distances in **5a** and **5b** is in the range observed for the related derivative containing a symmetric dithioimidodiphosphinato ligand, Bi[(SPPPh₂)₂N]₃,²⁴ which also exhibits short [2.609(6)-2.714(6) Å] and long [2.858(6)-2.886(6) Å] bismuth-sulfur bonds. Similar isobidentate coordination of the phosphorus ligand was reported for [2-

(Me₂NCH₂)C₆H₄]BiCl[(SPPH₂)₂N] [Bi-S 2.847(2) / 2.825(2) Å].²⁸ The resulting octahedral BiS₆ core is distorted as reflected by the S-Bi-S bond angles (Table 2). In both molecules the sulfur atoms attached to equivalent phosphorus atoms (*i.e.* [S(1), S(1a) and S(1b)] and [S(2), S(2a) and S(2b)] which belong to SPPH₂ and SPMe₂ groups, respectively) describe parallel trigonal faces of the coordination octahedron.

The difference in the coordination pattern of the dithioimidodiphosphinato ligand is reflected in a smaller ligand "bite" in **5a** [S(1)⋯S(2a) 3.950(2) Å] than in **5b** [S(3)⋯S(4c) 4.141(2) Å], thus reflecting the flexibility of the SPNPS skeleton. By contrast, the Bi-S-P angles are significantly larger in **5a** [110.36(7) / 112.55(7)^o] than in **5b** [106.45(7) / 106.80(7)^o].

In both independent molecules **5a** and **5b**, regardless the different coordination pattern of the phosphorus ligand, the phosphorus-sulfur distances [range: 2.001(2)-2.015(2) Å; cf. (SPMe₂)(SPPH₂)NH.²⁹ P=S 1.962(3), 1.946(3) Å; [2-(Me₂NCH₂)C₆H₄]Te-S-PPh₂=N-PPh₂=S.³⁰ P-S 2.057(1), P=S 1.945(1) Å] and the phosphorus-nitrogen distances [range 1.578(5)-1.592(5) Å; cf. (SPMe₂)(SPPH₂)NH.²⁹ P-N 1.698(7), 1.692(6) Å; [2-(Me₂NCH₂)C₆H₄]Te-S-PPh₂=N-PPh₂=S.³⁰ P-N 1.612(3), P=N 1.557(3) Å] are intermediate between single P-X and double P=X bonds (X = S, N), thus suggesting considerable double bond character.

The molecular structure of the unexpected mixed-ligand complex Bi[(OPPh₂)₂N]₂[(OPPh₂)(SPPH₂)N] (**7**) features a distorted octahedral BiSO₅ core as result of the monometallic biconnective coordination of both type of phosphorus ligands. By contrast to the Bi[(OPPh₂)₂N]₃, for which the imidodiphosphinato ligands exhibit an anisobidentate pattern with short [2.256(7)-2.281(7) Å] and long [2.337(8)-2.404(8) Å] bismuth-oxygen bonds,²¹ in compound **7** the [(OPPh₂)₂N] ligands are symmetrically coordinated to the metal center through both oxygen atoms [Bi(1)-O(2) 2.348(6) Å / Bi(1)-O(3) 2.334(6) Å, and Bi(1)-O(4) 2.378(7) Å / Bi(1)-O(5) 2.355(6) Å]. The monothioimidodiphosphinato unit is primarily bonded to bismuth through the oxygen atom [the shortest Bi(1)-O(1) 2.304(6) Å] and coordinated intramolecularly through the sulfur atom [Bi(1)-S(1) 2.941(3) Å, *c.f.* the sum of covalent and van der Waals radii for the corresponding atoms, respectively: $\Sigma r_{cov}(\text{Bi},\text{S})$ 2.56 Å; $\Sigma r_{vdw}(\text{Bi},\text{S})$

4.25 Å].³¹ The later bond is considerably longer than Bi-S bonds observed in **5** or in the related [2-(Me₂NCH₂)C₆H₄]BiCl[(OPMe₂)(SPPH₂)N] [Bi-O 2.389(6) Å, Bi-S 2.765(3) Å].²⁸

Within the XPNPY skeletons of **7** the phosphorus-oxygen and phosphorus-nitrogen bonds in the symmetric ligand moieties are equivalent within experimental error, as are the phosphorus-nitrogen bonds in the asymmetric monothioimidodiphosphinato unit (Table 3). Their lengths suggest single phosphorus-sulfur [2.013(3) Å] and -oxygen [1.527(6)-1.582(6) Å] bonds and considerable double bond character for the phosphorus-nitrogen [1.573(8)-1.588(7) Å] bonds [*c.f.* Bi[(OPPh₂)₂N]₃.²¹ P-O 1.509(8)-1.539(9) Å; P-N 1.568(12)-1.593(9) Å; Ph₂P(=O)OH.³² P-O 1.526(6), P=O 1.486(6) Å; Me₃Sb[(OPPh₂)(SPPH₂)N]₂.³³ P-O 1.544(6) / 1.556(5) Å, P=S 1.962(3) / 1.972(3) Å, P=O=N 1.571(7) / 1.564(6) Å, P_S-N 1.601(7) / 1.618(6) Å].

Although some delocalization of the π -electrons over the XPNPY systems in both **5** and **7** is suggested by the magnitude of the bonds, the six-membered BiXYP₂N rings are not planar as reflected by the torsion angles (Table 4). The conformation of both BiS₂P₂N rings in both molecules **5a** and **5b** is similar, *i.e.* distorted boat, with P(1)/S(2a) and P(3)/S(4c) atoms in the apices, respectively. By contrast, the conformation of the six-membered metallacyclic rings in **7** is different. The BiOSP₂N ring is again of boat conformation, but with Bi(1) and N(1) atoms in the apices, while the BiO₂P₂N rings are folded along the O(2)⋯O(3) and O(4)⋯O(5) axis [dihedral angles: O(2)Bi(1)O(3)/O(2)P(3)N(2)P(4)O(3) 22.6^o; O(4)Bi(1)O(5)/O(4)P(5)N(3)P(6)O(5) 25.7^o]

EXPERIMENTAL

The organophosphorus starting materials were prepared according to literature methods: (OPPh₂)₂NH,³⁴ (SPMe₂)₂NH,³⁵ (SPPH₂)₂NH,³⁴ (SPMe₂)(SPPH₂)NH,²⁹ K[(SPMe₂)(SPPH₂)N],³⁶ K[(OPPh₂)(SPPH₂)N].³⁷ The synthesis were carried out under argon atmosphere, using Schlenk techniques. Solvents were dried and distilled prior to use. ¹H, ¹³C and ³¹P NMR spectra were recorded on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively, using solutions in CDCl₃ and DMSO-d₆. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (*ref.* CHCl₃: ¹H 7.26, ¹³C 77.0 ppm; DMSO-d₆: ¹H 2.50, ¹³C 39.43 ppm) and H₃PO₄ 85%, respectively. Infrared spectra were recorded in the 4000–400 cm⁻¹ range as KBr discs on a PERKIN ELMER FT-IR SPEKTRUM 1000 spectrometer and are reported in cm⁻¹.

General procedure for the preparation of BiCl₃[(XPR₂)(YPR'₂)NH] (Table 5)

A mixture of anhydrous BiCl₃ and (XPR₂)(YPR'₂)NH (1:1 molar ratio) in 40 mL anhydrous solvent was stirred for 24 h, at room temperature, in argon atmosphere. The resulting solid

product was separated by filtration and dried under vacuum. Details of the preparations, yields and melting points are given in Table 5. Microanalyses (C, H, N) and NMR spectra are consistent with the given composition of the isolated products.

Table 4

Torsion angles (°) for the BiXYP ₂ N rings in Bi[(SPMe ₂)(SPPH ₂)N] ₃ (5) and Bi[(OPPh ₂) ₂ N] ₂ [(OPPh ₂)(SPPH ₂)N] (7)					
5a		5b			
Bi(1)S(1)P(1)N(1a)	38.5	Bi(2)S(3)P(3)N(2c)	41.7		
S(1)P(1)N(1a)P(2a)	-64.1	S(3)P(3)N(2c)P(4c)	-86.0		
P(1)N(1a)P(2a)S(2a)	13.3	P(3)N(2c)P(4c)S(4c)	36.5		
N(1a)P(2a)S(2a)Bi(1)	44.7	N(2c)P(4c)S(4c)Bi(2)	29.1		
P(2a)S(2a)Bi(1)S(1)	-42.2	P(4c)S(4c)Bi(2)S(3)	-39.8		
S(2a)Bi(1)S(1)P(1)	7.6	S(4c)Bi(2)S(3)P(3)	9.1		
7					
Bi(1)O(1)P(1)N(1)	17.3	Bi(1)O(2)P(3)N(2)	20.7	Bi(1)O(4)P(5)N(3)	27.2
O(1)P(1)N(1)P(2)	28.5	O(2)P(3)N(2)P(4)	-0.4	O(4)P(5)N(3)P(6)	-0.2
P(1)N(1)P(2)S(1)	-11.6	P(3)N(2)P(4)O(3)	0.7	P(5)N(3)P(6)O(5)	-7.1
N(1)P(2)S(1)Bi(1)	-29.9	N(2)P(4)O(3)Bi(1)	-22.1	N(3)P(6)O(5)Bi(1)	-15.0
P(2)S(1)Bi(1)O(1)	43.4	P(4)O(3)Bi(1)O(2)	30.0	P(6)O(5)Bi(1)O(4)	29.0
S(1)Bi(1)O(1)P(1)	-45.4	O(3)Bi(1)O(2)P(3)	-28.6	O(5)Bi(1)O(4)P(5)	-33.7

Table 5

Preparation data and m.p. for BiCl₃[(XPR₂)(YPR'₂)NH] derivatives

Starting materials			Product	m.p.
BiCl ₃ g / mmol	(XPR ₂)(YPR' ₂)NH g / mmol	Solvent	[yield: g (%)]	(°C)
0.310 / 1.00	(OPPh ₂) ₂ NH 0.42 / 1.00	benzene	BiCl ₃ [(OPPh ₂) ₂ NH] (1) 0.69 (95)	220-224
0.206 / 0.65	(SPPH ₂) ₂ NH 0.293 / 0.65	benzene	BiCl ₃ [(SPPH ₂) ₂ NH] (2) 0.33 (66)	212-214
0.488 / 1.55	(SPMe ₂) ₂ NH 0.311 / 1.55	CH ₃ CN	BiCl ₃ [(SPMe ₂) ₂ NH] (3) 0.71 (77)	148-150
0.394 / 1.25	(SPMe ₂)(SPPH ₂)NH 0.406 / 1.25	benzene	BiCl ₃ [(SPMe ₂)(SPPH ₂)NH] (4) 0.75 (94)	113-115

Trichloro[bis(diphenylphosphinyl)imine]bismut(III), BiCl₃[(OPPh₂)₂NH] (1). IR: ν(PO) 1135vs, ν_{as}(P₂NH) 940m. ¹H NMR (CDCl₃): 7.28m (4H, C₆H₅-para), 7.40m (8H, C₆H₅-meta), 7.81dd (8H, C₆H₅-ortho, ³J_{PH} 12.8, ³J_{HH} 7.8 Hz). ³¹P NMR (CDCl₃): 24.5s (¹J_{PC} 60.6 Hz).

Trichloro[bis(diphenylthiophosphinyl)imine]bismut(III), BiCl₃[(SPPH₂)₂NH] (2). IR: ν(NH) 2610w, ν_{as}(P₂NH) 920vs, ν(PS) 645vs, 610s. ¹H NMR (DMSO-d₆): 3.38s (1H, NH), 7.47m (12H, C₆H₅-meta+para), 7.85dd (8H, C₆H₅-ortho, ³J_{PH} 13.0, ³J_{HH} 7.4 Hz). ³¹P NMR (DMSO-d₆): 54.5s.

Trichloro[bis(dimethylthiophosphinyl)imine]bismut(III), BiCl₃[(OPPh₂)₂NH] (3). IR: ν(NH) 2650s, ν_{as}(P₂NH) 960vs, ν(PS) 565s, 540s. ¹H NMR (CDCl₃+DMSO-d₆): 1.42m (CH₃, ²J_{PH}+⁴J_{PH} 12.9 Hz). ¹³C NMR (CDCl₃+DMSO-d₆): 25.52m (CH₃, ¹J_{PC}+³J_{PC} 68.9 Hz). ³¹P NMR (CDCl₃+DMSO-d₆): 58.2s. ¹H NMR (DMSO-d₆): 1.92m (CH₃, ²J_{PH}+⁴J_{PH} 12.9 Hz). ¹³C NMR (DMSO-d₆): 25.6m (CH₃, ¹J_{PC}+³J_{PC} 70.9 Hz). ³¹P NMR (DMSO-d₆): 59.7s.

Trichloro[(dimethylthiophosphinyl)(diphenylthiophosphinyl)imine]bismut(III), BiCl₃[(SPMe₂)(SPPH₂)NH] (4). IR: ν(NH) 2610w, ν_{as}(P₂NH) 940vs, ν(PS) 610s (Ph), 555s (Me). ¹H

NMR (CDCl₃): 2.08d (6H, CH₃, ²J_{PH} 14.0 Hz), 4.09s,br (1H, NH), 7.53m (6H, C₆H₅-meta+para), 7.86dd (4H, C₆H₅-ortho, ³J_{PH} 14.0, ³J_{HH} 7.2 Hz). ¹³C NMR (CDCl₃): 25.23d (CH₃, ¹J_{PC} 66.5 Hz), 128.89d (C_m, ³J_{PC} 13.3 Hz), 131.09d (C_o, ²J_{PC} 12.1 Hz), 132.40s (C_p), 134.57d (C_i, ¹J_{PC} 101.3 Hz). ³¹P NMR (CDCl₃): 53.0d (SP-C₆H₅, ²J_{PP} 22.5 Hz), 65.8d (SP-CH₃, ²J_{PP} 21.6 Hz).

Synthesis of tris(P,P-dimethyl-P',P'-diphenyl-P,P'-dithioimidodiphosphinato)bismuth(II), Bi[(SPMe₂)(SPPH₂)N]₃ (5)

Anhydrous BiCl₃ (0.15 g, 0.47 mmol) and K[(SPMe₂)(SPPH₂)N] (0.52 g, 1.43 mmol) were stirred in 20 mL THF, at room temperature for 24 hours, under argon. The solvent was removed from the yellow reaction mixture under reduced pressure and the remaining yellow oily product was treated with CH₂Cl₂. The KCl was filtered off from the reaction mixture, solvent was removed under reduced pressure and the resulted sticky solid was stirred with hexane, when a yellow solid deposited. The solid was filtered off and was recrystallized from methylene dichloride / n-hexane (1:5 by volume). Yield: 0.32 g (57 %). M.p. 98°C. ¹H NMR (CDCl₃):

1.80s,br (18H, CH₃), 7.35s,br (18H, P-C₆H₅-*meta*+*para*), 7.84dd (12H, P-C₆H₅-*ortho*, ³J_{PH} 13.7, ³J_{HH} 7.2 Hz). ¹³C NMR (CDCl₃): 25.89d (CH₃, ¹J_{PC} 72.4 Hz), 128.00s,br (C_m, C_p), 131.21m (C_o, ¹J_{PC} 11.4 Hz); the resonance for the C_i atoms was not observed. ³¹P NMR (CDCl₃): 34.4s,br (SP-C₆H₅), 40.4s,br (SP-CH₃).

Synthesis of tris(P,P,P',P'-tetraphenyl-P'-thioimidodiphosphinato)bismuth(II), Bi[(OPPh₂)(SPPPh₂)N]₃ (6)

Anhydrous BiCl₃ (0.124 g, 0.39 mmol) and K[(OPPh₂)(SPPPh₂)N] (0.56 g, 1.19 mmol) were stirred in 20 mL THF, at room temperature for 24 hours, under argon. The solvent was removed from the yellowish reaction mixture under reduced pressure. The solid product was treated with CH₂Cl₂ and the insoluble KCl was filtered off. After the removal of the solvent the title compound was isolated as a yellowish solid powder. Yield: 0.28 g (47 %). M.p. 187°C. ¹H NMR (CDCl₃): 7.09m [24H, P(S)-C₆H₅, P(O)-C₆H₅-*meta*], 7.24s,br [12H, P(S)-C₆H₅, P(O)-C₆H₅-*para*], 7.53dd [12H,

P(O)-C₆H₅-*ortho*, ³J_{PH} 11.6, ³J_{HH} 7.5 Hz], 7.70dd [8H, P(S)-C₆H₅-*ortho*, ³J_{PH} 13.0, ³J_{HH} 7.2 Hz]. ¹³C NMR (CDCl₃): 127.53d (C_m, ³J_{PC} 13.5 Hz), 130.00s (C_p), 131.09d [C_o, P(O)-C₆H₅, ²J_{PC} 11.7 Hz], 131.46d [C_o, P(S)-C₆H₅, ²J_{PC} 10.4 Hz], the resonances for the C_i atoms were not observed. ³¹P NMR (CDCl₃): 19.5s,br (Ph₂PO), 32.0s,br (Ph₂PS).

Crystal structure determination

Block crystals of Bi[(SPMe₂)(SPPPh₂)N]₃ (5) and Bi[(OPPh₂)₂N]₂[(OPPh₂)(SPPPh₂)N] (7) were mounted on a cryoloop. Data collection and processing was carried on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Cell refinement gave cell constants corresponding to rhombohedral cell for 5 and triclinic cell for 7 (space group R-3 for 5 and P-1 for 7), whose dimensions are given in Table 6 along with other experimental parameters.

Table 6

Crystallographic data for Bi[(SPMe₂)(SPPPh₂)N]₃ (5) and Bi[(OPPh₂)₂N]₂[(OPPh₂)(SPPPh₂)N] (7)

Compound	5	7
Molecular formula	C ₁₆₈ H ₁₉₂ Bi ₄ N ₁₂ P ₂₄ S ₂₄	C ₇₂ H ₆₀ BiN ₃ O ₅ P ₆ S
<i>M</i>	4848.32	1474.09
Crystal system	Rhombohedral	Triclinic
Space group	R-3	P-1
Temperature (K)	297(2)	297(2)
<i>a</i> /Å	15.1776(5)	11.1239(12)
<i>b</i> /Å	15.1776(5)	14.0630(15)
<i>c</i> /Å	79.434(5)	23.214(2)
α°	90	80.381(2)
β°	90	79.081(2)
γ°	120	70.070(2)
<i>V</i> /Å ³	15846.8(12)	3331.4(6)
<i>Z</i>	3	2
<i>D</i> _{calc} /gcm ⁻³	1.524	1.470
<i>F</i> (000)	7260	1484
μ (Mo-K α)/mm ⁻¹	3.790	2.874
Crystal size (mm ³)	0.40 x 0.35 x 0.30	0.28 x 0.21 x 0.17
θ range for data collection (°)	0.77 to 26.37	0.90 to 26.37
Reflections collected	42867	35411
Independent reflections	7203 [<i>R</i> _{int} = 0.0493]	13543 [<i>R</i> _{int} = 0.0731]
Maximum and minimum transmissions	0.3960 and 0.3124	0.6407 and 0.5000
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	7203 / 0 / 368	13543 / 0 / 781
Goodness-of-fit on <i>F</i> ²	1.156	1.045
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0442 <i>wR</i> ₂ = 0.1049	<i>R</i> ₁ = 0.0711 <i>wR</i> ₂ = 0.1521
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0523 <i>wR</i> ₂ = 0.1095	<i>R</i> ₁ = 0.1011 <i>wR</i> ₂ = 0.1669
Largest difference peak and hole (e Å ⁻³)	1.314 and -1.178	2.696 and -2.019

^a Definition of the *R* values: $R_1 = (\sum |F_o| - |F_c|) / \sum |F_o|$; $wR_2 = \{[\sum (F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

An absorption correction was applied.³⁸ The structures were solved by direct methods³⁹ and refined using SHELX-97.⁴⁰ All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached, except the methyl protons for which the isotropic thermal parameters were set at 1.5. The drawings were created with the Diamond program.⁴¹

Supplementary material

Crystallographic data for the structural analysis of 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 632109 (1), 632110 (2)]. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http:// www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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