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Hypervalent 5–*Bi*–12 derivatives containing dichalcogenoimidodiphosphinato ligands. Crystal structure and solution behaviour of [2-(Me_2NCH_2)C_6H_4]BiCl[(XPR_2)(YPR'_2)N] (X, Y = O, S, Se; R, R′ = Me, Ph)

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The reaction between [2-(Me_2NCH_2)C_6H_4]$BiCl_2$ and M[(XPR_2)(YPR'_2)N] in 1 : 1 molar ratio affords the new functionalised [2-(Me_2NCH_2)C_6H_4]BiCl[(XPR_2)(YPR'_2)N] derivatives [R = Me, R′ = Ph, X = O, Y = S (**1**); R = R′ = Ph, X = Y = S (**2**), Se (**3**)]. Variable-temperature NMR studies suggest a fluxional behaviour in solution. The investigation of the molecular structures of **1**–**3** by single-crystal X-ray diffraction revealed that the N atoms of the pendant CH_2NMe_2 arm are strongly coordinated to the Bi atom and the organophosphorus ligands act as a bidentate moiety through both chalcogens, thus resulting in a square pyramidal coordination geometry around the metal atoms. The analysis of the crystal packing of **2** and **3** reveals the presence of pairs of enantiomers (the metal center is chiral) associated through weak intermolecular Bi ··· Cl interactions. The crystal of **1** contains only the *trans*-O–Bi–Cl isomer as a 1 : 1 mixture of the two enantiomers, in a unique square pyramidal (*C*,*N*)BiCl(*O*,*S*) coordination geometry with five different atoms attached to the metal atom.

Introduction

The chemistry of hypervalent compounds received much attention both from organic and inorganic chemists and a rapid development in this area has been noted in the last 20 years.[1] To describe hypervalent molecules the designation *N*–*X*–*L* is generally used [*N* = number of formally assignable electrons in the valence shell; *X* = central atom; *L* = number of ligands (substituents) directly bound to the central atom].[2] The use of *ortho*-functionalized aromatic ligands with potential ability for additional intramolecular coordination is a common modality to stabilise organometallic derivatives of main group elements. The most straightforward substituent for this purpose is possibly the 2-(dimethylaminomethyl)phenyl group, able to establish strong, intramolecular N⟶M coordination. A recent review of the structural chemistry of organobismuth compounds[3] revealed that only few bismuth(III) derivatives containing 2-(Me_2NCH_2)C_6H_4 groups are known.[4–7] When anionic groups as [(XPR_2)(YPR'_2)N]$^-$, able to exhibit a chelating pattern, are attached to a [2-(Me_2NCH_2)C_6H_4]Bi fragment either a chalcogen⟶Bi *vs.* N⟶Bi competition or a further increase of the coordination number of the metal centre might arise. Such dichalcogenoimidodiphosphinato anions, [(XPR_2)(YPR'_2)N]$^-$, are versatile ligands able to adjust to various coordination geometries required by metal centres due to the flexibility of the XPNPY skeleton.[8] So far, only inorganic Bi[($XPPh_2$)$_2$N]$_3$ (X = O,[9] S,[10] Se[11]) derivatives have been described with a slightly distorted BiX_6 core regardless the nature of the chalcogen atom.

We herein report on the synthesis, solution behaviour and solid state molecular structure of the first organo(chloro)-bismuth(III) compounds of the type [2-(Me_2NCH_2)C_6H_4]BiCl[(XPR_2)(YPR'_2)N].

Results and discussion

Synthesis

The synthesis of three new [2-(Me_2NCH_2)C_6H_4]BiCl[(XPR_2)(YPR'_2)N] derivatives was achieved in good yield according to eqn. (1), by reacting [2-(Me_2NCH_2)C_6H_4]$BiCl_2$ with M[(XPR_2)(YPR'_2)N] (1 : 1 molar ratio) at room temperature, in toluene.

$$[2\text{-}(Me_2NCH_2)C_6H_4]BiCl_2 + M[(XPR_2)(YPR'_2)N] \longrightarrow [2\text{-}(Me_2NCH_2)C_6H_4]BiCl[(XPR_2)(YPR'_2)N] + MCl \quad (1)$$

	R	R'	X	Y
1	Me	Ph	O	S
2	Ph	Ph	S	S
3	Ph	Ph	Se	Se

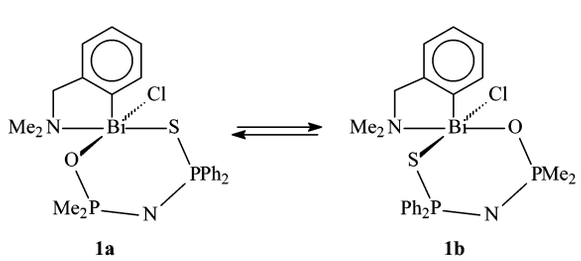
The compounds are white (**1**), white–yellow (**2**) and orange (**3**) solids, which can be recrystallized from chloroform or methylene dichloride. They were characterised using variable temperature NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction.

Single-crystal X-ray diffraction studies

Suitable crystals for X-ray diffraction analysis were grown by solvent diffusion from toluene–light petroleum (bp 40–60 °C) for **1**, toluene–hexane for **2**, and CH_2Cl_2–hexane for **3**.

From the mixture of the two isomers **1a** (Cl *trans* O) and **1b** (Cl *trans* S) (Scheme 1) only **1a** was obtained as colourless crystals by solvent diffusion from toluene–light petroleum at room temperature.

The solid material **1a** is racemic and crystallises in a centrosymmetric space group (*Pbca*) with one molecule in the asymmetric unit. Both compounds **2** and **3** crystallise in the



1a **1b**

Scheme 1

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Table 1 Selected bond distances (Å) and angles (°) for compounds **1a**, **2** and **3**

1a		**2**		**3**	
Bi(1)–C(1)	2.221(8)	Bi(1)–C(1)	2.246(7)	Bi(1)–C(1)	2.266(9)
Bi(1)–N(1)	2.553(7)	Bi(1)–N(1)	2.554(6)	Bi(1)–N(1)	2.575(8)
Bi(1)–Cl(1)	2.666(2)	Bi(1)–Cl(1)	2.669(2)	Bi(1)–Cl(1)	2.647(3)
Bi(1)–O(1)	2.389(6)	Bi(1)–S(1)	2.847(2)	Bi(1)–Se(2)	2.890(16)
Bi(1)–S(1)	2.765(3)	Bi(1)–S(2)	2.825(18)	Bi(1)–Se(1)	3.018(16)
P(1)–O(1)	1.524(6)	P(1)–S(1)	2.020(3)	P(1)–Se(1)	2.159(2)
P(2)–S(1)	2.018(3)	P(2)–S(2)	2.010(3)	P(2)–Se(2)	2.176(3)
P(1)–N(2)	1.608(7)	P(1)–N(2)	1.590(6)	P(1)–N(2)	1.605(8)
P(2)–N(2)	1.588(8)	P(2)–N(2)	1.603(6)	P(2)–N(2)	1.577(7)
C(1)–Bi(1)–N(1)	74.4(3)	C(1)–Bi(1)–N(1)	73.1(2)	C(1)–Bi(1)–N(1)	72.9(3)
C(1)–Bi(1)–Cl(1)	88.2(2)	C(1)–Bi(1)–Cl(1)	85.7(2)	C(1)–Bi(1)–Cl(1)	85.5(2)
C(1)–Bi(1)–O(1)	85.8(3)	C(1)–Bi(1)–S(1)	82.6(2)	C(1)–Bi(1)–Se(1)	81.4(2)
C(1)–Bi(1)–S(1)	88.7(2)	C(1)–Bi(1)–S(2)	89.11(2)	C(1)–Bi(1)–Se(2)	92.7(2)
N(1)–Bi(1)–Cl(1)	99.15(19)	N(1)–Bi(1)–Cl(1)	98.64(15)	N(1)–Bi(1)–Cl(1)	95.12(18)
N(1)–Bi(1)–O(1)	80.5(2)	N(1)–Bi(1)–S(1)	84.02(14)	N(1)–Bi(1)–Se(1)	86.73(17)
N(1)–Bi(1)–S(1)	159.21(17)	N(1)–Bi(1)–S(2)	159.62(14)	N(1)–Bi(1)–Se(2)	164.81(17)
Cl(1)–Bi(1)–S(1)	92.21(9)	Cl(1)–Bi(1)–S(2)	89.71(6)	Cl(1)–Bi(1)–Se(2)	88.54(6)
Cl(1)–Bi(1)–O(1)	173.83(16)	Cl(1)–Bi(1)–S(1)	166.65(6)	Cl(1)–Bi(1)–Se(1)	165.65(6)
O(1)–Bi(1)–S(1)	86.34(15)	S(2)–Bi(1)–S(1)	83.80(6)	Se(2)–Bi(1)–Se(1)	86.18(4)
P(1)–O(1)–Bi(1)	124.1(3)	P(1)–S(1)–Bi(1)	91.99(9)	P(1)–Se(1)–Bi(1)	87.16(7)
P(2)–S(1)–Bi(1)	92.60(12)	P(2)–S(2)–Bi(1)	94.69(9)	P(2)–Se(2)–Bi(1)	92.59(7)

monoclinic crystal system ($P2_1/c$ and $P2_1/n$, respectively). Important molecular parameters are given in Table 1 and the molecular structures of **1a** and **2** with the atom numbering schemes are shown in Figs. 1 and 2. The structure of **3** is similar to that of **2**.

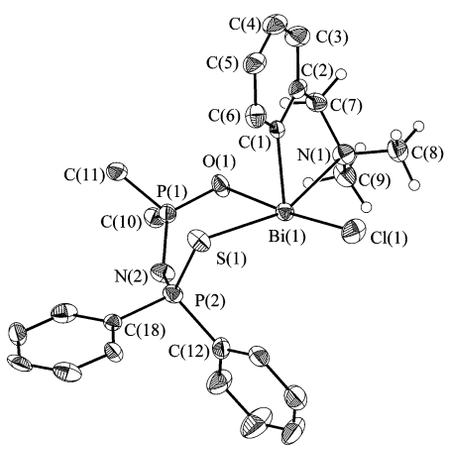


Fig. 1 Molecular structure of the enantiomer *S*-**1a**. The atoms are drawn with 50% probability ellipsoids.

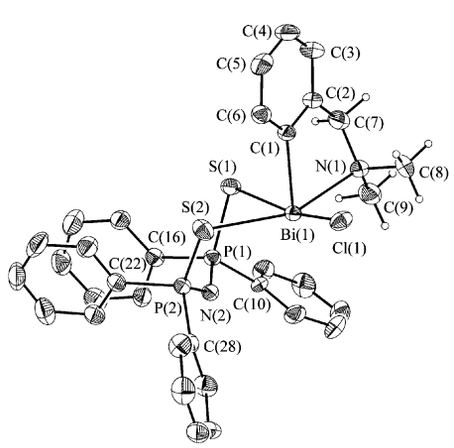


Fig. 2 Molecular structure of **2**. The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms on the aromatic rings are omitted for clarity.

The [2-(Me_2NCH_2)C_6H_4]Bi moiety in all three compounds exhibits a common feature, *i.e.* the nitrogen atom of the pendant CH_2NMe_2 arm is strongly coordinated to the metal center [Bi–N 2.553(7), 2.553(6) and 2.575(7) Å in **1a**, **2** and **3**, respectively]. Weaker intramolecular Bi–N interactions were reported for [2-(Me_2NCH_2)C_6H_4]$_3$Bi (2.97–3.15 Å)[4] and [2-(Me_2NCH_2)C_6H_4]$_2$BiCl (Bi–N 2.570 Å),[5] while in [2-(Me_2-NCH_2)C_6H_4]BiI_2 the value of the Bi–N distance (2.503 Å) suggests a stronger intramolecular interaction.[5]

The dichalcogenoimidodiphosphinato ligands act as monometallic biconnective units regardless the nature of the chalcogens, resulting in hypervalent 5–*Bi*–12 derivatives.[1,2] In **1a** the monothioimidodiphosphinato ligand is coordinated through the sulfur and the oxygen atoms to the metal centre [Bi(1)–O(1) 2.389(6), Bi(1)–S(1) 2.765(3) Å]. The bismuth–sulfur bonds are equivalent in **2** [Bi(1)–S(1) 2.847(19), Bi(1)–S(2) 2.825(18) Å], while the coordination in **3** is slightly asymmetric [Bi(1)–Se(2) 2.890(12) and Bi(1)–Se(1) 3.018(14) Å]. In all three compounds the bond distances are within the range of bismuth–chalcogen bond lengths observed in the inorganic derivatives Bi[($OPPh_2$)$_2$N]$_3$ [2.256(7)–2.404(8) Å],[9] Bi[($SPPh_2$)$_2$N]$_3$ [2.728(3)–2.986(3) Å],[10] and Bi[($SePPh_2$)$_2$N]$_3$ [2.835(3)–3.047(3) Å],[11] respectively.

The coordination environment around the bismuth atom in **1a** is unique, with five different atoms describing a distorted square pyramidal (*C*,*N*)BiCl(*O*,*S*) core. The apical position is occupied by the carbon atom, while the O(1), S(1), Cl(1) and N(1) atoms are placed in the corners of the basal plane, with the oxygen *trans* to the chlorine [Cl(1)–Bi(1)–O(1) 173.83(16)°] and the sulfur *trans* to the nitrogen [N(1)–Bi(1)–S(1) 159.21(17)°]. The coordination geometry around the Bi atom in the molecules of **2** and **3** is also distorted square pyramidal, with the Cl and N atoms *trans* to the S atoms [Cl(1)–Bi(1)–S(1) 166.65(6), N(1)–Bi(1)–S(2) 159.62(14)°] and Se atoms [Cl(1)–Bi(1)–Se(1) 165.65(6) N(1)–Bi(1)–Se(2) 164.81(17)°], respectively. The distortion of the coordination geometry in the molecular unit in **1a**, **2** and **3**, with the bismuth atom situated 0.26, 0.71 and 0.77 Å below the best basal plane (mean deviation 0.124, 0.12 and 0.12 Å, respectively) is mainly due to the constraint imposed by the five-membered BiC_3N ring formed as result of the intramolecular N⟶Bi coordination.

In spite of the similar molecular aspects, the crystal of **1a** contains distinct monomeric molecules, while dimeric associations through Bi–Cl ··· Bi bridges (planar Bi_2Cl_2 cores) are found for **2** (Fig. 3) and **3**. The intermolecular Bi(1) ··· Cl(1′)

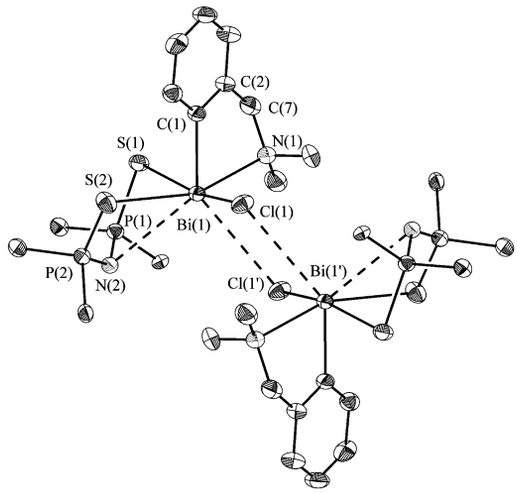


Fig. 3 Dimeric association in the crystal of **2**.

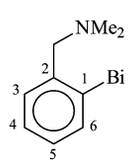
distances [3.526(8) Å for **2** and 3.576(2) Å for **3**] are considerably longer than in the chain polymeric association of $PhBiCl_2 \cdot THF$ (Bi ··· Cl 2.934 Å),[12] but shorter than in the dimer associations of $(4\text{-}MeC_6H_4)[2\text{-}(Me_2NCH_2)C_6H_4]BiCl$ (Bi ··· Cl 3.94 Å)[12] or the sum of the van der Waals radii of Bi and Cl atoms [Σ_{vdW} (Bi,Cl) 4.2 Å].[13]

Regardless the nature of the chalcogens and organic groups on phosphorus atoms, the six-membered $BiXYP_2N$ rings exhibit a distorted boat conformation with different atoms in the apices. For **2** and **3** the Bi and N atoms are in the apices, thus bringing the nitrogen atom close to the metal centre (3.35 and 3.37 Å, respectively) and suggesting a weak additional intramolecular interaction. For **1a** the S(1) and P(1) atoms are in the apices, the transannular bismuth–nitrogen distance is somewhat longer (3.66 Å), but shorter than the sum of the van der Waals radii of Bi and N atoms [Σ_{vdW} (Bi,N) 4.0 Å].[13]

The phosphorus–sulfur, phosphorus–selenium and phosphorus–nitrogen bonds in the symmetric ligand moiety in **2** and **3** are equivalent within experimental error (Table 1), as are the phosphorus–nitrogen bonds in the asymmetric oxothioimidodiphosphinato unit in **1a**. Their lengths suggest single phosphorus–sulfur and –oxygen bonds and considerable double bond character for the phosphorus–selenium and –nitrogen bonds (*cf.* $[2\text{-}(Me_2NCH_2)C_6H_4]Te\text{–}S\text{–}PPh_2{=}N\text{–}PPh_2{=}S$:[14] P–S 2.057(1), P=S 1.945(1), P–N 1.612(3), P=N 1.557(3)°; $Me_2C[PhP(=Se)]_2Se$:[15] P–Se 2.279(2), 2.283(2), P=Se 2.096(2), 2.101(2) Å; $Ph_2P(=O)OH$:[16] P–O 1.526(6), P=O 1.486(6) Å).

Solution behaviour

The aromatic ^1H resonances for the organic group attached to bismuth were assigned according to the Scheme 2.



Scheme 2

The ^1H NMR spectra ($CDCl_3$) of the two derivatives containing symmetric imidodiphosphinato ligands, $[2\text{-}(Me_2NCH_2)\text{-}C_6H_4]BiCl[(XPR_2)_2N]$ [X = S (**2**), Se (**3**)], showed at −45 °C an AB system for the CH_2 protons and two sharp singlets for the $N(CH_3)_2$ protons (Fig. 4(a)).

At 25 °C in $CDCl_3$, an unresolved AB system for the methylene protons was observed indicating the stability of the configuration at Bi at this temperature, although in the presence of two potential intramolecularly coordinating groups a very fast

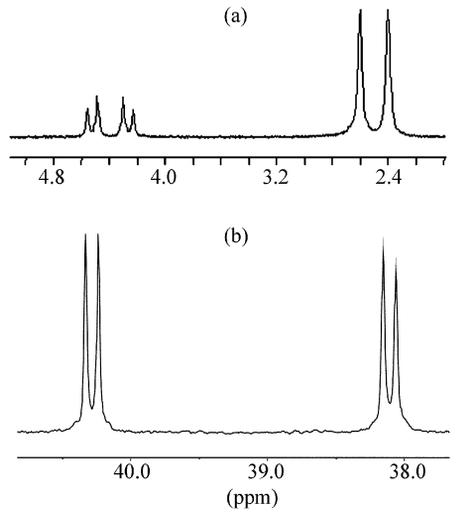


Fig. 4 (a) The alkyl region of the ^1H NMR spectrum and (b) the ^{31}P NMR spectrum of **2** (at −45 °C, $CDCl_3$ solution).

bismuth inversion was expected to take place.[17] By contrast, the two singlets for the methyl protons of the dimethylamino group showed coalescence at 25 °C in $CDCl_3$ ($\Delta G^{\ddagger}$ = 14.7 kcal mol^{-1} for **2** and 14.8 kcal mol^{-1} for **3**, respectively). This process corresponds to the dissociation–recoordination between the nitrogen and the bismuth atoms, with inversion at a three-coordinated nitrogen atom and rotation of the $(H_2)C\text{–}N$ bond (Scheme 3).

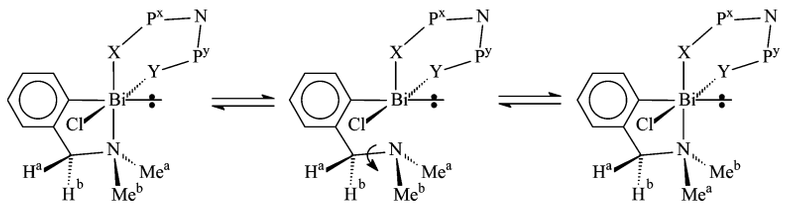
Two sharp doublets [δ 38.1, 40.3 ($^2J_{PP}$ 7.6 Hz) (split width ($\Delta\nu$) 176 Hz) for **2** (Fig. 4(b)), and δ 27.6, 32.5 ($^2J_{PP}$ 6.8 Hz) (split width ($\Delta\nu$) 397 Hz) for **3**] were observed in the ^{31}P NMR spectra at −45 °C, due to the non-equivalent phosphorus atoms in a rigid structure with chalcogens *trans* to chlorine and nitrogen atoms as observed in the solid state. The coalescence of the phosphorus signals was observed at 25 °C in $CDCl_3$ and the free energy of activation for the chalcogen exchange process was calculated to be $\Delta G^{\ddagger}$ = 13.9 and 13.4 kcal mol^{-1}, respectively.[18] A possible mechanism is shown in Scheme 4.

The inversion barrier upon the Bi atom was reported to be diminished by nucleophilic solvents.[17] Indeed, the ^1H NMR spectra of both **2** and **3** at 25 °C in DMSO-d_6 showed sharp singlet signals for the methylene protons, thus suggesting a coordinating solvent-assisted *edge* inversion (Scheme 5).

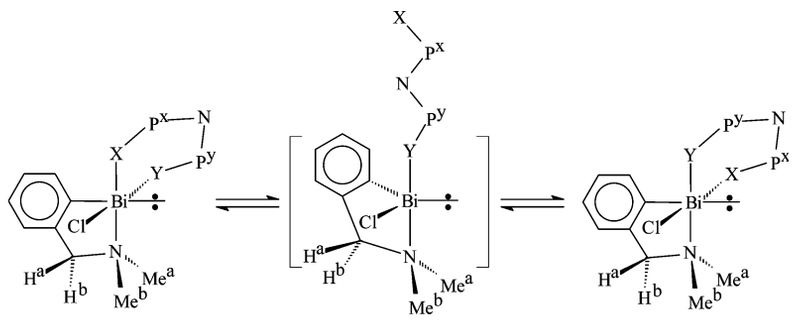
The ^{31}P NMR spectrum of **1** recorded at −45 °C showed two sets of doublet resonances assigned to the isomers **1a** and **1b** (Scheme 1) by comparison with the spectra of the free imidodiphosphinato acid and its sodium salt,[19] and taking into account the shielding effect of the atoms *trans* to the sulfur atoms. The molar ratio **1a** : **1b** is 3.5 : 1 (from integrals). At +20 °C, only two broad resonances at δ 32.16 (P_O) and 42.11 (P_S), were observed for **1** (Fig. 5), thus suggesting a rapid chalcogen exchange.

The ^1H NMR spectrum ($CDCl_3$) at −45 °C is also consistent with the presence of two sets of resonances for the isomers **1a** and **1b**. In the aromatic region two doublets for the H-6 proton of the organic group attached to bismuth were observed at δ 8.88 (isomer **1a**) and 9.38 (isomer **1b**). The alkyl region (Fig. 6) showed an AB system for the methylene protons and two singlets for the $N(CH_3)_2$ protons of isomer **1a**, which partially overlap the resonance signals corresponding to the isomer **1b**. By contrast, the resonances of the methyl groups attached to phosphorus are well separated for the two isomers. The pattern of these signals, *i.e.* two doublets for each isomer [δ 1.63 ($^2J_{PH}$ 14.0 Hz), 1.71 ($^2J_{PH}$ 15.1 Hz) for **1a**, and 1.19 ($^2J_{PH}$ 13.5 Hz), 1.52 ($^2J_{PH}$ 14.0 Hz) for **1b**], indicates the non-equivalence of the two methyl groups in the phosphorus ligand unit in the frozen molecules of isomers **1a** and **1b**, respectively.

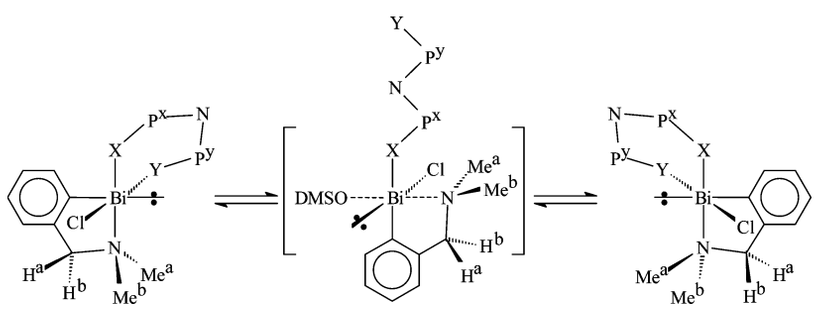
At +20 °C, in $CDCl_3$, the ^1H NMR spectrum of **1** exhibits only an unresolved doublet for the H-6 proton (δ 9.11) (at



Scheme 3



Scheme 4



Scheme 5

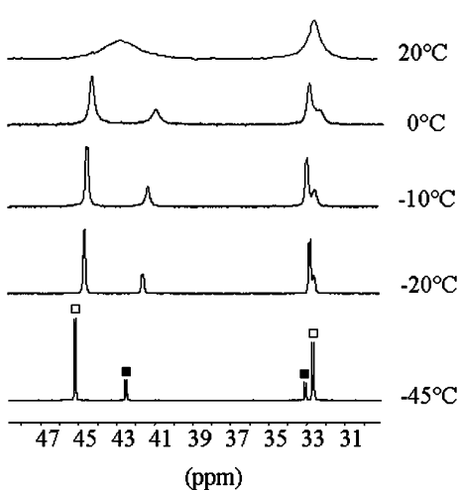


Fig. 5 Variable-temperature ^{31}P NMR spectra of **1**: (□) isomer **1a**; (■) isomer **1b**.

+60 °C this resonance is resolved as a doublet, $^{3}J_{HH}$ 7.1 Hz), singlet resonances for the CH_2 (δ 4.37) and $N(CH_3)_2$ (δ 2.73) protons of the [2-$(Me_2NCH_2)C_6H_4$] group, as well as a doublet [δ 1.54 ($^{2}J_{PH}$ 13.3 Hz)] for the $P(CH_3)_2$ protons of the phosphorus ligand. This behaviour indicates fast inversion and isomerisation processes at this temperature in $CDCl_3$. No concentration dependence was observed at room temperature, in $CDCl_3$, for compound **1**. The NMR spectra of **1** in DMSO-d_6, at 25 °C, exhibit a similar pattern as in $CDCl_3$. A detailed NMR study of this compound is in progress in order to investigate the solvent effect and activation parameters.

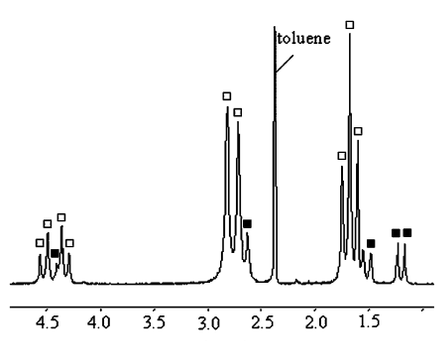


Fig. 6 The alkyl region of the ^{1}H NMR spectrum of **1** (at −45 °C, $CDCl_3$ solution): (□) isomer **1a**; (■) isomer **1b**.

Conclusions

The isolation of the first functionalised organobismuth(III) derivatives containing dichalcogenoimidodiphosphinato ligands open new perspectives for the synthesis of further mixed-ligand compounds and studies of hypervalent organobismuth derivatives.

Experimental

General procedures

The syntheses were carried out using dried solvents freshly distilled under argon. The starting materials were prepared according to literature methods: [2-$(Me_2NCH_2)C_6H_4$]$BiCl_2$,[5] $Na[(OPMe_2)(SPPh_2)N]$,[19] $K[(XPPh_2)_2N]$ (X = S,[20] Se[21]). The ^{1}H

Table 2 Crystallographic data for compounds **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{23}H_{28}BiClN_2OP_2S$	$C_{33}H_{32}BiClN_2P_2S_2$	$C_{33}H_{32}BiClN_2P_2Se_2$
Formula weight	686.90	827.10	920.90
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_1/n$
a/Å	12.489(1)	15.121(3)	12.111(3)
b/Å	19.234(1)	11.3420(10)	14.046(3)
c/Å	21.543(2)	20.027(2)	20.102(8)
β/°	90	107.470(10)	103.60(2)
V/Å^3	5174.9(7)	3276.3(8)	3323.7(17)
Z	8	4	4
λ/Å	0.71073	0.71073	0.71073
Absorption correction	DIFABS[24]	Empirical	Empirical (SHELXA)
μ(Mo-Kα)/mm^{-1}	7.140	5.714	7.697
$R1$ [$I > 2\sigma(I)$]	0.0503	0.0397	0.0544
$wR2$	0.0771	0.0780	0.0932
GOF	1.001	1.009	1.003

and ^{31}P NMR spectra were recorded on a Bruker DPX 200 instrument, using $CDCl_3$ and DMSO-d_6 solutions. The chemical shifts are reported in ppm relative to TMS and 85% H_3PO_4, respectively. For the mass spectrometry a Finnigan MAT 8222 instrument was used.

Synthesis of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl[(OPMe$_2$)(SPPh$_2$)N] (1). A mixture of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl$_2$ (0.5 g, 1.20 mmol) and Na[(OPMe$_2$)(SPPh$_2$)N] (0.399 g, 1.20 mmol) in toluene (30 ml) was stirred at room temperature for 24 h. The solvent was removed with a syringe and the solid product was washed with methanol (20 ml) to remove the KCl. The remaining white powder was dried in vacuum and colourless single crystals were obtained by solvent diffusion from toluene–light petroleum (bp 40–60 °C); yield 0.58 g (70%); mp 115 °C. ^{1}H NMR (200 MHz, +25 °C, DMSO-d_6), δ 1.34 (6 H, d, PCH_3, $^2J_{PH}$ 14.2 Hz), 2.63 (6 H, s, NCH_3), 4.36 (2 H, s, CH_2N), 7.32 [7 H, m, H-4 + PC_6H_5 (*meta* + *para*)], 7.65 (1 H, t, H-5, $^3J_{HH}$ 7.3 Hz), 7.83 [5 H, dm, H-4 + PC_6H_5 (*ortho*), $^3J_{PH}$ 13.7 Hz], 9.04 (1 H, d, H-6, $^3J_{HH}$ 7.3 Hz); ^{1}H NMR (200 MHz, +20 °C, $CDCl_3$), δ 1.54 (6 H, d, PCH_3, $^2J_{PH}$ 13.3 Hz), 2.73 (6 H, s, NCH_3), 4.37 (2 H, s, CH_2N), 7.3–7.9 (33 H, m, all aromatic protons except H-6), 9.11 (1 H, br s, H-6); ^{1}H NMR (200 MHz, −45 °C, $CDCl_3$), δ 1.63 (3 H, d, PCH_3, $^2J_{PH}$ 14.0 Hz), 1.71 (3 H, d, PCH_3, $^2J_{PH}$ 15.1 Hz), 2.71 (3 H, s, NCH_3), 2.81 (3 H, s, NCH_3), AB spin system with A: 4.32, B: 4.52 (4 H, CH_2N, $^2J_{HH}$ 14.6 Hz), 8.88 (1 H, d, H-6, $^3J_{HH}$ 7.3 Hz) for isomer **1a**, and δ 1.19 (3 H, d, PCH_3, $^2J_{PH}$ 13.5 Hz), 1.52 (3 H, d, PCH_3, $^2J_{PH}$ 14.0 Hz), 2.62 (3 H, s, NCH_3), 2.81 (3 H, s, NCH_3), 9.38 (1 H, d, H-6, $^3J_{HH}$ 7.0 Hz) for isomer **1b**; the AB system for CH_2N protons of isomer **1b** is overlapped by that corresponding to isomer **1a**, and the all aromatic protons except H-6 for both isomers are in the region δ 7.15–8.10; ^{31}P NMR (81 MHz, +25 °C, DMSO-d_6, rel. to H_3PO_4), δ 32.94 (br s, PO), 40.14 (br s, PS); ^{31}P NMR (81 MHz, +20 °C, $CDCl_3$, rel. to H_3PO_4), δ 32.16 (s, PO), 42.11 (br s, PS); ^{31}P NMR (81 MHz, −45 °C, $CDCl_3$, rel. to H_3PO_4), δ 32.74 (d, PO, $^2J_{PP}$ 7.3 Hz), 45.24 (d, PS, $^2J_{PP}$ 7.4 Hz) for isomer **1a**, and δ 33.15 (d, PO, $^2J_{PP}$ 7.0 Hz), 42.57 (d, PS, $^2J_{PP}$ 7.1 Hz) for isomer **1b**. MS (CI, NH_3) *m*/*z* (%), positive: 651 (5) [M^+ − Cl], 427 (40) [Ph_2PSBi^+], 292 (100) [$Me_2PNPPh_2S^+$], 170 (50) [RCl^+], 134 (85) [R^+]; negative: 547 (90) [M^+ − 2Ph + NH_3], 308 (100) [$OMe_2PNPPh_2S^+$].

Synthesis of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl[(SPPh$_2$)$_2$N] (2). A mixture of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl$_2$[5] (0.5 g, 1.20 mmol) and K[(SPPh$_2$)$_2$N] (0.59 g, 1.20 mmol) in toluene (30 ml) was stirred at room temperature for 24 h. The solvent was removed with a syringe and the solid product was washed with methanol (20 ml) to remove the KCl. The remaining yellowish powder was dried in vacuum and a crystalline solid was obtained by solvent diffusion from hexane–toluene; yield 0.7 g (80%); mp 210 °C. ^{1}H NMR (200 MHz, +25 °C, DMSO-d_6), δ 2.60 (6 H, s, NCH_3), 4.35 (2 H, s, CH_2N), 7.32 [12 H, m, PC_6H_5 (*meta* + *para*)], 7.49 (1 H, t, H-4, $^3J_{HH}$ 7.3 Hz), 7.68 [1 H, t, H-5, $^3J_{HH}$ 7.3 Hz], 7.88 [9 H, m, H-3 + PC_6H_5 (*ortho*)], 9.18 (1 H, d, H-6, $^3J_{HH}$ 6.5 Hz); ^{1}H NMR (200 MHz, +25 °C, $CDCl_3$), δ 2.58 (6 H, br s, NCH_3), unresolved AB spin system with A: 4.19, B: 4.42 (4H; CH_2N), 7.2–7.9 (23 H, m, all aromatic protons except H-6), 9.41 (1 H, d, H-6, $^3J_{HH}$ 7.5 Hz); ^{1}H NMR (200 MHz, −45 °C, $CDCl_3$), δ 2.39 (3 H, s, NCH_3), 2.59 (3 H, s, NCH_3), AB spin system with A: 4.265, B: 4.515 (4H; CH_2N, $^2J_{HH}$ 13.8 Hz), 7.07–8.15 (23 H, m, all aromatic protons except H-6), 9.48 (1 H, d, H-6, $^3J_{HH}$ 7.3 Hz). ^{31}P NMR (81 MHz, +25 °C, DMSO-d_6, rel. to H_3PO_4), δ 37.2 (br s); ^{31}P NMR (81 MHz, +25 °C, $CDCl_3$, rel. to H_3PO_4), δ 38.3 (s); ^{31}P NMR (81 MHz, −45 °C, $CDCl_3$, rel. to H_3PO_4), δ 38.1 (d, $^2J_{PP}$ 7.6 Hz), 40.3 (d, $^2J_{PP}$ 7.6 Hz).

Synthesis of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl[(SePPh$_2$)$_2$N] (3). A mixture of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl$_2$[5] (0.169 g, 0.4 mmol) and K[(SePPh$_2$)$_2$N] (0.238 g, 0.4 mmol) in toluene (20 ml) was stirred at room temperature for 24 h. The solvent was removed with a syringe and the solid product was washed with methanol (20 ml) to remove the KCl. The remaining yellowish powder was dried in vacuum and a crystalline solid was obtained by solvent diffusion from hexane–methylene chloride; yield 0.3 g (82%); mp 190 °C. ^{1}H NMR (200 MHz, +25 °C, $CDCl_3$), δ 2.50 (6 H, br s, NCH_3), unresolved AB spin system with A: 4.11, B: 4.45 (4H; CH_2N), 7.18–7.76 (23 H, m, all aromatic protons except H-6), 9.53 (1 H, d, H-6, $^3J_{HH}$ 7.4 Hz); ^{1}H NMR (200 MHz, −45 °C, $CDCl_3$), δ 2.37 (3 H, s, NCH_3), 2.56 (3 H, s, NCH_3), AB spin system with A: 4.11, B: 4.52 (4H; CH_2N, $^2J_{HH}$ 13.6 Hz), 7.17–8.07 (23 H, m, all aromatic protons except H-6), 9.62 (1H, d, H-6, $^3J_{HH}$ 6.1 Hz). ^{31}P NMR (81 MHz, +25 °C, DMSO-d_6, rel. to H_3PO_4), δ 30.4 (br s); ^{31}P NMR (81 MHz, +25 °C, $CDCl_3$, rel. to H_3PO_4), δ 29.9 (s); ^{31}P NMR (81 MHz, −45 °C, $CDCl_3$, rel. to H_3PO_4), δ 27.6 (d, $^2J_{PP}$ 6.8 Hz), 32.5 (d, $^2J_{PP}$ 6.8 Hz).

Crystal structures

Experimental details relating to the single-crystal X-ray crystallographic study of compounds **1**–**3** are given in Table 2. Data were collected on a Siemens P4 diffractometer at 170 K. The refinement method was full-matrix least squares on F^2. The structure solution and refinement was carried out using the SHELX-97 program.[22] For the figures the Diamond program was used.[23] All non-hydrogen atoms were refined anisotropically and H-positions were set geometrically.

CCDC reference numbers 183181 (**1**), 186865 (**2**) and 186866 (**3**).

See http://www.rsc.org/suppdata/dt/b3/b301290e/ for crystallographic data in CIF or other electronic format.

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