

Dedicated to Professor Valer Farcasan  
on the occasion of his 95th anniversary

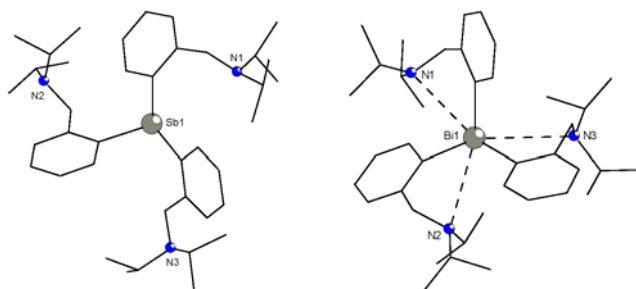
## HOMOLEPTIC ORGANOMETALLIC COMPOUNDS OF HEAVY PNICOGENS. CRYSTAL AND MOLECULAR STRUCTURE OF [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M (M = Sb, Bi)

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Two new homoleptic triorganopnicogen(III) species, [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M [M = Sb (**2**), Bi (**3**)] were obtained by reacting [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>MgBr (prepared *in situ* from [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Br (**1**) and Mg filings] with MCl<sub>3</sub>. The compounds were characterized by multinuclear NMR solution studies and the crystal and molecular structure of **2** and **3** was established by single-crystal X-ray diffraction. The NMR data are consistent with one type of organic group attached to the metal atom in **2** and **3**. The main difference between the molecules of the organometallic species is observed in the solid state. While for the antimony(III) compound all pendant arms are twisted to push the nitrogen atoms far from the metal centre, in the bismuth(III) derivative weak intramolecular N→Bi interactions are established for all three nitrogen atoms, thus increasing the coordination number from three to six in a distorted octahedral (C,N)<sub>3</sub>Bi core.



### INTRODUCTION

The organometallic chemistry of heavy pnicogens (antimony, bismuth) with aromatic ligands bearing one or two pendant arms containing nitrogen as donor atom, *e.g.* 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>, 2-[E(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>, 2-(RN=CH)C<sub>6</sub>H<sub>4</sub>, RN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>, 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-[E(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub> or related derivatives, raised continuous interest both due to fundamental approaches<sup>1-17</sup> and the potential biological properties<sup>1,18</sup> or applications in catalysis,<sup>1</sup> including

CO<sub>2</sub> fixation,<sup>1,19,20</sup> or bismuth-based C–H bond activation.<sup>1,21-23</sup>

The organopnicogen(III) mono- and dichlorides are basic starting materials for the synthesis of new organopnicogen species and a useful method to prepare these halides is the redistribution reaction between R<sub>3</sub>M and MCl<sub>3</sub>, in solution or in absence of a solvent.<sup>24-28</sup> We report here on the synthesis, the spectroscopic characterization in solution as well as the molecular structure of two new triorganopnicogen(III) derivatives, *i.e.* [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M [M = Sb (**2**), Bi (**3**)], which

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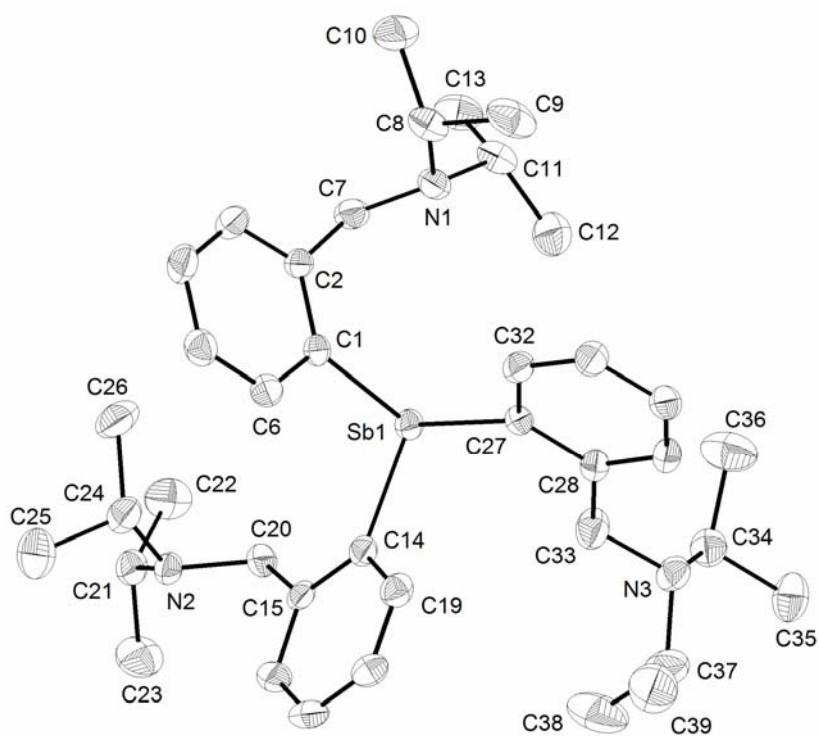


Fig. 1 – ORTEP representation at 25% probability and atom numbering scheme for [2-(*i*-Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Sb (2). Hydrogen atoms are omitted for clarity.

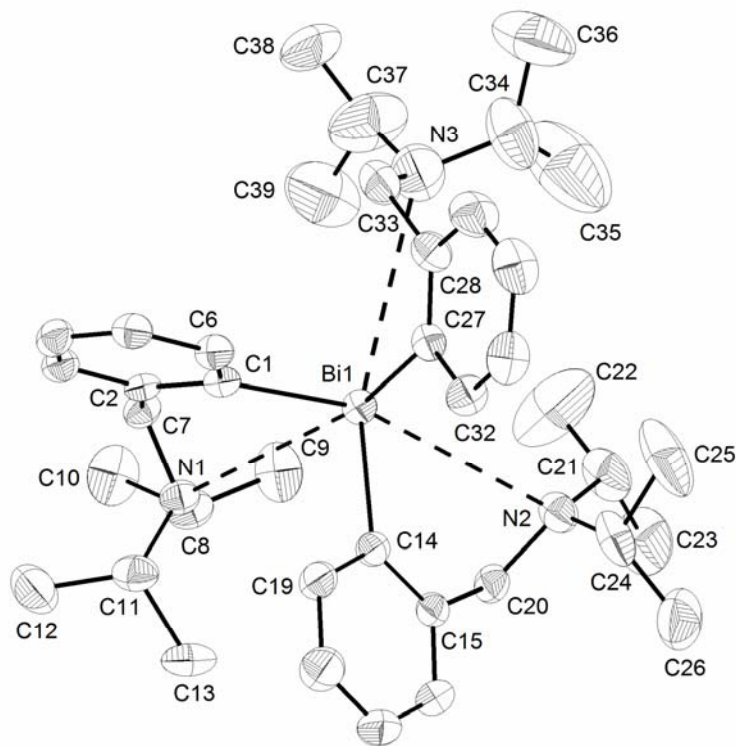


Fig. 2 – ORTEP representation at 25% probability and atom numbering scheme for [2-(*i*-Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (3). Hydrogen atoms are omitted for clarity.

Table 1

Selected interatomic distances (Å) and angles (deg) in  $[2-(^i\text{Pr}_2\text{NCH}_2)\text{C}_6\text{H}_4]_3\text{M}$  [M = Sb (**2**), Bi (**3**)]

<b>2</b>		<b>3</b>	
Sb(1)–C(1)	2.158(4)	Bi(1)–C(1)	2.269(7)
Sb(1)–C(14)	2.168(3)	Bi(1)–C(14)	2.260(6)
Sb(1)–C(27)	2.164(4)	Bi(1)–C(27)	2.261(6)
		Bi(1)⋯N(1)	3.401(6)
		Bi(1)⋯N(2)	3.397(7)
		Bi(1)⋯N(3)	3.573(11)
N(1)–C(7)	1.454(5)	N(1)–C(7)	1.460(8)
N(1)–C(8)	1.453(5)	N(1)–C(8)	1.502(9)
N(1)–C(11)	1.492(5)	N(1)–C(11)	1.476(9)
N(2)–C(20)	1.445(4)	N(2)–C(20)	1.470(8)
N(2)–C(21)	1.476(5)	N(2)–C(21)	1.484(11)
N(2)–C(24)	1.456(5)	N(2)–C(24)	1.456(11)
N(3)–C(33)	1.451(5)	N(3)–C(33)	1.304(13)
N(3)–C(34)	1.478(5)	N(3)–C(34)	1.516(15)
N(3)–C(37)	1.477(5)	N(3)–C(37)	1.537(16)
C(1)–Sb(1)–C(14)	96.27(13)	C(1)–Bi(1)–C(14)	95.1(2)
C(1)–Sb(1)–C(27)	99.51(14)	C(1)–Bi(1)–C(27)	90.8(2)
C(14)–Sb(1)–C(27)	96.40(13)	C(14)–Bi(1)–C(27)	94.6(2)
		N(1)–Bi(1)–N(2)	113.45(14)
		N(1)–Bi(1)–N(3)	90.1(3)
		N(2)–Bi(1)–N(3)	104.6(3)
		N(1)–Bi(1)–C(27)	154.1(2)
		N(2)–Bi(1)–C(1)	158.6(2)
		N(3)–Bi(1)–C(14)	154.4(2)
		N(1)–Bi(1)–C(1)	64.1(2)
		N(2)–Bi(1)–C(14)	63.9(2)
		N(3)–Bi(1)–C(27)	61.6(2)
		N(1)–Bi(1)–C(14)	82.2(2)
		N(2)–Bi(1)–C(27)	87.5(2)
		N(3)–Bi(1)–C(1)	94.5(3)
C(7)–N(1)–C(8)	114.9(3)	C(7)–N(1)–C(8)	112.3(6)
C(7)–N(1)–C(11)	113.5(3)	C(7)–N(1)–C(11)	112.7(6)
C(8)–N(1)–C(11)	114.5(3)	C(8)–N(1)–C(11)	116.0(6)
		Bi(1)–N(1)–C(7)	79.9(3)
		Bi(1)–N(1)–C(8)	116.3(4)
		Bi(1)–N(1)–C(11)	114.2(4)
C(20)–N(2)–C(21)	114.4(3)	C(20)–N(2)–C(21)	114.1(7)
C(20)–N(2)–C(24)	113.2(3)	C(20)–N(2)–C(24)	112.1(6)
C(21)–N(2)–C(24)	116.4(3)	C(21)–N(2)–C(24)	115.4(8)
		Bi(1)–N(2)–C(20)	78.2(4)
		Bi(1)–N(2)–C(21)	113.3(5)
		Bi(1)–N(2)–C(24)	118.2(5)
C(33)–N(3)–C(34)	111.7(3)	C(33)–N(3)–C(34)	115.2(11)
C(33)–N(3)–C(37)	112.6(3)	C(33)–N(3)–C(37)	120.2(13)
C(34)–N(3)–C(37)	114.2(3)	C(34)–N(3)–C(37)	105.5(13)
		Bi(1)–N(3)–C(33)	74.9(6)
		Bi(1)–N(3)–C(34)	126.4(8)
		Bi(1)–N(3)–C(37)	113.2(8)

## DISCUSSION

## Solution behavior

The presence of only one set of  $^1\text{H}$  and  $^{13}\text{C}$  resonances, respectively, in both compounds **2** and **3** is consistent with equivalent 2-( $\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$  groups attached to the same metal in solution at the NMR time scale. This suggests either the lack of intramolecular  $\text{N}\rightarrow\text{M}$  interactions in solution or a fast dynamic process which consists in de-coordination – inversion of configuration at nitrogen – re-coordination of the donor atoms to the metal centre.

## Solid state structure

In solid state there are significant differences between the title triorganopnictogen(III) compounds. In the molecule of **2** (Fig. 1) the pendant arms are twisted to push the nitrogen atoms far from the metal centre, probably due to steric repulsions between bulky isopropyl groups attached to nitrogen, thus preventing any intramolecular  $\text{N}\rightarrow\text{Sb}$  interaction [shorter non-bonding  $\text{Sb}(1)\cdots\text{N}(1)$  3.735(4) Å; c.f. the sum of the corresponding van der Waals radii,  $\Sigma r_{\text{vdW}}(\text{Sb},\text{N})$  3.74 Å].<sup>32</sup> As result the antimony atom in **2** remains three-coordinated in a trigonal pyramidal  $\text{C}_3\text{Sb}$  core (metal atom in the apical position). This contrasts with the situation observed in related triorganoantimony(III) compounds for which an increased coordination number is achieved based on three ( $C,N$ )-ligands, e.g. [2-( $\text{Me}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $_3\text{Sb}$  [ $\text{N}\rightarrow\text{Sb}$  3.03(2) - 3.041(11) Å,<sup>33</sup> 2.970(4) - 3.034(5) Å<sup>34</sup>] or [2-

{ $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2$ ] $\text{C}_6\text{H}_4$ ] $_3\text{Sb}$  [ $\text{N}\rightarrow\text{Sb}$  3.15(1) Å]<sup>35</sup> with an octahedral ( $C,N$ ) $_3\text{Sb}$  core, or two ( $C,N$ )-ligands, e.g. [2- $\{(S)\text{-Me}_2\text{NCH}(\text{Me})\}$ ] $\text{C}_6\text{H}_4$ ] $_3\text{Sb}$  [ $\text{N}\rightarrow\text{Sb}$  2.920(4) / 2.988(5) Å]<sup>34</sup> with a square pyramidal ( $C,N$ ) $_2\text{SbC}$  core.

In the crystal of **2** weak intermolecular  $\text{C}-\text{H}_{\text{aryl}}\cdots\pi$  ( $\text{Ph}_{\text{centroid}}$ ) interactions (*i.e.*  $\text{H}\cdots\text{Ph}_{\text{centroid}}$  contact shorter than 3.1 Å, with an angle  $\gamma$  between the normal to the phenyl ring and the line defined by the H atom and  $\text{Ph}_{\text{centroid}}$  smaller than  $30^\circ$ )<sup>36</sup> are established between pairs of molecules thus resulting in dimer associations [ $\text{C}(5)-\text{H}(5)\cdots\text{Ph}_{\text{centroid}}\{\text{C}(27a)-\text{C}(32a)\}$  2.98 Å;  $\gamma = 15.9^\circ$ ] (Fig. 3).

By contrast, the crystal of the bismuth(III) analogue **3** contains discrete molecules, with no intermolecular interactions based on contacts which involve the hydrogen atoms. In this case the nitrogen atoms from all three pendant arms are coordinated to the metal centre, probably due to a larger volume of the metal atom and its increased electropositive character. The resulted coordination geometry is distorted octahedral, with opposite trigonal faces described by the carbon atoms and by the nitrogen atoms, respectively. The bulkiness of the organic groups attached to nitrogen atoms is however reflected in the magnitude of the intramolecular  $\text{N}\rightarrow\text{Bi}$  interactions which are considerably longer in **3** [ $\text{Bi}(1)\cdots\text{N}$  range: 3.397(7) - 3.573(11) Å; c.f. the sum of the corresponding van der Waals radii,  $\Sigma r_{\text{vdW}}(\text{Bi},\text{N})$  3.94 Å]<sup>32</sup> than in other related species, e.g. [2-( $\text{R}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $_3\text{Bi}$  [ $\text{N}\rightarrow\text{Bi}$  3.04(2) - 3.11(3) Å for  $\text{R} = \text{Me}$ ;<sup>33</sup> 3.214(7) Å for  $\text{R} = \text{Et}$ <sup>37</sup>] or [2- $\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2$ ] $\text{C}_6\text{H}_4$ ] $_3\text{Bi}$  [ $\text{N}\rightarrow\text{Bi}$  3.170(7) Å for  $\text{E} = \text{O}$ ; 3.211(5) Å for  $\text{E} = \text{MeN}$ ].<sup>38</sup>

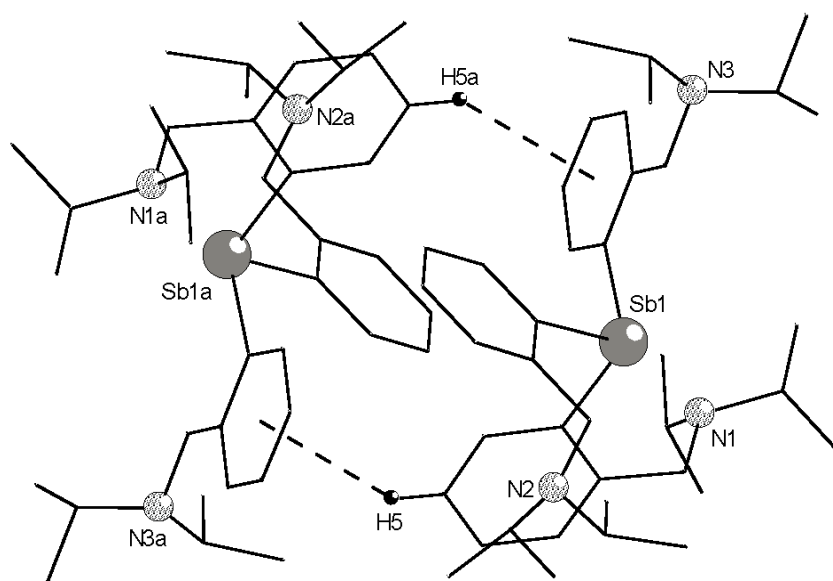


Fig. 3 – View of the dimer association in the crystal of **2** based on intermolecular  $\text{C}-\text{H}_{\text{aryl}}\cdots\pi$  ( $\text{Ph}_{\text{centroid}}$ ) interactions (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms ( $1-x$ ,  $1-y$ ,  $-z$ ) are given by “a”].

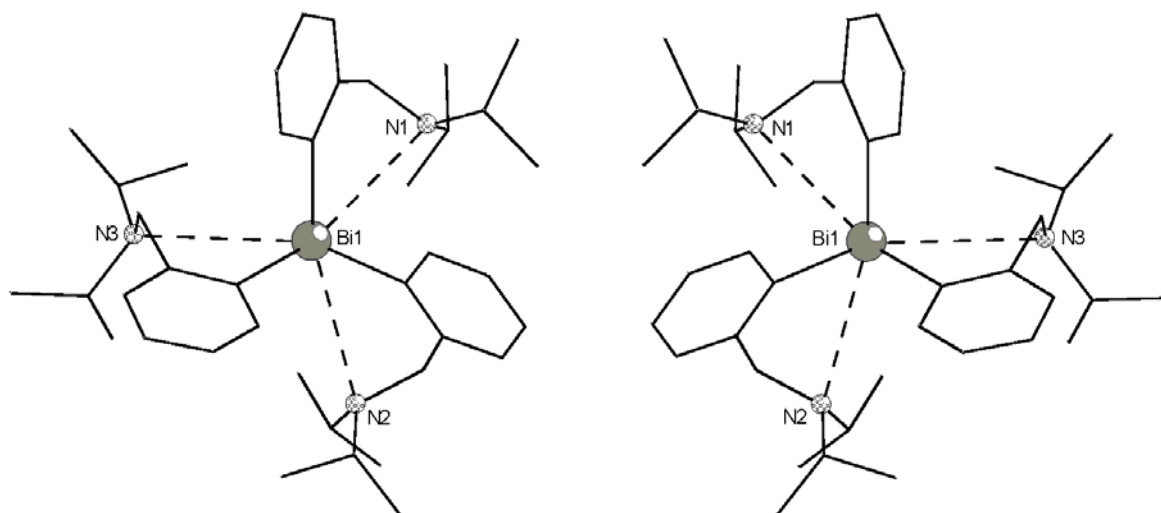


Fig. 4 – Molecular structure of isomers  $M$ -( $pR_{N1}, pR_{N2}, pS_{N3}$ )-3 (left) and  $P$ -( $pS_{N1}, pS_{N2}, pR_{N3}$ )-3 (right) in the crystal of **3**.

To minimize the sterical repulsions the three ( $C,N$ )-ligands adopt a propeller-like conformation in **3**, as observed in solid state for most of the homoleptic triarylplnicogen(III) derivatives with an octahedral ( $C,N$ )<sub>3</sub>Bi core.<sup>1</sup> As a result helicoidal chirality can be considered, *i.e.*  $M$ -helicoidal and  $P$ -helicoidal isomers with respect to the left-handed or right-handed helicity of the aromatic rings along a  $C_3$ -axis passing through the metal centre. Moreover, the five-membered BiC<sub>3</sub>N chelate rings are not planar and this induces planar chirality [with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively].<sup>39</sup> Consequently, the crystal of **3** consists of a 1:1 mixture of  $M$ -( $pR_{N1}, pR_{N2}, pS_{N3}$ ) and  $P$ -( $pS_{N1}, pS_{N2}, pR_{N3}$ ) isomers (Fig. 4).

## EXPERIMENTAL

All manipulations were carried out under an inert atmosphere of argon using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. Other starting materials such as 2-(BrCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br, SbCl<sub>3</sub> and BiCl<sub>3</sub> were obtained from Aldrich or Merck, and were used as received. <sup>1</sup>H, <sup>13</sup>C and 2D NMR spectra were recorded at room temperature on Bruker Avance 300 or Bruker Avance III 600 instruments, using solutions in CDCl<sub>3</sub>. The <sup>1</sup>H chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of the deuterated solvent (CHCl<sub>3</sub>, 7.26 ppm). The <sup>13</sup>C chemical shifts are reported in  $\delta$  units (ppm) relative to the peak of the deuterated solvent (CDCl<sub>3</sub>, 77.16 ppm).<sup>40</sup> <sup>1</sup>H and <sup>13</sup>C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC). The NMR spectra were processed using the *MestReC* and *MestReNova* software.<sup>41</sup> HRMS APCI(+) spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic patterns were carried out with the Xcalibur software package.<sup>42</sup>

### Synthesis of 2-(di-isopropylaminomethyl)phenyl bromide, 2-(*i*-Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (**1**)

A solution of 2-bromobenzyl bromide (126.2 g, 0.50 mol) in 100 mL benzene was added dropwise to a solution of 210 mL di-isopropylamine (212.4 mL, 152.95 g, 1.51 mol) in 500 mL benzene. A white precipitate was formed after a few hours and the solution turned yellow. The reaction mixture was refluxed for 36 h and after cooling to room temperature the solid was filtered off and washed with 150 mL benzene. Benzene and excess of di-isopropylamine were removed from the clear yellow filtrate *in vacuo*. The remaining residue was further distilled under vacuum to give **1** as a pale yellow liquid (b.p. 69 °C at 10<sup>-3</sup> mbar), which should be stored in dark under inert atmosphere. Yield: 101.2 g (75%). <sup>1</sup>H NMR (300 MHz):  $\delta$  1.10 [12H, d, -CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz], 3.12 [2H, hept, -CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz], 3.76 (2H, s, H-7), 7.10 (1H, ddd, H-5, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz), 7.33 (1H, ddd, H-4, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz), 7.54 (1H, dd, H-6, <sup>3</sup>J<sub>HH</sub> = 7.9, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz), 7.78 (1H, dd, H-3, <sup>3</sup>J<sub>HH</sub> = 7.8, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz). <sup>13</sup>C NMR (75.5 MHz):  $\delta$  20.97 [s, -CH(CH<sub>3</sub>)<sub>2</sub>], 48.87 [s, -CH(CH<sub>3</sub>)<sub>2</sub>], 49.23 (s, C-7), 123.38 (s, C-1), 127.11 (s, C-4), 127.58 (s, C-5), 130.23 (s, C-3), 132.18 (s, C-6), 142.13 (s, C-2). MS (APCI+, MeCN):  $m/z$  (%) 270.09 (55) [M+H]<sup>+</sup>, 254.05 (100) [M-Me]<sup>+</sup>. HRMS (APCI+): Calc. for [C<sub>13</sub>H<sub>21</sub>BrN]<sup>+</sup> 270.08521. Found: 270.08519.

### Synthesis of tris[2-(di-isopropylaminomethyl)phenyl]antimony(III), [2-(*i*-Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Sb (**2**)

A solution of **1** (6.00 g, 22.20 mmol) in 50 mL anhydrous diethyl ether was added dropwise, under stirring, to magnesium filings (0.675 g, 27.78 mmol, 25% excess) activated with 1,2-dibromoethane (1.04 g, 5.55 mmol). The reaction mixture was stirred for 3 h under reflux, which resulted in complete consumption of magnesium. To the solution of the organomagnesium derivative thus obtained and cooled at -78 °C was added dropwise, under stirring, a solution of SbCl<sub>3</sub> (0.844 g, 3.70 mmol) in 30 mL toluene, at -78 °C. The reaction mixture was left to reach the room temperature and was stirred at this temperature for 12 h. The distilled water was added (90 mL) and the organic phase was separated and dried over anhydrous MgSO<sub>4</sub>. The solid was filtered off and the solvent was removed *in vacuo* from the clear solution to give a viscous residue. Its treatment with acetonitrile (40 mL) afforded the isolation of **2** as a white solid after separation by filtration and drying under reduced

pressure. Yield: 1.49 g (58%). M.p. = 100–102 °C.  $^1\text{H}$  NMR (300 MHz):  $\delta$  0.91 [36H, d,  $-\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz], 2.95 [6H, hept,  $-\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz], 3.78 (6H, s, H<sub>7</sub>), 7.01 (6H, m, H-5 + H-6), 7.27 (3H, m, H-4), 7.62 (3H, d, H-3,  $^3J_{\text{HH}} = 7.6$  Hz).  $^{13}\text{C}$  NMR (75.5 MHz):  $\delta$  20.80 [s,  $-\text{CH}(\text{CH}_3)_2$ ], 47.81 [s,  $-\text{CH}(\text{CH}_3)_2$ ], 51.63 (s, C-7), 127.01 (s, C-5), 128.38 (s, C-4), 128.56 (s, C-3), 136.69 (s, C-6), 138.69 (s, C-1), 148.00 (s, C-2). MS (APCI+, MeCN):  $m/z$  (%) 692.39 (7)  $[\text{M}+\text{H}]^+$ , 501.22 (100)  $[\text{M}-\text{R}]^+$  [R = 2-( $^i\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ]. HRMS (APCI+): Calc. for  $[\text{C}_{39}\text{H}_{61}\text{N}_3\text{Sb}]^+$  692.38982. Found: 692.38885.

*Synthesis of tris[2-(di-isopropylaminomethyl)phenyl]bismuth(III), [2-( $^i\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $_3\text{Bi}$  (3)*

Compound **3** was prepared as above by reacting [2-( $^i\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $\text{MgBr}$  [obtained *in situ* from **1** (6.00 g, 22.20 mmol) and Mg filings (0.675 g, 27.78 mmol) activated with 1,2-dibromoethane] in anhydrous  $\text{Et}_2\text{O}$  (60 mL) and  $\text{BiCl}_3$  (1.167 g, 3.70 mmol) in  $\text{Et}_2\text{O}$  (30 mL), at 0 °C. The reaction mixture was stirred at room temperature for 12 h, then treated with distilled water (80 mL). The organic phase was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solid was filtered off, removal of the solvent from the clear solution left an oily residue. Treatment with acetonitrile (30 mL) afforded the isolation of **3** as a white solid after separation by filtration and drying under reduced pressure. Yield: 1.53 g (53%). M.p. = 96–98 °C.  $^1\text{H}$  NMR (600 MHz):  $\delta$  0.95 [36H, d,

$-\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.8$  Hz], 2.99 [6H, hept,  $-\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz], 3.78 (6H, s, H-7), 7.07 (3H, ddd, H-5,  $^3J_{\text{HH}} = 7.3$ ,  $^4J_{\text{HH}} = 1.4$  Hz), 7.30 (3H, dd, H-4,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.4$  Hz), 7.60 (3H, d, H-6,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HH}} = 1.4$  Hz), 7.63 (3H, d, H-3,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.3$  Hz).  $^{13}\text{C}$  NMR (75.5 MHz):  $\delta$  20.80 [s,  $-\text{CH}(\text{CH}_3)_2$ ], 47.69 [s,  $-\text{CH}(\text{CH}_3)_2$ ], 53.68 (s, C-7), 127.37 (s, C-4), 129.32 (s, C-5), 129.50 (s, C-3), 139.65 (s, C-6), 147.38 (s, C-2), 158.68 (s, C-1). MS (APCI+, MeCN):  $m/z$  (%) 778.45 (1)  $[\text{M}-\text{H}]^+$ , 589.30 (100)  $[\text{M}-\text{R}]^+$  [R = 2-( $^i\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ]. HRMS (APCI+): Calc. for  $[\text{C}_{39}\text{H}_{59}\text{N}_3\text{Bi}]^+$  778.45073. Found: 778.44733.

### Crystal structure determination

Block colorless crystals of **2** and **3** were attached on cryoloops using epoxy glue. The details of the crystal structure determination and refinement are given in Table 2. Data collection and processing was carried on a Bruker SMART APEX system using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), at room temperature.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.<sup>44</sup> The drawings were created with the Diamond program.<sup>45</sup>

Table 2

Crystallographic data for [2-( $^i\text{Pr}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ ] $_3\text{M}$  [M = Sb (**2**), Bi (**3**)]

Compound	<b>2</b>	<b>3</b>
Molecular formula	$\text{C}_{39}\text{H}_{60}\text{N}_3\text{Sb}$	$\text{C}_{39}\text{H}_{60}\text{BiN}_3$
$M$	692.65	779.88
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
Temperature (K)	297(2)	297(2)
$a/\text{Å}$	12.607(4)	13.3380(18)
$b/\text{Å}$	13.111(4)	13.4359(18)
$c/\text{Å}$	13.557(5)	21.751(3)
$\alpha^\circ$	68.239(6)	90
$\beta^\circ$	70.176(6)	94.278(3)
$\gamma^\circ$	69.626(5)	90
$V/\text{Å}^3$	1893.3(11)	3887.0(9)
$Z$	2	4
$D_{\text{calc}}/\text{gcm}^{-3}$	1.215	1.333
$F(000)$	732	1592
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.757	4.563
Crystal size ( $\text{mm}^3$ )	0.50 x 0.25 x 0.25	0.40 x 0.34 x 0.30
$\theta$ range for data collection ( $^\circ$ )	1.67 to 25.00	1.53 to 25.00
Reflections collected	18369	36790
Independent reflections	6655 [ $R_{\text{int}} = 0.1045$ ]	6853 [ $R_{\text{int}} = 0.0896$ ]
Absorption correction	Multi-Scan <sup>43</sup>	Multi-Scan <sup>43</sup>
Maximum and minimum transmissions	0.8333 and 0.7034	0.3414 and 0.2626
Data / restraints / parameters	6655 / 0 / 400	6853 / 0 / 400
Goodness-of-fit on $F^2$	0.973	1.048
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0459$ $wR_2 = 0.0851$	$R_1 = 0.0462$ $wR_2 = 0.1079$
$R$ indices (all data)	$R_1 = 0.0576$ $wR_2 = 0.0888$	$R_1 = 0.0620$ $wR_2 = 0.1140$
Largest difference peak and hole ( $e \text{ Å}^{-3}$ )	1.210 and $-0.490$	1.092 and $-1.123$

## SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 1042954 (**2**) and 1042953 (**3**)]. 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).

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