

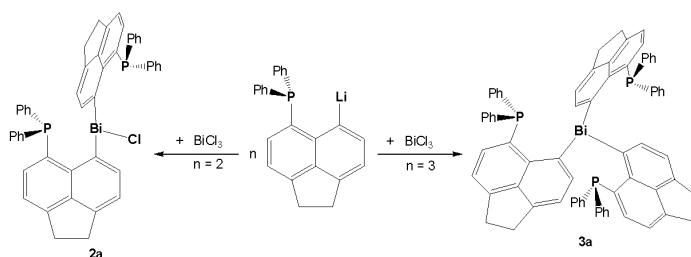
SYNTHESIS AND STRUCTURE  
OF 6-DIPHENYLPHOSPHINOACENAPHTH-5-YL BISMUTH COMPOUNDS

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Received July 11, 2019

The di- and tri-substituted arylbismuth compounds  $R_2BiCl$  and  $R_3Bi$  ( $R = 6$ -diphenylphosphinoacenaphth-5-yl) were prepared and fully characterized. Both compounds contain intramolecularly coordinating P-donor atoms that provide electron density to the bismuth atoms.



## INTRODUCTION

There is a growing interest in arylbismuth compounds containing intramolecularly coordinating donor ligands, which are able to block potential coordination sites at the bismuth atom and to (partly) compensate the inherent Lewis acidity.<sup>1</sup> Alternatively, the donor ligands may also bind to transition metal ions giving rise to interesting complexes that involve metal bismuth interactions. The vast majority of these ligands possess N-donors,<sup>2-8</sup> whereas as P-donors are only occasionally encountered.<sup>9-15</sup> As part of our research programme on *peri*-substituted scaffolds, we recently prepared the monoarylbismuth dichloride  $RBiCl_2$  (**1a**,  $R = 6$ -diphenylphosphinoacenaphth-5-yl), the analogous arylantimony dichloride  $RSbCl_2$  (**1b**)<sup>16</sup> as well as the

diarylantimony chloride  $R_2SbCl$  (**2b**) and the triarylantimony  $R_3Sb$  (**3b**).<sup>17</sup> The latter two compounds were also used as (coordination non-innocent) ligands towards late transition metals. In an effort to complete the series of bismuth compounds, we now also report on the synthesis and structure of diarylbismuth chloride  $R_2BiCl$  (**2a**) and the triarylbismuth  $R_3Bi$  (**3a**), which also hold potential as ligands for the preparation of transition metal complexes.

## RESULTS AND DISCUSSION

The synthesis of **2a** and **3a** was achieved by the stoichiometry controlled reaction between the aryl lithium  $RLi$  and  $BiCl_3$  at  $-78^\circ C$  ( $R = 6$ -diphenylphosphinoacenaphth-5-yl, Scheme 1).<sup>18</sup>

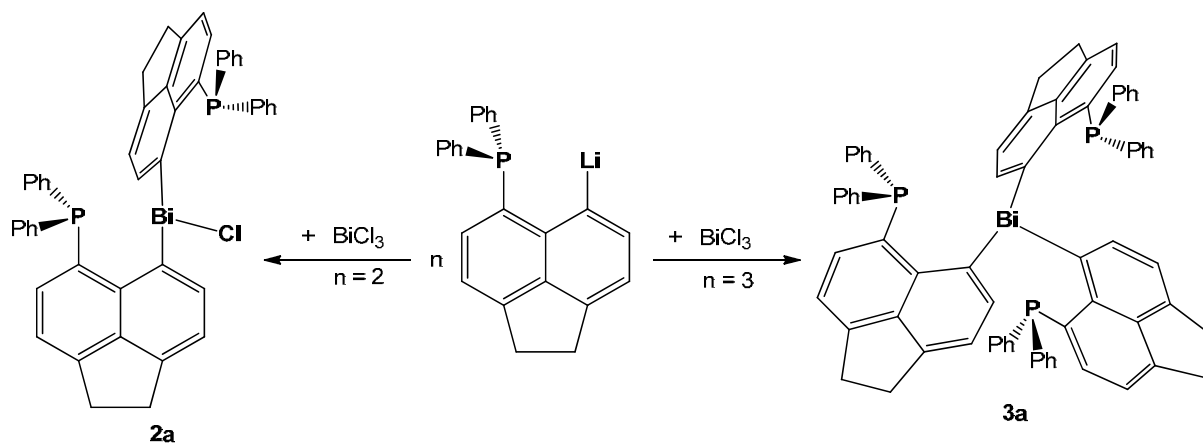
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The products **2a** and **3a** were obtained as pale yellow crystalline solids in 85 and 73% yield, respectively. The molecular structures of **2a** and **3a** are shown in Figure 1. There are two crystallographically independent, yet very similar conformers of **2a** in the crystal lattice. In both compounds, the spatial arrangement of the Bi atoms is trigonal pyramidal when bearing in mind the first coordination sphere.

In addition, there are significant Bi...P *peri*-interactions that are shorter than the sum of van der Waals radii. One Bi...P bond length of **2a** [2.8990(13) Å, (2.8614(14) Å)] is significantly shorter than the other [3.3555(13) Å, (3.2704(12) Å)] and slightly longer than the Bi...P distance of **1a** (2.7696(8) Å).<sup>16</sup> The Bi...P bond lengths of **3a** (3.2166(7), 3.2660(5), 3.2745(7) Å) are between

the respective distances found for **2a**. Overall, the bond situation closely resembles that of the Sb...P bond lengths of **1b** (2.8080(9) Å),<sup>16</sup> **2b** (2.7738(8), 3.2660(7) Å) and **3b** (3.1713(8), 3.2293(7), 3.2427(9) Å)<sup>17</sup> as well as of the related R<sub>3</sub>Bi species (R' = 6-di-*iso*-propylphosphinoacenaphth-5-yl; 3.218(3)-3.279(4) Å).<sup>19</sup>

Compounds **2a** and **3a** are soluble in common organic solvents, such as dichloromethane, tetrahydrofuran and toluene. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>) of **2a** and **3a** show single resonances at δ = -20.9 ppm and -30.6 ppm, respectively, indicating magnetic equivalence of the 6-diphenylphosphinoacenaphth-5-yl groups in solution at room temperature. These values compare well with those of the antimony analogues **2b** (δ = -20.3) and **3b** (δ = -26.8 ppm).



Scheme 1 – Synthesis of **2a** and **3a**.

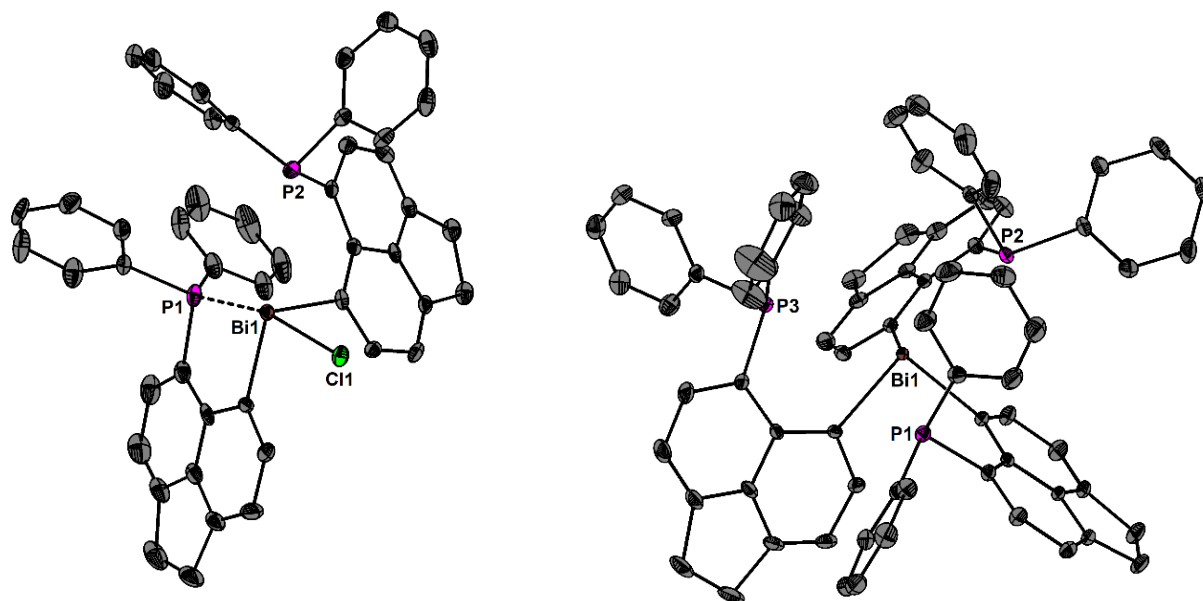


Fig. 1 – Molecular structures of R<sub>2</sub>BiCl (**2a**, left) and R<sub>3</sub>Bi (**3a**, right) showing 50% probability ellipsoids (R = 6-diphenylphosphinoacenaphth-5-yl).

## EXPERIMENTAL

**General.** Reagents were obtained commercially (Sigma-Aldrich, Germany) and were used as received. Dry solvents were collected from a SPS800 mBraun solvent system. The starting material 5-bromo-6-diphenylphosphinoacenaphthene was prepared according to literature procedures.<sup>20</sup>  $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded at room temperature (unless otherwise stated) using Bruker Avance 360 and Neo 600 spectrometer and are referenced to tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and phosphoric acid (85% in water) ( $^{31}\text{P}$ ). Chemical shifts are reported in parts per million (ppm) and coupling constants ( $J$ ) are given in Hertz (Hz). Electrospray ionization mass spectrometry (ESI-MS) was carried out using a Bruker Impact II. Acetonitrile solution was injected directly into the spectrometer at a flow rate of  $3\ \mu\text{L}\ \text{min}^{-1}$ . Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 4 L/min and a pressure of 0.4 bar. The spectra were collected for one minute and averaged.

**Synthesis of bis(6-(diphenylphosphino)acenaphth-5-yl)bismuth chloride (2a).** *n*-Butyllithium (1.20 mmol, 2.5 M in *n*-hexane) and *N,N,N',N'*-tetramethylethylenediamine (139.7 mg, 1.20 mmol) were added at  $-78^\circ\text{C}$  to a suspension of

5-bromo-6-diphenylphosphino-acenaphthene (500 mg, 1.20 mmol) in diethyl ether (15 mL) and stirred for 2 h. The suspension was allowed to warm up to room temperature, stirred for 1 h, and was added at  $-78^\circ\text{C}$  to a solution of bismuth trichloride (190.0 mg, 0.60 mmol) and diethyl ether (15 mL). Temperature of the reaction mixture was slowly raised to room temperature overnight. After settling of the precipitate, the supernatant was decanted and dichloromethane added. Aqueous workup and removal of the solvent via rotary evaporation led to **2a** as pale yellow solid (470 mg, 0.51 mmol, 85%, mp  $192^\circ\text{C}$  (dec.)). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a dichloromethane solution at room temperature.

$^1\text{H-NMR}$  (360.3 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.16$  (d,  $^3J(^1\text{H} - ^1\text{H}) = 7.0$  Hz, 2H), 7.42 (d,  $^3J(^1\text{H} - ^1\text{H}) = 7.1$  Hz, 3H), 7.31–6.85 (m, 23H), 3.44–3.30 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (90.6 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 152.1$  (s), 147.3 (s), 144.0 (s), 143.0 (d,  $^3J(^{31}\text{P}-^{13}\text{C}) = 10.2$  Hz), 137.2 (s), 133.6 (d), 132.7 (d), 131.0 (d,  $J(^{31}\text{P}-^{13}\text{C}) = 6.9$  Hz), 129.8 (s), 128.9 (d,  $^3J(^{31}\text{P}-^{13}\text{C}) = 4.1$  Hz), 125.2 (s), 120.2 (d,  $^2J(^{31}\text{P}-^{13}\text{C}) = 2.1$  Hz), 30.9 (s), 30.7 (s).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (145.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = -20.9$  (s). **HR-ESI MS:** ( $\text{CH}_2\text{Cl}_2/\text{MeCN}$  1:100, positive mode): calcd for  $\text{C}_{48}\text{H}_{36}\text{P}_2\text{Bi} [\text{M}-\text{Cl}]^+$ , 883.20907; found, 883.20772.

Table 1

Crystal data and structure refinement of **2a** and **3a**

	<b>2a</b>	<b>3a</b> · $\text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{48}\text{H}_{36}\text{BiClP}_2$	$\text{C}_{73}\text{H}_{56}\text{BiCl}_2\text{P}_3$
Formula weight, $\text{g mol}^{-1}$	919.14	1305.96
Crystal system	triclinic	triclinic
Crystal size, mm	$0.20 \times 0.10 \times 0.10$	$0.08 \times 0.08 \times 0.06$
Space group	$P\bar{1}$	$P\bar{1}$
$a$ , Å	12.2176(3)	12.7530(4)
$b$ , Å	19.4901(4)	14.4881(4)
$c$ , Å	20.2705(5)	17.8021(6)
$\alpha$ , °	114.407(1)	74.605(1)
$\beta$ , °	102.483(1)	79.599(1)
$\gamma$ , °	98.766(1)	64.512(1)
$V$ , Å <sup>3</sup>	4129.9(2)	2854.3(2)
$Z$ ( $Z'$ )	4 (2)	2 (1)
$\rho_{\text{calcd}}$ , $\text{Mg m}^{-3}$	1.478	1.520
$T$ , K	100	100
$\mu$ (Mo $K\alpha$ ), $\text{mm}^{-1}$	4.443	3.312
$F(000)$	1816	1312
$\theta$ range, deg	2.32 to 25.50	2.61 to 33.19
Index ranges	$-14 \leq h \leq 14$ $-23 \leq k \leq 23$ $-24 \leq l \leq 24$	$-18 \leq h \leq 19$ $-21 \leq k \leq 22$ $-27 \leq l \leq 27$
No. of reflns collected	33470	72740
Completeness to $\theta_{\text{max}}$	97.4%	99.9%
No. indep. Reflns	14966	21891
No. obsd reflns with ( $I > 2\sigma(I)$ )	11605	18918
No. refined params	937	712
GooF ( $F^2$ )	0.966	1.031
$R_1$ ( $F$ ) ( $I > 2\sigma(I)$ )	0.0274	0.0325
$wR_2$ ( $F^2$ ) (all data)	0.0612	0.0643
$(\Delta/\sigma)_{\text{max}}$	0.004	0.005
Largest diff peak/hole, $\text{e Å}^{-3}$	2.194 / -0.677	1.832 / -1.182
CCDC	1939481	1939482

**Synthesis of tris((6-(diphenylphosphino)acenaphth-5-yl)bismuth (3a).** *n*-Butyllithium (2.88 mmol, 2.5 M in *n*-hexane) and *N,N,N',N'*-tetramethylethylenediamine (334.7 mg, 2.88 mmol) were added at  $-78^{\circ}\text{C}$  to a suspension of 5-bromo-6-diphenylphosphinoacenaphthene (1.00 g, 2.40 mmol) in diethyl ether (50 mL) and stirred for 2 h at this temperature. The suspension was allowed to warm up to room temperature, stirred for 1 h and cooled to  $-78^{\circ}\text{C}$  again before a solution of bismuth trichloride (252 mg, 0.80 mmol) in diethyl ether (15 mL) was added. The reaction mixture was slowly raised to room temperature overnight. The precipitate was filtered, washed with acetonitrile ( $3 \times 50$  mL), solved in dichloromethane and filtered a second time. Removal of the solvent via rotary evaporation led to **3a** as pale yellow solid (710 mg, 0.58 mmol, 73%, mp  $178^{\circ}\text{C}$  (dec.)). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a dichloromethane solution at room temperature.

**$^1\text{H-NMR}$  (600.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta = 8.68$  (d,  $^3J(\text{H}-\text{H}) = 6.7$  Hz, 3H), 7.24–7.21 (m, 10H), 7.14 (d,  $^3J(\text{H}-\text{H}) = 7.5$  Hz, 6H), 7.12–7.09 (m, 4H), 6.99–6.96 (m, 14H), 6.55–6.53 (m, 5H), 3.46–3.29 (m, 12H).  **$^{13}\text{C}\{^1\text{H}\}$ -NMR (151.0 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta = 150.2$  (s), 145.7 (s), 145.2 (s), 141.5–141.4 (m), 138.4–138.3 (m), 137.5 (s,  $\text{C}_a$  or  $\text{C}_b$ ), 133.6–133.5 (m), 132.6–132.5 (m), 128.2 (m), 128.1 (s), 127.7 (m), 127.4 (s), 123.7 (s), 119.0 (s), 30.3 (s), 30.1 (s).  **$^{31}\text{P}\{^1\text{H}\}$ -NMR (243.0 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta = -30.6$  (s). **HR-ESI MS** ( $\text{CH}_2\text{Cl}_2/\text{MeCN}$  1:100, positive mode): calcd for  $\text{C}_{72}\text{H}_{54}\text{BiK}_3$   $[\text{M}+\text{K}]^+$ , 1259.28739; found, 1259.28742.

**X-ray crystallography.** Intensity data of **2a** and **3a** was collected on a Bruker Venture D8 diffractometer with graphite-monochromated Mo-K $\alpha$  (0.7107 Å) radiation. The structure was solved by direct methods and difference Fourier synthesis with subsequent Full-matrix least-squares refinements on  $F^2$ , using all data.<sup>21</sup> All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Strongly disordered THF molecules in the crystal lattice of **2a** were accounted for using the SQUEEZE routine.<sup>22</sup> Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND.<sup>23</sup> Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre. Copies of this 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 <http://www.ccdc.cam.ac.uk>).

## CONCLUSIONS

We present the synthesis of the P-stabilized diarylbismuthchloride **2a** and the triarylbismuth species **3a** along with its structural properties derived by single crystal diffraction measurements and NMR spectroscopy. The synthetic potential of

both compounds for the preparation of transition metal complexes is currently under investigation.

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