

Dedicated to Prof. Ion Grosu
on the occasion of his 70th anniversary

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF HOMOLEPTIC TRIORGANOPNICTOGEN(III) COMPOUNDS – USEFUL PRECURSORS FOR FUNCTIONALIZED MATERIALS. MOLECULAR STRUCTURE OF [4-((CH₂O)₂CH)C₆H₄]₃Sb

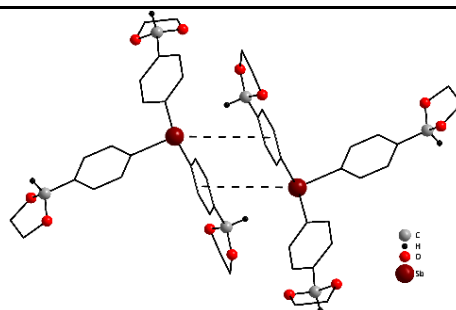
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[4-((CH₂O)₂CH)C₆H₄]₃Pn [Pn = Sb (**2**), Bi (**3**)] were obtained by treatment of heavy pnictogen(III) halides, PnCl₃, either with 4-((CH₂O)₂CH)C₆H₄MgBr or 4-((CH₂O)₂CH)C₆H₄Li [obtained *in situ* from 4-((CH₂O)₂CH)C₆H₄Br (**1**)]. Deprotection of the *para* substituents in **2** and **3** gave the carbonyl-substituted compounds [4-(O=CH)C₆H₄]₃Pn [Pn = Sb (**4**), Bi (**5**)], which afforded isolation of [4-(ⁱPrN=CH)C₆H₄]₃Pn [Pn = Sb (**6**), Bi (**7**)] and [4-((EtO)₃Si(CH₂)₃N=CH)C₆H₄]₃Bi [Pn = Sb (**8**), Bi (**9**)], following condensation reactions with ⁱPrNH₂ and (EtO)₃Si(CH₂)₃NH₂, respectively. The compounds were characterized by multinuclear NMR [¹H, ¹³C{¹H}], and ²⁹Si{¹H}], where appropriate] in solution and IR spectroscopies as well as mass spectrometry. The crystal and molecular structure of **2** was established by single-crystal X-ray diffraction. Weak intermolecular Sb···π (A_{Tcentroid}) interactions were found in solid state, thus resulting in a dimer association of molecules of **2** in the crystal. Compounds **4–9** might be potential useful precursors for functionalized materials.



INTRODUCTION

The organometallic chemistry of heavy pnictogens, antimony and bismuth, produced several outstanding results in the last three decades,¹ thus stimulating a continuous general interest in this field among several groups of scientists. Important achievements were obtained in a variety of topics related to both (i) *fundamental chemistry*, e.g. synthesis, structure and reactivity of

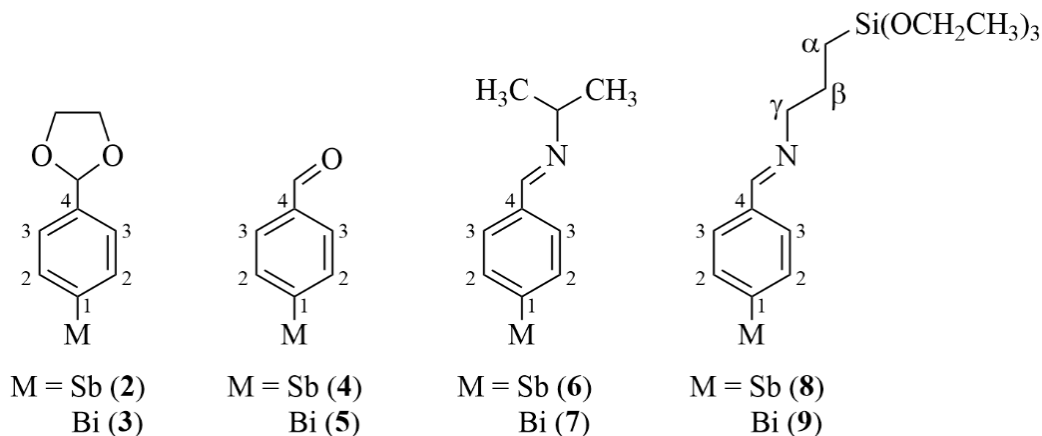
organopnictogen compounds,² exploring mononuclear and dinuclear organopnictogen(I)³ and other unusual organopnictogen species,⁴ the use of organopnictogen compounds in lower oxidation state as ligands for main group⁵ or transition metals,⁶ as well as understanding the nature of metal-metal bond,^{4d,6e,f,i,j,m,7} or aspects related to supramolecular chemistry,⁸ and (ii) and *applied chemistry*, e.g. investigation of photophysical

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peaks were the molecular $[M]^+$ and protonated molecular $[M + H]^+$ ions, respectively.

In the IR spectra typical medium to very strong bands were assigned to the C–O acetal group stretching ($940\text{--}970$, 939 cm^{-1}) for **2** and **3**, and C=O stretching vibration (ca. 1700 cm^{-1}) for **4** and **5**.¹⁹ For compounds **6–9** a strong band in the region $1630\text{--}1650\text{ cm}^{-1}$ was assigned to the stretching vibration of the C=N double bond as typical for compounds containing Schiff-base ligands.¹⁹

All compounds were characterized in CDCl_3 solution, at room temperature, by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy as well as $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy for compounds **8** and **9**. The NMR spectra are consistent with the investigated organopnictogen(III) compounds and the assignment of the observed ^1H and ^{13}C resonances was made using 2D NMR experiments, according to the numbering schemes shown in Scheme 2.



Scheme 2 – Numbering scheme for ^1H and ^{13}C NMR assignments.

The structure of compound **2** was established by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$. All the 1,3-dioxolan-2-yl rings are disordered over two positions and were modelled with site occupancies of 60:40,

60:40 and 94:6, respectively. The ORTEP-like representation of the molecular structure of **2**, with the atom numbering scheme, is depicted in Fig. 1. Selected interatomic distances and bond angles are listed in Table 1.

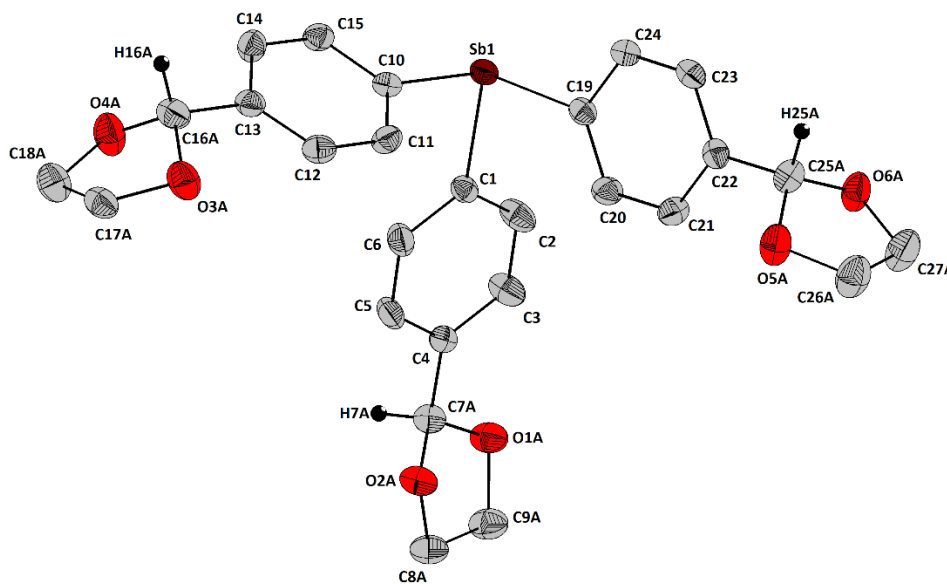


Fig. 1 – Thermal ellipsoid (probability 15%) representation of the molecular structure of **2** (*M* isomer). Hydrogen atoms bonded to carbon atoms, except those of *CH* of the acetal rings were omitted for clarity. The minor components of the disordered acetal rings are not shown.

Table 1
Selected interatomic distances (Å) and angles (deg) for [4- $\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4\}_3\text{Sb}$ (**2**)^a

Sb(1)–C(1)	2.161(4)	Sb(1)–C(10)	2.157(6)
Sb(1)–C(19)	2.169(5)		
O(1A)–C(7A) [O(1B)–C(7B)]	1.381(13) [1.377(19)]	O(2A)–C(7A) [O(2B)–C(7B)]	1.355(10) [1.377(19)]
O(1A)–C(9A) [O(1B)–C(9B)]	1.42(2) [1.44(3)]	O(2A)–C(8A) [O(2B)–C(8B)]	1.410(15) [1.41(2)]
O(3A)–C(16A) [O(3B)–C(16B)]	1.442(11) [1.347(15)]	O(4A)–C(16A) [O(4B)–C(16B)]	1.353(14) [1.433(14)]
O(3A)–C(17A) [O(3B)–C(17B)]	1.43(2) [1.42(3)]	O(4A)–C(18A) [O(4B)–C(18B)]	1.43(3) [1.44(4)]
O(5A)–C(25A) [O(5B)–C(25B)]	1.363(9) [1.39(6)]	O(6A)–C(25A) [O(6B)–C(25B)]	1.389(8) [1.36(6)]
O(5A)–C(26A) [O(5B)–C(26B)]	1.406(10) [1.42(13)]	O(6A)–C(27A) [O(6B)–C(27B)]	1.410(11) [1.41(10)]
C(1)–Sb(1)–C(10)	94.95(17)	C(1)–Sb(1)–C(19)	95.58(17)
C(10)–Sb(1)–C(19)	97.76(17)		
C(4)–C(7A)–O(1A) [C(4)–C(7B)–O(1B)]	113.1(7) [114.8(9)]	C(4)–C(7A)–O(2A) [C(4)–C(7B)–O(2B)]	113.1(6) [107.7(7)]
O(1A)–C(7A)–O(2A) [O(1B)–C(7B)–O(2B)]	110.7(7) [100.7(10)]		
C(13)–C(16A)–O(3A) [C(13)–C(16B)–O(3B)]	109.5(7) [118.1(9)]	C(13)–C(16A)–O(4A) [C(13)–C(16B)–O(4B)]	111.4(9) [108.4(10)]
O(3A)–C(16A)–O(4A) [O(3B)–C(16B)–O(4B)]	105.4(8) [106.0(10)]		
C(22)–C(25A)–O(5A) [C(22)–C(25B)–O(5B)]	111.5(5) [112(3)]	C(22)–C(25A)–O(6A) [C(22)–C(25B)–O(6B)]	111.0(5) [126(2)]
O(5A)–C(25A)–O(6A) [O(5B)–C(25B)–O(6B)]	106.5(5) [101(4)]		

^a Site occupancies for acetal heterocycles are: (i) 60:40 for C(7A)O(1A)C(9A)C(8A)O(2A) / C(7B)O(1B)C(9B)C(8B)O(2B); (ii) 60:40 for C(16A)O(3A)C(17A)C(18A)O(4A) / C(16B)O(3B)C(17B)C(18B)O(4B), and (iii) 94:6 for C(25A)O(5A)C(26A)C(27A)O(6A) / C(25B)O(5B)C(26B)C(27B)O(6B), respectively.

DISCUSSION

Solution behaviour of compounds 2–9

The NMR data agree with the presence of only one organometallic species in solution of compounds **2–9**. Only one set of expected ¹H and ¹³C resonances, respectively, both in the aliphatic and the aromatic regions, were observed. This behaviour is consistent with the equivalence of the organic substituents attached to a heavy pnictogen atom and the lack of any intramolecular or intermolecular interactions. The chemical shifts observed for the ¹H resonances assigned to the CH group placed in position 4 of the aromatic substituents are indicative of the transformations carried out during the conversion of compounds **2** and **3** to compounds **4** and **5**, respectively, and then further to *imino* species **6–9**. Thus, they shift from δ 5.8 ppm for the acetal substituent $(\text{CH}_2\text{O})_2\text{CH}-$ in **2** and **3**, to δ 10.0 ppm for the aldehyde function $\text{O}=\text{CH}-$ in **4** and **5**, and δ 8.2–8.3 ppm for the imine function $-\text{N}=\text{CH}-$ in **6–9**. Similar significant shifts were observed for the singlet resonance assigned to the CH group in the ¹³C{¹H} NMR spectra, *i.e.* δ 103.73 and 103.93 ppm for **2** and **3** [$(\text{CH}_2\text{O})_2\text{CH}-$], and 192.27 and 192.55 ppm for **4** and **5** ($\text{O}=\text{CH}-$), while for compounds **6–9** chemical shifts in the range

158.27–161.28 ppm are indicative for the presence of only imine-containing organometallic species in solution.

Solid state structure of [4- $\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4\}_3\text{Sb}$ (**2**)

The molecule of compound **2** (Fig. 1) exhibits a distorted trigonal pyramidal SbC₃ core, with the antimony atom in the apex and C–Sb–C bond angles in the range 94.95(17)–97.76(17)°. The Sb–C bond lengths [range 2.157(6)–2.169(5) Å] in the molecule of **2** are like those found in other related homoleptic triarylantimony(III) compounds, *i.e.* (4-MeC₆H₄)₃Sb [2.146(2) Å],²⁰ (2,4,6-Me₃C₆H₂)₃Sb [range 2.182(8)–2.185(8) Å],²¹ or (2,4,6-ⁱPr₃C₆H₂)₃Sb [range 2.195(2)–2.206(2) Å].²²

The relative orientation of the three aromatic rings attached to the pnictogen atom mimics a propeller-like conformation which results in helicoidal chirality of an Ar₃Sb molecule, with the metal atom on a C₃-axis.²³ Indeed, the crystal of **2** contains a racemic of *M* and *P* isomers with respect to the left-handed or right-handed helicity of the aromatic rings. Two such *M* and *P* isomers are connected into a dimer association (Fig. 2) through weak Sb(lone pair)⋯π(Ar_{centroid}) interactions²⁴ [Sb(1)⋯Ar_{centroid}{C(1a)–C(6a)} 4.32 Å; $\gamma = 22.3^\circ$ (angle between the normal to the aryl ring and the line defined by the metal atom and Ar_{centroid}); *cf.* 1.9 Å as the upper value estimated for half the centroid–

centroid distance in parallel phenyl rings,²⁵ and the van der Waals radius of antimony (2.47 Å)²⁶. A similar dimer association was found in the crystal of tris[4-(7-

azaindol-1-yl)phenyl]stibine (Sb...Ar_{centroid} 3.89 Å; $\gamma = 4.5^\circ$).²⁷ No further contacts are established between the centrosymmetric dimers in the crystal of **2**.

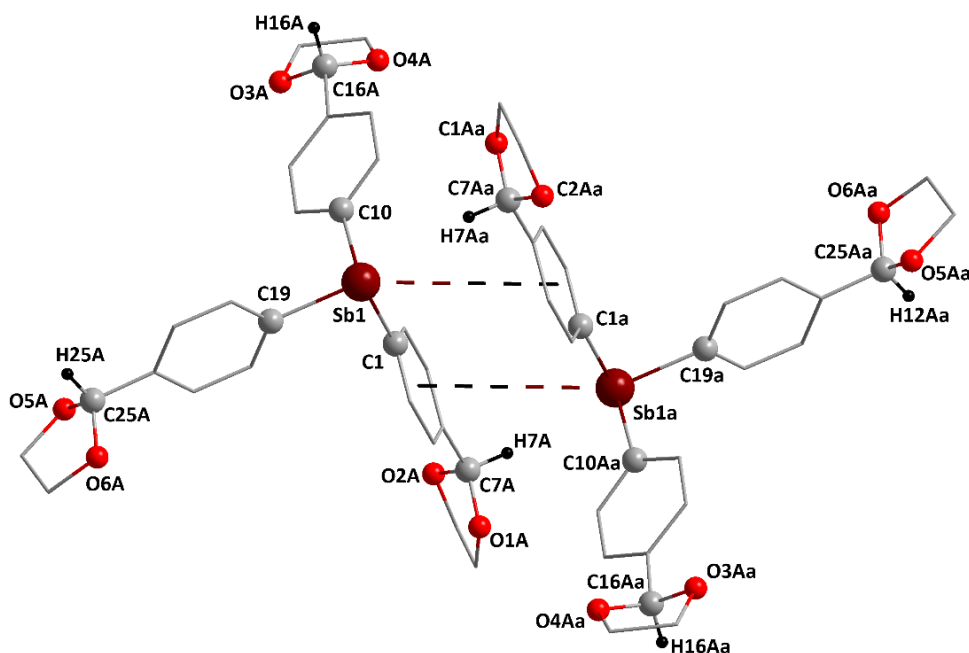


Fig. 2 – Dimer association through weak Sb... π (Ar_{centroid}) interactions between *M*- and *P*-helicoidal isomers in the crystal of **2** [symmetry equivalent atoms ($2-x, -y, 1-z$) are given by “a”].

EXPERIMENTAL

Most reactions and manipulation of the compounds were carried out under argon atmosphere using Schlenk techniques. When appropriate, solvents were dried and freshly distilled under argon prior to use. Starting materials such as SbCl₃, BiCl₃, 4-(O=CH)C₆H₄Br, anhydrous ethylene glycol, *p*-toluene sulfonic acid monohydrate, isopropyl amine, (3-aminopropyl)triethoxysilane (APTES), *n*-butyllithium (1.6 M in hexane), anhydrous MgSO₄ and Mg fillings were obtained from Aldrich or Merck. SbCl₃ and BiCl₃ were freshly sublimed prior to use and kept under inert atmosphere, while the other reagents were used as received. The ¹H, ¹³C{¹H}, ²⁹Si{¹H} and 2D NMR spectra were recorded at room temperature on Bruker Avance III 400 or 600 MHz instruments, using solutions in CDCl₃. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl₃, 7.26 ppm) for ¹H spectra, and relative to the peak of the deuterated solvent (CDCl₃, 77.16 ppm) for ¹³C{¹H} spectra.²⁸ The ¹H and ¹³C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC). The NMR spectra were processed using the *MestReNova*

software.²⁹ APCI+ mass spectra were recorded on a Thermo Scientific Orbitrap XL spectrometer equipped with a standard APCI source. Data analyses were carried out with the *Xcalibur* software package.³⁰ The IR ATR spectra were recorded in the range 4000–500 cm⁻¹ on a FT/IR-610 spectrometer (JASCO Corp.). Melting points were measured in capillary tubes on a Gallenkamp Melting Point Apparatus and were not corrected. Elemental analyses were carried out using a Thermo Flash EA-1112 analyser.

Synthesis of 4-[(CH₂O)₂CH]C₆H₄Br (**1**)

The title organic bromide was obtained as a colourless oil using a procedure already described,¹⁶ starting from 4-bromobenzaldehyde (8.0 g, 43.2 mmol), excess of anhydrous ethylene glycol (3 g, 2.7 mL, 48 mmol) and *p*-toluene sulfonic acid monohydrate (0.2 mg, 1 mmol), in toluene (50 mL). Yield: 8.9 g (90%). The ¹H and ¹³C NMR data (recorded in CDCl₃, on a Bruker Avance III 600 MHz instrument) are identical with the previously reported ones.¹⁶

Synthesis of [4-[(CH₂O)₂CH]C₆H₄]₃Sb (**2**)

Method A. A solution of **1** (6.0 g, 26.2 mmol) in anhydrous THF (100 mL) was added dropwise,

under stirring to magnesium fillings (0.79 g, 32.8 mmol), activated with 1,2-dibromoethane (1.24 g, 6.6 mmol) in anhydrous THF (10 mL). The addition was completed after 0.5 h. The reaction mixture was stirred for further 5 h under reflux, then it was cooled to $-40\text{ }^{\circ}\text{C}$ and a solution of SbCl_3 (1.0 g, 4.38 mmol) in anhydrous THF (50 mL) was dropwise added under stirring to the resulted organomagnesium derivative. The stirring was maintained for 4 h to reach room temperature, then distilled water (10 mL) was added, and the stirring was continued for 12 h. The solvent was distilled to reduce the volume to about one third, the solid was filtered off and the organic phase was dried over anhydrous MgSO_4 . After filtration, the solvent was completely removed in vacuum from the clear solution and the solid residue was extracted with CH_2Cl_2 . Evaporation of the solvent resulted in a precipitate which was washed with Et_2O to remove organic impurities, then dried in vacuum to give compound **2** as a white solid. Yield: 0.75 g (30%, calcd. based on SbCl_3).

Method B. A solution of **1** (6.0 g, 26.2 mmol) in anhydrous THF (40 mL) was added dropwise, under stirring, to $^n\text{BuLi}$ (1.68 g, 16.4 mL, 1.6 M in hexane, 26.2 mmol) in THF (40 mL) at $-100\text{ }^{\circ}\text{C}$, and left to stir for 2 h. Then a solution of SbCl_3 (1.49 g, 6.5 mmol) in anhydrous THF (40 mL) was added dropwise, maintaining the temperature of the reaction mixture at $-100\text{ }^{\circ}\text{C}$. The reaction mixture was stirred to reach room temperature, then the solvent was removed and anhydrous EtOH (100 mL) was added to the reaction mixture, resulting in a white precipitate and a yellowish solution. The precipitate was filtered off and was washed with a mixture of Et_2O /hexane (1:1, v/v), then dried under vacuum to give compound **2** as a white solid. Yield: 3.42 g (92%, calcd. based on SbCl_3). M.p. = $176\text{--}178\text{ }^{\circ}\text{C}$. **Elemental analysis:** calcd. for $\text{C}_{27}\text{H}_{27}\text{O}_6\text{Sb}$ (MW 569.27): C, 56.97; H, 4.78%; found: C, 56.48; H, 5.59%. $^1\text{H NMR}$ (600 MHz, 295 K): δ 4.01–4.06 [m, 6H, $(\text{CH}_2\text{O})_2\text{CH}$], 4.10–4.15 [m, 6H, $(\text{CH}_2\text{O})_2\text{CH}$], 5.79 [s, 3H, $(\text{CH}_2\text{O})_2\text{CH-}$], 7.42 (d, $^3J_{\text{HH}} = 8.1\text{ Hz}$, 6H, *H-3*, C_6H_4), 7.45 (d, $^3J_{\text{HH}} = 8.0\text{ Hz}$, 6H, *H-2*, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 295 K): δ 65.50 [s, $(\text{CH}_2\text{O})_2\text{CH-}$], 103.73 [s, $(\text{CH}_2\text{O})_2\text{CH-}$], 127.03 (s, *C-3*, C_6H_4), 136.44 (s, *C-2*, C_6H_4), 138.50 (s, *C-4*, C_6H_4), 139.58 (s, *C-1*, C_6H_4). **FTIR** (cm^{-1}): ν 2964 (w), 2888 (m), 2772 (w), 1595 (w), 1480 (w), 1415 (s), 1382 (s), 1307 (m), 1272 (m), 1220 (s), 1104 (m), 1074 (vs), 1051 (vs), 1013 (s), 970 (s), 942 (vs) (C–O acetal group stretching), 881 (m), 856 (m), 811 (vs), 726 (m), 704

(w), 667 (s), 631 (m), 536 (m), 512 (s). **MS** (APCI+, MeCN), m/z (relative intensity, %): 570.35 (21) $[\text{M} + \text{H}]^+$, 299.12 (100) $[(\text{CH}_2\text{O})_2\text{CHC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CH}(\text{OCH}_2)_2 + \text{H}]^+$, 255.16 (41) $[\text{O}=\text{CHC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CH}(\text{OCH}_2)_2 + \text{H}]^+$.

Synthesis of [4- $\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4\text{]}_3\text{Bi}$ (**3**)

Method A. Prepared as described for the triorganoantimony(III) derivative **2** from [4- $\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4\text{]MgBr}$ [obtained from bromide **1** (6.0 g, 26.2 mmol) and magnesium fillings (0.79 g, 32.8 mmol), activated with $\text{BrCH}_2\text{CH}_2\text{Br}$ (1.24 g, 6.6 mmol), in anhydrous THF (100 mL)] and BiCl_3 (1.38 g, 4.38 mmol) in anhydrous THF (50 mL). The isolated crude solid was washed with acetonitrile to remove organic impurities, then dried in vacuum to give compound **3** as a white solid. Yield: 0.50 g (17%, calcd. based on BiCl_3).

Method B. Prepared as described for **2** from [4- $\{(\text{CH}_2\text{O})_2\text{CH}\}\text{C}_6\text{H}_4\text{]Li}$ [obtained from bromide **1** (6.0 g, 26.2 mmol) and $^n\text{BuLi}$ (1.68 g, 16.4 mL, 1.6 M in hexane, 26.2 mmol), in anhydrous THF (80 mL)] and BiCl_3 (2.05 g, 6.5 mmol) in anhydrous THF (40 mL). The isolated crude solid was washed with a mixture of Et_2O /hexane (1:1, v/v), then dried under vacuum to give compound **3** as a white solid. Yield: 3.95 g (93%). M.p. = $148\text{--}150\text{ }^{\circ}\text{C}$. **Elemental analysis:** calcd. for $\text{C}_{27}\text{H}_{27}\text{BiO}_6$ (MW 656.49): C, 49.40; H, 4.15%; found: C, 49.26; H, 4.35%. $^1\text{H NMR}$ (400 MHz, 295 K): δ 3.99–4.07 [m, 6H, $(\text{CH}_2\text{O})_2\text{CH}$], 4.08–4.16 [m, 6H, $(\text{CH}_2\text{O})_2\text{CH}$], 5.78 [s, 3H, $(\text{CH}_2\text{O})_2\text{CH-}$], 7.48 (d, $^3J_{\text{HH}} = 7.9\text{ Hz}$, 6H, *H-3*, C_6H_4), 7.75 (d, $^3J_{\text{HH}} = 8.0\text{ Hz}$, 6H, *H-2*, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 295 K): δ 65.46 [s, $(\text{CH}_2\text{O})_2\text{CH-}$], 103.93 [s, $(\text{CH}_2\text{O})_2\text{CH-}$], 128.63 (s, *C-3*, C_6H_4), 137.57 (s, *C-4*, C_6H_4), 137.77 (s, *C-2*, C_6H_4), 136.43 (s, *C-1*, C_6H_4). **FTIR** (cm^{-1}): ν 2965 (w), 2890 (m), 2769 (w), 1591 (w), 1481 (w), 1415 (s), 1380 (m), 1306 (m), 1272 (w), 1220 (m), 1138 (w), 1101 (w), 1070 (vs), 1045 (vs), 1011 (s), 968 (vs), 942 (vs) (C–O acetal group stretching), 879 (w), 856 (w), 808 (vs), 724 (m), 663 (s), 583 (w), 522 (m). **MS** (APCI+, MeOH), m/z (relative intensity, %): 657.17 (13) $[\text{M} + \text{H}]^+$, 299.12 (100) $[(\text{CH}_2\text{O})_2\text{CHC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CH}(\text{OCH}_2)_2 + \text{H}]^+$, 255.16 (54) $[\text{O}=\text{CHC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CH}(\text{OCH}_2)_2 + \text{H}]^+$.

Synthesis of [4- $(\text{O}=\text{CH})\text{C}_6\text{H}_4\text{]}_3\text{Sb}$ (**4**)

Compound **2** (1.30 g, 2.29 mmol) was dissolved in hot acetone (40 mL) and a solution HCl 0.01 M (10 mL) was added dropwise. The reaction mixture was refluxed for 6 h, then it was left to stir overnight to reach room temperature. The solvent was

removed in a rotary evaporator, then CH_2Cl_2 (75 mL) was added to the residual compound, and the reaction mixture was filtered. From the clear solution the solvent was removed in vacuum to give compound **4** as a pale-yellow solid. Yield: 0.70 g (70%). M.p. = 147–149 °C. **Elemental analysis:** calcd. for $\text{C}_{21}\text{H}_{15}\text{O}_3\text{Sb}$ (MW 437.11): C, 57.70; H, 3.46%; found: C, 57.30; H, 4.60%. **^1H NMR** (400 MHz, 294 K): δ 7.61 (d, $^3J_{\text{HH}} = 8.1$ Hz, 6H, *H*-2, C_6H_4), 7.85 (d, $^3J_{\text{HH}} = 8.1$ Hz, 6H, *H*-3, C_6H_4), 10.02 [s, 3H, $\text{O}=\text{CH}-$]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, 295 K): δ 129.99 (s, *C*-3, C_6H_4), 136.89 (s, *C*-2, *C*-4, C_6H_4), 146.19 (s, *C*-1, C_6H_4), 192.27 [s, $\text{O}=\text{CH}-$]. **FTIR** (cm^{-1}): ν 2832 (w), 2793 (w), 2739 (w), 2708 (w), 2361 (w), 1697 (vs) ($\text{C}=\text{O}$ stretching), 1659 (s), 1581 (vs), 1556 (s), 1488 (w), 1405 (w), 1378 (s), 1351 (w), 1308 (m), 1274 (m), 1206 (s), 1174 (m), 1111 (w), 1093 (w), 1055 (m), 1010 (m), 959 (m), 829 (vs), 806 (vs), 705 (w), 668 (vs), 626 (s), 515 (m). **MS** (APCI+, MeCN), *m/z* (relative intensity, %): 437.01 (100) [$\text{M}]^+$, 226.94 (24) [$\text{O}=\text{CHC}_6\text{H}_4\text{Sb} + \text{H}]^+$, 211.07 (52) [$\text{O}=\text{CHC}_6\text{H}_4-\text{C}_6\text{H}_4\text{CH}=\text{O} + \text{H}]^+$.

Synthesis of [4-($\text{O}=\text{CH}$) C_6H_4] $_3\text{Bi}$ (**5**)

Prepared as described for compound **4** from **3** (1.00 g, 1.52 mmol). An excess of aqueous HCl solution should be avoided to prevent potential Bi–C bond cleavage. Removal in vacuum of the solvent from a clear CH_2Cl_2 solution afforded isolation of compound **5** as a pale-yellow solid. Yield: 0.64 g (80%; c.f. 34% in ref. 18). M.p. = 145–147 °C (c.f. 132–133 °C in ref. 18). **Elemental analysis:** calcd. for $\text{C}_{21}\text{H}_{15}\text{BiO}_3$ (MW 524.33): C, 48.11; H, 2.88%; found: C, 48.10; H, 2.95%. **^1H NMR** (400 MHz, 294 K): δ 7.86–7.95 (m, 12H, *H*-2,3, C_6H_4), 10.00 [s, 3H, $\text{O}=\text{CH}-$]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, 295 K): δ 131.67 (s, *C*-3, C_6H_4), 138.26 (s, *C*-4, C_6H_4), 138.26 (s, *C*-2, C_6H_4), 164.41 (s, *C*-1, C_6H_4), 192.55 [s, $\text{O}=\text{CH}-$]. **FTIR** (cm^{-1}): ν 2964 (w), 2889 (w), 2831 (m), 2791 (w), 2738 (w), 2361 (w), 1693 (vs) ($\text{C}=\text{O}$ stretching), 1652 (s), 1575 (s), 1556 (s), 1487 (m), 1375 (vs), 1307 (s), 1274 (m), 1205 (s), 1172 (s), 1074 (s), 1048 (s), 1006 (s), 944 (m), 825 (vs), 803 (vs), 718 (m), 665 (vs), 625 (s), 511 (s). **MS** (APCI+, MeOH), *m/z* (relative intensity, %): 525.09 (100) [$\text{M} + \text{H}]^+$.

Synthesis of [4-($^i\text{PrN}=\text{CH}$) C_6H_4] $_3\text{Sb}$ (**6**)

A solution of isopropylamine (0.12 g, 2.06 mmol) in anhydrous CH_2Cl_2 (20 mL) was added dropwise to a solution of compound **4** (0.30 g, 0.68 mmol) in anhydrous CH_2Cl_2 (20 mL). The reaction mixture was stirred for 12 h, at room temperature,

resulting in an orange solution. The solvent was removed using a rotary evaporator and anhydrous Et_2O (50 mL) was added to the resulting orange oil. The suspension was filtered on celite, the solvent was removed in vacuum to give compound **6** as a yellow oil. Yield: 0.19 g (50%). **Elemental analysis:** calcd. for $\text{C}_{30}\text{H}_{36}\text{N}_3\text{Sb}$ (MW 560.40): C, 64.30; H, 6.48; N, 7.50%; found: C, 63.86; H, 6.83; N, 7.05%. **^1H NMR** (400 MHz, 294 K): δ 1.25 [d, $^3J_{\text{HH}} = 6.3$ Hz, 18H, $(\text{CH}_3)_2\text{CHN}=\text{}$], 3.53 (hept, $^3J_{\text{HH}} = 6.3$ Hz, 3H, $(\text{CH}_3)_2\text{CHN}=\text{}$), 7.46 (d, $^3J_{\text{HH}} = 8.1$ Hz, 6H, *H*-2, C_6H_4), 7.66 (d, $^3J_{\text{HH}} = 8.2$ Hz, 6H, *H*-3, C_6H_4), 8.28 [s, 3H, $-\text{N}=\text{CH}-$]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, 295 K): δ 24.29 [s, $(\text{CH}_3)_2\text{CHN}=\text{}$], 61.91 (s, $(\text{CH}_3)_2\text{CHN}=\text{}$), 128.44 (s, *C*-3, C_6H_4), 136.55 (s, *C*-2, C_6H_4), 137.01 (s, *C*-4, C_6H_4), 141.31 (s, *C*-1, C_6H_4), 158.27 [s, $-\text{N}=\text{CH}-$]. **FTIR** (cm^{-1}): ν 2965 (s), 2924 (m), 2863 (m), 2601 (w), 2360 (m), 2341 (m), 1637 (s) ($\text{C}=\text{N}$ stretching), 1587 (m), 1552 (m), 1462 (m), 1381 (s), 1359 (s), 1325 (m), 1303 (s), 1266 (m), 1220 (w), 1180 (w), 1142 (s), 1119 (m), 1056 (m), 1013 (s), 977 (s), 943 (m), 882 (s), 816 (vs), 736 (w), 715 (m), 652 (s), 633 (m), 543 (m), 529 (s), 511 (m). **MS** (APCI+, MeOH), *m/z* (relative intensity, %): 560.20 (100) [$\text{M} + \text{H}]^+$, 293.20 (20) [$^i\text{PrN}=\text{CHC}_6\text{H}_4-\text{C}_6\text{H}_4\text{CH}=\text{N}^i\text{Pr} + \text{H}]^+$, 251.15 (10) [$^i\text{PrN}=\text{CHC}_6\text{H}_4-\text{C}_6\text{H}_4\text{CH}=\text{NH} + \text{H}]^+$.

Synthesis of [4-($^i\text{PrN}=\text{CH}$) C_6H_4] $_3\text{Bi}$ (**7**)

A solution of isopropylamine (0.067 g, 1.14 mmol) in anhydrous THF (20 mL) was added dropwise to a solution of compound **5** (0.30 g, 0.38 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred for 12 h, at room temperature, resulting in an orange solution. The THF was removed in vacuum and anhydrous CH_2Cl_2 (50 mL) was added to the resulting orange oil. The suspension was filtered on celite, the solvent was removed in vacuum and treatment of the yellow oily residue with a mixture of Et_2O /hexane (1:1, v/v) (50 mL) afforded a precipitate. Following filtration and drying in vacuum compound **7** was isolated as a yellow solid. Yield: 0.13 g (53%). M.p. = 257 °C (decomp.). **^1H NMR** (400 MHz, 293 K): δ 1.25 [d, $^3J_{\text{HH}} = 6.3$ Hz, 18H, $(\text{CH}_3)_2\text{CHN}=\text{}$], 3.53 (hept, $^3J_{\text{HH}} = 6.3$ Hz, 3H, $(\text{CH}_3)_2\text{CHN}=\text{}$), 7.72 (d, $^3J_{\text{HH}} = 8.0$ Hz, 6H, *H*-3, C_6H_4), 7.76 (d, $^3J_{\text{HH}} = 8.2$ Hz, 6H, *H*-2, C_6H_4), 8.27 [s, 3H, $-\text{N}=\text{CH}-$]. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, 293 K): δ 24.27 [s, $(\text{CH}_3)_2\text{CHN}=\text{}$], 61.85 (s, $(\text{CH}_3)_2\text{CHN}=\text{}$), 130.04 (s, *C*-3, C_6H_4), 136.17 (s, *C*-4, C_6H_4), 137.90 (s, *C*-1, *C*-2, C_6H_4), 158.52 [s, $-\text{N}=\text{CH}-$]. **FTIR** (cm^{-1}): ν 3177 (w), 3056 (w),

2967 (m), 2929 (m), 2865 (w), 2653 (w), 2361 (m), 2341 (m), 2325 (m), 1640 (s) (C=N stretching), 1580 (vs), 1541 (s), 1378 (s), 1362 (vs), 1301 (s), 1261 (s), 1164 (m), 1141 (m), 1102 (m), 1049 (m), 1009 (s), 972 (m), 943 (m), 881 (m), 810 (s), 762 (m), 693 (m), 669 (m), 646 (m), 629 (m), 544 (s), 521 (vs). **MS** (APCI+, MeOH), m/z (relative intensity, %): 648.27 (100) [M + H]⁺, 293.20 (64) [ⁱPrN=CHC₆H₄-C₆H₄CH=NⁱPr + H]⁺.

Synthesis of [4-*t*-(EtO)₃Si(CH₂)₃N=CH]C₆H₄)₃Sb (**8**)

A solution of (3-aminopropyl)triethoxysilane (0.76 g, 3.42 mmol) in anhydrous THF (10 mL) was added dropwise to a solution of compound **4** (0.50 g, 1.14 mmol) in anhydrous THF (20 mL), and the reaction mixture was stirred for 24 h, at room temperature. The solvent was removed from the resulting orange solution using a rotary evaporator, and the remaining orange oil was treated with anhydrous CH₂Cl₂ (50 mL), then filtered on celite. Removal of the solvent in vacuum afforded isolation of compound **8** as a clear yellow oil. Yield: 0.97 g (81%). **Elemental analysis**: calcd. for C₄₈H₇₈N₃O₉SbSi₃ (MW 1047.18): C, 55.06; H, 7.51; N, 4.01%; found: C, 54.59; H, 7.77; N, 2.61%. **¹H NMR** (600 MHz, 295 K): δ 0.65–0.67 (m, 6H, H-α), 1.21 [t, ³J_{HH} = 7.0 Hz, 27H, Si(OCH₂CH₃)₃], 1.79–1.84 (m, 6H, H-β), 3.60 (t, ³J_{HH} = 7.0 Hz, 6H, H-γ), 3.81 [q, ³J_{HH} = 7.0 Hz, 18H, Si(OCH₂CH₃)₃], 7.47 (d, ³J_{HH} = 7.7 Hz, 6H, H-2, C₆H₄), 7.66 (d, ³J_{HH} = 7.8 Hz, 6H, H-3, C₆H₄), 8.24 [s, 3H, -N=CH-]. **¹³C{¹H} NMR** (151 MHz, 296 K): δ 8.13 (s, C-α), 18.42 [s, Si(OCH₂CH₃)₃], 24.35 (s, C-β), 58.47 [s, Si(OCH₂CH₃)₃], 64.46 (s, C-γ), 128.41 (s, C-3, C₆H₄), 136.54 (s, C-2, C₆H₄), 136.86 (s, C-4, C₆H₄), 141.37 (s, C-1, C₆H₄), 160.91 [s, -N=CH-]. **²⁹Si{¹H} NMR** (80 MHz, 294 K): δ -45.0. **FTIR** (cm⁻¹): ν 2972 (m), 2925 (m), 2882 (m), 2836 (w), 2361 (w), 2326 (w), 1644 (s) (C=N stretching), 1587 (w), 1554 (w), 1441 (w), 1390 (w), 1373 (w), 1342 (w), 1299 (w), 1164 (m), 1101 (vs), 1077 (vs), 1012 (m), 956 (s), 813 (m), 789 (m), 777 (m), 714 (w), 632 (s), 536 (vs), 511 (s). **MS** (APCI+, MeOH), m/z (relative intensity, %): 1048.47 (100) [M + H]⁺, 845.45 (11) [C₃₉H₆₂N₃O₆Si₂Sb]⁺.

Synthesis of [4-*t*-(EtO)₃Si(CH₂)₃N=CH]C₆H₄)₃Bi (**9**)

A solution of (3-aminopropyl)triethoxysilane (0.25 g, 1.14 mmol) in anhydrous THF (20 mL) was added dropwise to a solution of compound **5** (0.20 g, 0.38 mmol) in anhydrous THF (20 mL), and the reaction mixture was stirred for 12 h, at room

temperature. The solvent was removed from the resulting orange solution using a rotary evaporator, and the remaining orange oil was treated with anhydrous CH₂Cl₂ (50 mL), then filtered on celite. Removal of the solvent in vacuum afforded isolation of compound **9** as a clear yellow oil. Yield: 0.14 g (32%). **Elemental analysis**: calcd. for C₄₈H₇₈BiN₃O₉Si₃ (MW 1134.40): C, 50.82; H, 6.93; N, 3.70%; found: C, 49.31; H, 7.07; N, 3.69%. **¹H NMR** (400 MHz, 293 K): δ 0.61–0.68 (m, 6H, H-α), 1.21 [t, ³J_{HH} = 7.0 Hz, 27H, Si(OCH₂CH₃)₃], 1.77–1.85 (m, 6H, H-β), 3.63 (t, ³J_{HH} = 7.0 Hz, 6H, H-γ), 3.84 [q, ³J_{HH} = 7.0 Hz, 18H, Si(OCH₂CH₃)₃], 7.50 (d, ³J_{HH} = 7.7 Hz, 6H, H-2, C₆H₄), 7.69 (d, ³J_{HH} = 7.8 Hz, 6H, H-3, C₆H₄), 8.27 [s, 3H, -N=CH-]. **¹³C{¹H} NMR** (100 MHz, 293 K): δ 8.10 (s, C-α), 18.42 [s, Si(OCH₂CH₃)₃], 24.33 (s, C-β), 58.48 [s, Si(OCH₂CH₃)₃], 64.46 (s, C-γ), 130.05 (s, C-3, C₆H₄), 136.02 (s, C-4, C₆H₄), 137.93 (s, C-2, C₆H₄), 158.64 (s, C-1, C₆H₄), 161.28 [s, -N=CH-]. **²⁹Si{¹H} NMR** (80 MHz, 294 K): δ -45.0. **FTIR** (cm⁻¹): ν 2971 (m), 2925 (m), 2882 (m), 2736 (w), 2650 (w), 2360 (m), 2341 (w), 1643 (s) (C=N stretching), 1584 (w), 1554 (w), 1442 (w), 1388 (m), 1370 (m), 1342 (w), 1303 (m), 1164 (s), 1100 (vs), 1074 (vs), 1010 (s), 953 (s), 882 (m), 813 (s), 791 (m), 776 (m), 716 (w), 652 (m), 633 (s), 543 (s), 535 (s), 511 (m). **MS** (APCI+, MeOH), m/z (relative intensity, %): 1134.50 (100) [M]⁺.

Crystal structure determination

Single crystals were obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution of **2**. An appropriate crystal was mounted on a cryoloop and data were collected at 297 K on a Bruker SMART APEX diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was refined with anisotropic thermal parameters for non-H atoms. The hydrogen atoms were placed in fixed, idealized positions, and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-2019 was used.³¹ Further details of the crystal structure determination and refinement are given in Table 2. The disordered 1,3-dioxolan-2-yl rings were modelled over two positions, with site occupancies of 60:40, 60:40 and 94:6, respectively. The representations of the molecular structure and those describing the supramolecular architecture were created using the Diamond program.³²

Table 2

Crystallographic data for [4-((CH₂O)₂CH)C₆H₄]₃Sb (**2**)

Empirical formula	C ₂₇ H ₂₇ O ₆ Sb
Formula weight	569.25
Crystal size /mm	0.17 x 0.20 x 0.25
Crystal habit	colourless block
Wavelength MoK α (Å)	0.71073
Temperature (K)	297(2)
Crystal system	monoclinic
Space group	P2 ₁ /c (No. 14)
a (Å)	11.623(2)
b (Å)	19.402(4)
c (Å)	10.927(2)
α (°)	90
β (°)	92.557(4)
γ (°)	90
Volume (Å ³)	2461.7(8)
Z	4
Density (calculated) (g cm ⁻³)	1.536
Absorption coefficient μ (MoK α) (mm ⁻¹)	1.161
<i>F</i> (000)	1152
θ range for data collections (°)	1.8 – 25.0
T _{max} / T _{min}	0.820 / 0.748
Reflections collected	23550
Independent reflections, <i>R</i> _{int}	4318, 0.059
Absorption corrections	Multi-Scan ³³
Miller indices, h, k, l (min/max)	–13/13, –23/23, –12/12
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4318 / 426 / 416
Goodness-of-fit on F ²	1.03
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0484
	<i>wR</i> ₂ = 0.1164
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0695
	<i>wR</i> ₂ = 0.1325
Largest diff. peak and hole, eÅ ⁻³	–0.26, 1.10

CONCLUSIONS

Eight homoleptic triarylpnictogen(III) compounds of the type (4-RC₆H₄)₃Pn [Pn = Sb, Bi; R = (CH₂O)₂CH, O=CH, ⁱPrN=CH, (EtO)₃Si(CH₂)₃N=CH] were prepared and characterized, both in solution and in solid state, by IR and multinuclear (¹H, ¹³C, ²⁹Si) NMR spectroscopies, as well as mass spectrometry. The room temperature NMR spectra, recorded in CDCl₃ solution, are consistent with the equivalence of the aromatic substituents attached to pnictogen atom. A single-crystal X-ray diffraction study revealed a trigonal SbC₃ core and helical chirality for the molecular [4-((CH₂O)₂CH)C₆H₄]₃Sb compound. Its crystal contains a 1:1 mixture of *M*-helical and *P*-helical isomers which are associated in loosely centrosymmetric (*M,P*) dimers through Sb(lone pair)⋯ π (Ar_{centroid}) interactions.

Supplementary material

The CCDC reference number for **2** is 2416581. The supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

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