



*Dedicated to Professor Cristian Silvestru
on the occasion of his 65th anniversary*

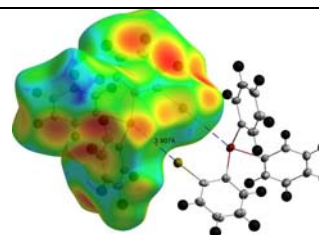
MOLECULAR STRUCTURES OF (2-BROMOPHENYL)DIPHENYLSTIBANE AND {2'-BROMO-[1,1'-BIPHENYL]-2-YL}DIPHENYLSTIBANE

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The synthesis of 2-BrC₆H₄SbPh₂ (**1**) and the serendipitous formation 2-(2'-BrC₆H₄)C₆H₄SbPh₂ (**2**) are reported. Compounds **1** and **2** were characterized in solution by NMR spectroscopy and their identity was confirmed by high-resolution mass spectrometry. The molecular structures of both compounds were determined by single-crystal X-ray diffraction.



INTRODUCTION

The synthesis and characterization of organoantimony(III) compounds of type 2-(Ph₂E)C₆H₄SbPh₂ (E = P,¹ As,¹ Sb²) was mainly promoted by their prospective use as soft bidentate chelating ligands in the coordination chemistry of late transition metals.^{1,3-5} The mass spectra and elemental analysis data for the related bismuthane 2-(Ph₂Sb)C₆H₄BiPh₂ were also reported.⁶ In the last decade, compounds with Lewis acidic functional groups containing antimony were shown to have applications in anion^{7,8} or molecular sensing,⁹ and catalysis.^{10,11}

We report an alternative method with fewer steps and better yield for the synthesis for (2-bromophenyl)diphenylstibane, 2-BrC₆H₄SbPh₂ (**1**) and the serendipitous formation of the {2'-bromo-

[1,1'-biphenyl]-2-yl}diphenylstibane, 2-(2'-BrC₆H₄)C₆H₄SbPh₂ (**2**). Both compounds were characterized by NMR spectroscopy, by high-resolution mass spectrometry and their structures were determined by single-crystal X-ray diffraction.

RESULTS AND DISCUSSION

The synthesis of compound **1** by the reaction of 2-BrC₆H₄SbCl₂ with PhMgBr was reported McAuliffe *et al.*² The dichlorostibane used in the reaction involves the synthesis and subsequent reduction of 2-bromophenylstibonic acid in an overall moderate reported yield (20%).¹² Bearing in mind the potential applications of organoantimony(III) compounds reported in the literature (*vide supra*) and aiming to improve the

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synthesis of compound **1**, we sought an alternative synthetic protocol starting from the commercially available 1,2-Br₂C₆H₄ (Scheme 1). The reaction of 1,2-Br₂C₆H₄ with *n*-BuLi, in a 1:1 mixture of Et₂O and THF, followed by the reaction of the organolithium derivative obtained *in situ* with Ph₂SbCl, afforded **1** in low yield together with small amounts of **2**. Formation of **2** is not unexpected as occurrence of 2-(2'-LiC₆H₄)C₆H₄Br in the reaction of 1,2-Br₂C₆H₄ with *n*-BuLi *via* aryne intermediates is well documented.¹³ Thus considering the high temperature sensitivity of the 2-LiC₆H₄Br intermediate, the reaction with *i*-PrMgCl·LiCl, in which milder conditions are required,¹⁴ was attempted. Using the Grignard intermediate approach, compound **1** was obtained in one step and with higher yield (75%) than in the previously reported methods.

¹H NMR spectra of compounds **1** and **2** exhibit multiplet signals in the aromatic region. The most deshielded hydrogen atoms are those in position *ortho* to the bromine atom (**1**: 7.61 – 7.54; **2**: 7.70 – 7.60 ppm). The most shielded hydrogen atoms are those in position *meta* to the bromine atom and *ortho* to the antimony atom (**1**: 7.05 – 7.01 ppm) or carbon atom (**2**: 7.11 – 7.06 ppm).

In the ¹³C NMR spectra of **1** there are 10 resonance signals, whereas in the spectra of **2** there are 19 resonance signals, indicating the non-equivalence of the Ph groups due to the presence of a chirality axis in the molecule. Two resonance signals in ¹³C NMR of **2** are overlapped.

In APCI+ high resolution mass spectra of **1** and **2** protonated molecular ions were observed. Fragmentation of [M+H]⁺ ions led to the [Ph₂Sb-H]⁺ for **1** and [M-Ph]⁺, [M-2Ph-H]⁺ [Ph₂Sb-H]⁺ for **2**, respectively.

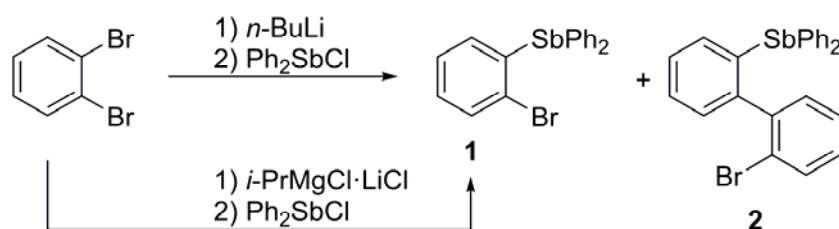
In the molecular structures of **1** (Figure 1) and **2** (Figure 2) the antimony atoms have a trigonal pyramidal geometry. The Sb–C bond lengths of **1** [2.157(6), 2.162(7), and 2.168(6) Å] and **2** [2.123(8), 2.153(8), and 2.160(9) Å] have values in the range of those reported for Ph₃Sb [2.143(6) –

2.169(10) Å],¹⁵ (*m*-Tol)₃Sb [2.146(3) – 2.152(3) Å],¹⁶ (*p*-Tol)₃Sb [2.141(3) Å],¹⁷ {4-(Me₂N)C₆H₄}₃Sb [2.133(3) – 2.147(3) Å],¹⁸ and slightly smaller than in the sterically crowded stibanes (2,6-Me₂C₆H₃)₃Sb [2.188(5) – 2.192(6) Å],¹⁹ Mes₃Sb [2.181(9) – 2.185(9) Å],²⁰ or {2,4,6-(*i*-Pr)₃C₆H₂}₃Sb [2.184(3) – 2.206(2) Å].²¹

Although the C–Sb–C bonding angles found in the molecular structures of **1** [94.1(3), 95.9(3), and 98.3(2)°] and **2** [96.4(3), 98.2(3), 94.8(3)°] are similar to those reported for Ph₃Sb [95.1(3) – 98.0(3)°],¹⁵ (*m*-Tol)₃Sb [96.49(11) – 97.28(11)°],¹⁶ (*p*-Tol)₃Sb [97.3(1)°],¹⁷ {4-(Me₂N)C₆H₄}₃Sb [94.52(11) – 97.61(11)°],¹⁸ they are smaller than in (2,6-Me₂C₆H₃)₃Sb [98.7(2) – 109.5(2)°],¹⁹ Mes₃Sb [103.7(3) – 106.4(4) Å],²⁰ or {2,4,6-(*i*-Pr)₃C₆H₂}₃Sb [101.90(10) – 112.11(9)°].²¹

In the molecular structure of **1**, the distance between Sb1 and Br1 [3.442(3) Å] is shorter than the sum of van der Waals radii of the respective elements [Σr_{vdw}(Br,Sb) = 3.89 Å].²² Second order perturbation theory analysis of Fock matrix in NBO basis,²³ carried out on the optimized molecular structure, of **1** indicates that electron donation from a bromine lone pair into a Sb–C antibonding orbital amounts 2.43 kcal/mol. If larger contact radii are considered,^{24,25} in the crystals of **1**, there are also weak intermolecular Br⋯Sb contacts [3.908(3) Å] which lead to the formation of dimers (see Synopsis). Analysis of the 2D fingerprint plots of *d_e* and *d_i* functions^{26,27} indicate that in the crystals of **1** the most abundant contacts are H⋯H (49.7%), followed by C⋯H (28.9%) and Br⋯H (13.5%).

In the crystals of **2**, intermolecular C–H⋯π interactions led to formation of chains (Figure 3). Similar intermolecular contacts as in crystals of **1** are observed [H⋯H (50.9%), C⋯H (31.3%), Br⋯H (12.0%)]. However, for **2**, no intra- or intermolecular Sb⋯Br contacts are established. The most important C–H⋯π interactions are depicted in Figure 3.



Scheme 1 – Preparation of compound **1** and generation of **2**.

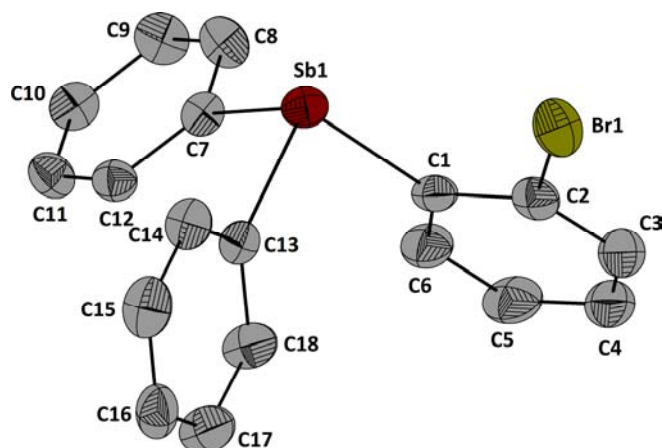


Fig. 1 – Thermal ellipsoid representation (25% probability) of the molecular structure of 2-BrC₆H₄SbPh₂ (**1**). Hydrogen atoms were omitted for clarity. Selected interatomic distances (Å) and angles (°): Sb1–C1 2.162(7), Sb1–C7 2.157(6), Sb1–C13 2.168(6), Br1–C2 1.907(7), Sb1⋯Br1 3.442(3); C1–Sb1–C7 94.1(3), C1–Sb1–C13 95.9(3), C7–Sb1–C13 98.3(2).

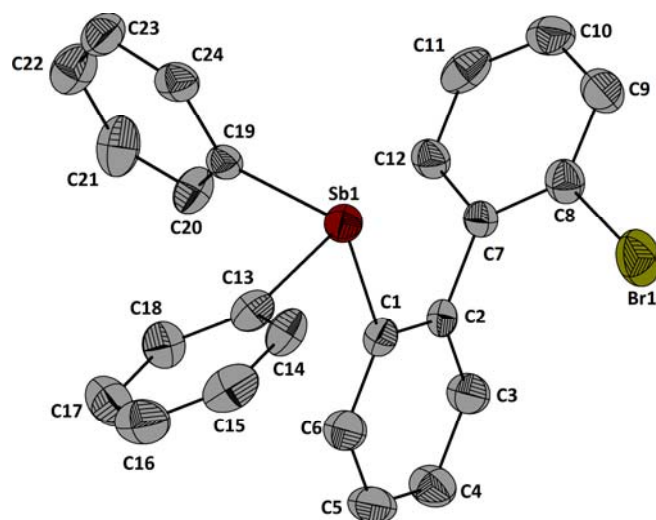


Fig. 2 – Thermal ellipsoid representation (25% probability) of the molecular structure of 2-(2'-BrC₆H₄)C₆H₄SbPh₂ (**2**). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–C1 2.153(8), Sb1–C13 2.160(9), Sb1–C19 2.123(8), Br1–C8 1.923(12); C1–Sb1–C13 96.4(3), C1–Sb1–C19 98.2(3), C13–Sb1–C19 94.8(3).

EXPERIMENTAL

General Considerations

Unless otherwise indicated, starting materials were used without further purification. The solvents were distilled, under argon atmosphere, from appropriate drying agents (sodium for diethylether, potassium for tetrahydrofuran) prior to use. All the other solvents were distilled using a rotary evaporator prior to use. Ph₂SbCl was prepared according to the methods described in the literature.^{28,29} *i*-PrMgCl·LiCl 1.3 M in THF was purchased and used as received.

For the column and thin layer chromatography was used 0.060–0.200 mm, 60 Å silica gel, and silica gel 60 coated aluminum sheets with F254 indicator, respectively.

The NMR spectra were recorded on a Bruker Avance III 400 spectrometer. ¹H and ¹³C{¹H} chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent (CHCl₃, 7.26 ppm) in the ¹H NMR spectra and to the peak of the deuterated solvent (CDCl₃, 77.16 ppm) in ¹³C{¹H} NMR spectra.³⁰

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.³¹

Crystals suitable for crystallographic determinations were obtained by slow evaporation of solvents from solutions in CHCl₃ and MeOH of **1** and **2**, respectively. Crystallographic data for **1** and **2** were collected at 297 K on a Bruker Smart APEX diffractometer, with graphite monochromator, using Mo Kα radiation (0.71073 Å). Crystals were mounted on a loop using Paratone oil. The structures were solved and refined with the SHELX-2018 software package.³² Compound **2** was refined as an inversion twin. All the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in riding positions with the isotropic thermal parameters set 1.2 times the thermal parameters of the carbon atoms directly attached for the aromatic hydrogen atoms. The ring centroids, intra- and intermolecular interactions were evaluated with PLATON software package.³³ The representation of the

molecular structures were carried out using Diamond.³⁴ Analysis of the intermolecular interactions was performed

with CrystalExplorer.³⁵ Crystal data and structure refinement for compounds **1** and **2** are listed in Table 1.

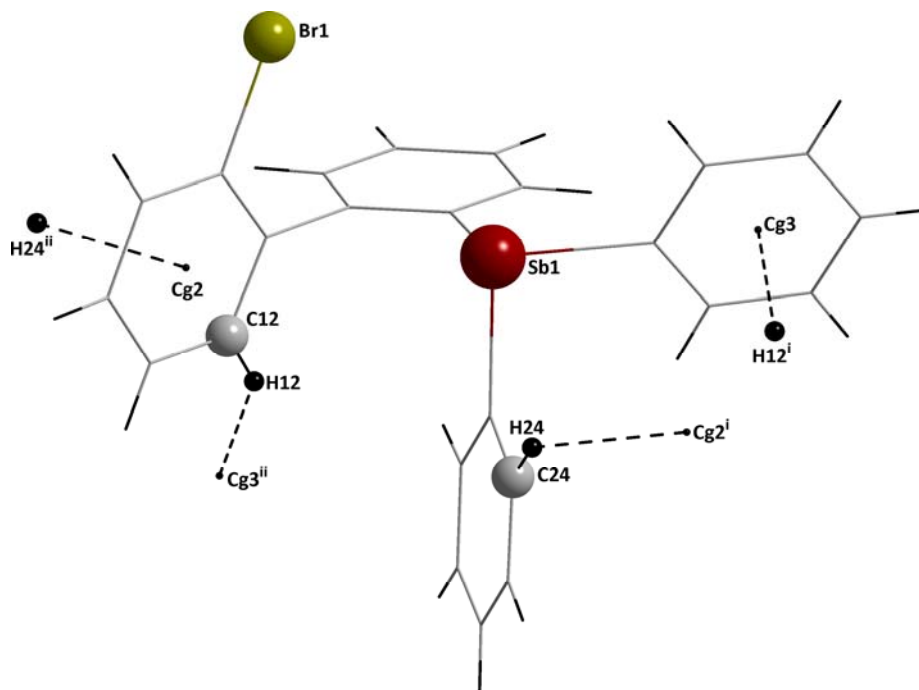


Fig. 3 – Intermolecular C–H \cdots π interactions in crystals of **2**. Selected bond lengths (\AA) and angles ($^\circ$): C12–H12 2.88, C12–H12 \cdots Cg3 143, H12 \cdots Cg3 3.669(11); C24–H24 2.87, C24–H24 \cdots Cg2 146, H24 \cdots Cg2 3.677(10). Symmetry codes: i) $1/2+x, 1/2-y, z$; ii) $-1/2+x, 1/2-y, z$. Cg2 and Cg3 are the centroids of the aromatic rings C7–C12 and C13–C18, respectively.

Table 1

Crystal data and structure refinement for compounds **1** and **2**

Compound	1	2
CCDC	1960088	1960089
Formula	$\text{C}_{18}\text{H}_{14}\text{BrSb}$	$\text{C}_{24}\text{H}_{18}\text{BrSb}$
Formula weight	431.95	508.04
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a, b, c [\AA]	10.554(9), 8.961(8), 17.403(15)	15.967(3), 9.0474(16), 14.232(3)
α, β, γ [$^\circ$]	90, 94.458(14), 90	90, 90, 90
V [\AA^3]	1641(2)	2056.0(7)
Z	4	4
D(calc) [$\text{g}\cdot\text{cm}^{-3}$]	1.748	1.641
μ (Mo $K\alpha$) [mm^{-1}]	4.104	3.289
F(000)	832	992
Crystal size [mm]	$0.28 \times 0.30 \times 0.31$	$0.23 \times 0.26 \times 0.28$
Temperature (K)	297	297
$\theta_{\text{min}}, \theta_{\text{max}}$ [$^\circ$]	2.3, 25.0	2.6, 25.0
Dataset	$\pm 12; \pm 10; \pm 20$	$\pm 18; \pm 10; \pm 16$
No. of measured reflections	11269	18513
No. of independent reflections	2896	3620
R_{int}	0.045	0.062
Observed data [$I > 2.0 \sigma(I)$]	2185	2790
No. of reflections	2896	3620
No. of parameters	181	236
$R[F^2 > 2\sigma(F^2)]$	0.0521	0.0379
$wR(F^2)$	0.1197	0.0749
S	1.05	0.97
Absolute structure parameter	-	0.02(2)
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e}\cdot\text{\AA}^{-3}$)	-0.43, 0.94	-0.24, 0.67

Theoretical calculations were performed with Gaussian 09, Revision E.01,³⁶ using the B3LYP functional,³⁷ and the def2-TZVP basis set.³⁸ The dispersion corrections were accounted for using the D3 version of Grimme's dispersion with Becke-Johnson damping.³⁹

Preparation of 2-BrC₆H₄SbPh₂ (1)

Over a solution of 1,2-dibromobenzene (7.55 g, 32.0 mmol) in THF (25 mL) cooled to -60 °C was added dropwise *i*-PrMgCl·LiCl (25 mL, 32.0 mmol, 1.3 M in THF). The reaction mixture was allowed to reach -20 °C within 3 h, after which Ph₂SbCl (10.00 g, 32.0 mmol) was added as solid to the Grignard solution. The stirring was continued for additional 30 min at rt then the solvent was removed at reduced pressure. Column chromatography using hexane as mobile phase afforded **1** (10.40 g, 20.5 mmol, 75%) as a colorless oil. Solid **1** was obtained after titration with MeOH, filtration and solvent removal at reduced pressure. Mp 54 – 56 °C (lit. 59 °C).² ¹H NMR (CDCl₃, 400 MHz): δ 7.60 – 7.55 (m, 1H), 7.48 – 7.41 (m, 4H), 7.39 – 7.32 (m, 6H), 7.24 – 7.14 (m, 2H), 7.05 – 7.01 (m, 1H). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ 142.77, 138.93, 137.49, 136.43, 132.61, 132.26, 130.69, 129.17, 128.89, 127.81. MS (APCI+, MeCN): *m/z* 272.97 ([Ph₂Sb–2H]⁺, 15), 354.89 ([M–Ph]⁺, 20), 430.94 ([M+H]⁺, 100). HRMS (APCI+, MeCN): *m/z* [M+H]⁺ calcd for C₁₈H₁₅BrSb, 430.93898; found, 430.93778.

Generation of 2-BrC₆H₄SbPh₂ (1) and 2-(2'-BrC₆H₄)C₆H₄SbPh₂ (2)

1,2-Dibromobenzene (2.241 g, 9.5 mmol) was dissolved, under argon atmosphere, in a mixture of Et₂O (20 mL) and tetrahydrofuran (20 mL). To the obtained solution, cooled to -120 °C, *n*-BuLi (6.3 mL, 10.0 mmol, 1.6 M in hexane) was added dropwise. After 20 min, maintaining the temperature at -120 °C, to the reaction mixture a solution of Ph₂SbCl (2.570 g, 8.3 mmol) in Et₂O (50 mL) was added dropwise over a time span of 10 min and the reaction mixture was allowed to reach rt overnight. The solvents were removed at reduced pressure and the work up of the reaction was carried out in air. The products were separated by column chromatography using heptane as mobile phase. Content of the collected fractions was assayed by TLC. Solvent removal from the combined fractions afforded dense oils which were titrated with MeOH (8 mL) and pentane (6 mL) to afford **1** (0.762 g, 1.5 mmol, 18%),⁴⁰ and **2** (0.554 g, 0.5 mmol, 6%), respectively.

2-(2'-BrC₆H₄)C₆H₄SbPh₂ (2). Mp 94 – 96 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.67 – 7.61 (m, 1H), 7.45 – 7.35 (m, 6H), 7.35 – 7.27 (m, 8H), 7.25 – 7.17 (m, 2H), 7.11 – 7.06 (m, 1H). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ 148.69, 144.05, 139.93, 139.06, 138.88, 136.45, 136.38, 136.28, 132.74, 131.93, 129.41, 129.33, 128.88, 128.62, 128.56, 128.51, 128.33, 127.05, 124.12. MS (APCI+, MeCN): *m/z* 428.92 ([M–Ph]⁺, 22), 506.97 ([M+H]⁺, 100). HRMS (APCI+, MeCN): *m/z* [M+H]⁺ calcd for C₂₄H₁₉BrSb, 506.97028; found, 506.96779.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1960088

and 1960089. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: (+44) 1223 336 408; Fax: (+44) 1223 336 033; e-mail deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

CONCLUSIONS

A faster and more efficient method of synthesis for 2-BrC₆H₄SbPh₂ (**1**) and spectroscopic and structural characterization of the serendipitous 2-(2'-BrC₆H₄)C₆H₄SbPh₂ (**2**) are reported.

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40. Conversions calculated with respect to amount of diphenylantimony(III) chloride used in the reaction.