Journal of Organometallic Chemistry, 470 (1994) 93–98

Syntheses and structures of dimesitylbismuth(III) bromide, Mes_2BiBr, and bis(diphenyldithiophosphinato)mesitylbismuth(III), $MesBi(S_2PPh_2)_2$

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(Received August 19, 1993)

Abstract

Addition of $BiBr_3$ to Mes_3Bi (Mes = 2, 4, 6-$Me_3C_6H_2$) in Et_2O gives 86% of Mes_2BiBr (**1**) as yellow crystals. Reaction of **1** with $Ph_2PS_2NH_4$ in a 1:1 molar ratio gives a quantitative yield of $MesBi(S_2PPh_2)_2$ (**2**) rather than the expected dimesitylbismuth compound. The crystal and molecular structures of **1** and **2** were determined at 153 K and 173 K, respectively. They contain Mes_2BiBr molecules with trigonal pyramidal coordination around Bi. The mean Bi–C bond distance is 2.27 Å and the Bi–Br bond distance is 2.690(2) Å. The angles around Bi vary between 89.4 and 106.4°. Intermolecular Bi...Br contacts of 3.795 Å, indicating weak secondary bonding, give rise to zig-zag shaped $(Bi–Br)_x$ chains. In the polymeric chain the coordination geometry around bismuth atoms can be described as pseudo-trigonal bipyramidal. The crystals of **2** consist of discrete monomeric $MesBi(S_2PPh_2)_2$ molecules with a symmetry plane containing the metal atom and the aromatic ring of the attached mesityl group. The dithiophosphinato ligands exhibit an anisobidentate coordination pattern with long and short phosphorus–sulfur bonds, *i.e.* P(1)–S(1) 2.051(31) Å and P(1)–S(2) 1.980(3) Å, related to short and long bismuth–sulfur distances, respectively, *i.e.* Bi–S(1) 2.662(2) Å and Bi–S(2) 3.123(3) Å. This leads to a square-pyramidal geometry around the bismuth atom, with the metal lying 0.33 Å above the basal plane formed by the four sulfur atoms.

Key words: Bismuth; Mesityl; Phosphorus; Bromide; Crystal structure

1. Introduction

The diarylbismuth bromides Ph_2BiBr and $(p\text{-tolyl})_2BiBr$ derivatives were made previously [1,2]. They are useful starting materials for a variety of reactions, including reduction to dibismuthanes [3] or halide substitution [1]. We report here on the preparation and the crystal structure of dimesitylbismuth(III) bromide (**1**) and on the synthesis and structure of bis(diphenyldithiophosphinato)mesitylbismuth(III) (**2**), the first organobismuth compound containing a dithiophosphorus ligand. Several inorganic compounds of Group 15 semi-metals and metals (As, Sb, Bi) containing dithiophosphorus ligands, *i.e.* diorganodithiophosphinato, $R_2PS_2^-$, and diorganodithiophosphato, $(RO)_2PS_2^-$, groups, are known and the molecular structures of some of them have been investigated by X-ray diffraction, *e.g.* $Sb(S_2PPh_2)_3$ [4,5], $Bi(S_2PMe_2)_3$ [6], $Bi(S_2PEt_2)_3$ [7], $Bi(S_2PPh_2)_3$ [5], and $Sb[S_2P(OR)_2]_3$ (R = Me, ^iPr) [8], $Sb[S_2P(OEt)_2]_3$ [9], $Bi[S_2P(O^iPr)_2]_3$ [10]. By contrast, the structures of organometallic derivatives of Group 15 elements with such ligands have been less studied. To the best of our knowledge, only the structures of $Ph_2Sb[S_2PPh_2]$ [11], $Ph_2Sb[S_2P(O^iPr)_2]$ [12] and $PhM[S_2P(O^iPr)_2]_2$ (M = As, Sb) [13] have been reported, and no organobismuth(III) dithiophosphinate or dithiophosphate compounds have been known until now. In addition, the structures of some monoorganobismuth(III) derivatives of dithiocarbamato and xanthato ligands have been determined, including $MeBi(S_2CNEt_2)_2$ [14], $PhBi(S_2CNEt_2)_2$ [15], and

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0022-328X/94/$7.00
SSDI 0022-328X(93)24190-G

$PhBi(S_2COMe)_2$ [16]. Usually significant structural differences were observed between inorganic and organometallic derivatives, depending on either the central metal atom, the nature of the dithiophosphorus ligand type, or the type of organic or alkoxy groups bound to phosphorus.

2. Results and discussion

2.1. Synthesis and structure of Mes_2BiBr (1)

Addition of a suspension of $BiBr_3$ in Et_2O to a solution of Mes_3Bi in the same solvent at room temperature leads to the formation of **1** according to eqn. (1):

$$2Mes_3Bi + BiBr_3 \longrightarrow \underset{\mathbf{(1)}}{3Mes_2BiBr} \qquad (1)$$

The bromide **1** separates from the solution as an air stable, yellow powder that gives yellow crystals on recrystallization from Et_2O. Compound **1** is soluble in common organic solvents, to give yellow solutions. Other methods for the synthesis of **1**, including addition of Br_2 to Mes_3Bi and subsequent distillation of MesBr or the reaction between Mes_3Bi and $BiBr_3$ in absence of a solvent at 80°C, offer no advantages. As a by-product of the redistribution reaction (1) MesH is sometimes formed. The identification of **1** is based on the elemental analysis, ^1H NMR data, the mass spectrum (which shows the molecular ion and the expected fragments) and the results of the X-ray study.

Crystal data are given in Table 1. The atomic coordinates and equivalent isotropic displacement coefficients are listed in Table 2. The structure of the monomeric unit is shown in Fig. 1, and the relevant bond angles and interatomic distances are given in Table 3. In the crystals of **1** there are Mes_2BiBr molecules with a trigonal pyramidal coordination at Bi (Fig. 1). The C–Bi and Bi–Br distances and angles are similar to the corresponding values for Mes_3Bi [17] or $BiBr_3$ [18]. The differences between the angles at Bi indicate some steric stress in the molecules. The relative wide angle Br(1)–Bi(1)–C(11) of 106.4(3)° may result from a contact of Br with the *ortho*-methyl group at C(19). In the crystal, the Mes_2BiBr molecules are associated *via* Bi···Br contacts of 3.795 Å to give zig-zag $(Bi–Br...)_x$ chains. These contacts are much longer than the Bi···Br contacts in the polymeric anions $(BiBr_4)_n^{n-}$ or $(BiBr_5)_n^{2n-}$, but are below the sum of van der Waals radii (*ca.* 4.2 Å), and indicate the presence of very weak interactions. In the polymeric chain, in solid state, the coordination around bismuth can be described as distorted pseudo-trigonal bipyramidal, with the axial positions occupied by the two bromine atoms (Br–Bi...Br bond angle 156.1(1)°) and the two mesityl groups in equatorial positions. Figure 2 shows the association of the molecules of **1** in the crystal. The weak Bi···Br secondary bonds are broken on dissolution of the compound. The fact that there is little intermolecular interaction in **1** is reflected in the fairly good solubility of the compound in organic solvents.

TABLE 1. Crystal data for compounds **1** and **2** (Mo Kα_1 radiation, 0.70926 Å)

	1	**2**
Crystal system	Monoclinic	Orthorombic
Crystal colour	Yellow	Yellow
Crystal size (mm)	0.5×0.4×0.2	0.8×0.6×0.6
Space group	$P2_1$	*Pnma*
Z	2	4
a (Å)	8.790(6)	16.400(6)
b (Å)	9.387(5)	21.571(6)
c (Å)	10.823(7)	9.210(4)
α (°)	90.00	90.00
β (°)	101.82(5)	90.00
γ (°)	90.00	90.00
V (Å^3)	874.0(9)	3258(2)
Molecular formula	$C_{18}H_{22}BiBr$	$C_{33}H_{31}BiP_2S_4$
Formula weight	527.26	826.7
$d_{röntg}$ (g cm^{-3})	2.003	1.685
R (%)	4.01	4.36
R_w (%)	4.81	5.32
$w = (\sigma^2(F) + gF^2)^{-1}$ g	0.0009	0.0015
GOF	1.18	1.03
T (°C)	−120	−100

2.2. Synthesis and structure of $MesBi(S_2PPh_2)_2$ (2)

Dimesitylbismuth(III) bromide (**1**) and ammonium diphenyldithiophosphinate were found to react to form $MesBi(S_2PPh_2)_2$ (**2**) rather than the expected dimesityl compound. The mono-mesityl derivative **2** was obtained as yellow crystals in almost quantitative yield (based on the amount of diphenyldithiophosphinate taken). Equation (2) depicts this unexpected reaction. The side product mesitylene was identified by NMR spectroscopy:

$$Mes_2BiBr + 2Ph_2PS_2NH_4 \longrightarrow \underset{\mathbf{(2)}}{MesBi(S_2PPh_2)_2} + NH_4Br + MesH + NH_3 \qquad (2)$$

The infrared spectrum of **2** shows two strong absorptions, at 636 cm^{-1} and 544 cm^{-1} for the asymmetric and the symmetric PS_2 stretching vibrations, respectively. The difference $\nu_{as}(PS_2) - \nu_s(PS_2)$ of 92 cm^{-1} is consistent with an anisobidentate coordination pattern of the dithiophosphinato groups [19], which leads to a five-coordinated bismuth atom.

The structure of $MesBi(S_2PPh_2)_2$ was determined by X-ray diffraction. It is similar to that of closely related compounds of the type $PhM[S_2P(O^iPr)_2]_2$ (M = As, Sb) [13]. It differs, however, from the structures of $PhBi(S_2CNEt_2)_2$ [15] and $MeBi(S_2CNEt_2)_2$ [14], which also contain a bidentate 1,1-dithiolato ligand; in the solid these compounds are dimers, associated through Bi ··· S secondary interactions, and exhibit a pentagonal bipyramidal coordination geometry around the metal. Obviously, the bulky mesityl groups prevent dimerization. This conclusion is supported by the fact that in inorganic bismuth(III) dithiophosphinates, the metal achieves higher coordination numbers: *e.g.* six in distorted octahedral $Bi(S_2PEt_2)_3$ [7] and seven in the dimers of $Bi(S_2PPh_2)_3$ [5], and $Bi(S_2PMe_2)_3$ [6]. In the mesityl derivative the coordination number of bismuth is only five.

The crystals of **2** consist of discrete molecules separated by distances longer than van der Waals contacts. Bond distances and angles are listed in Table 3. The molecular structure is presented in Fig. 3, together with the atom numbering scheme. The molecule has a symmetry plane that contains the bismuth atom and the aromatic ring of the attached mesityl group. The dithiophosphinato groups act as anisobidentate ligands. There are short Bi(1)–S(1) and Bi(1)–S(1A) bonds (2.662(2) Å) and long Bi(1) ··· S(2) and Bi(1) ··· S(2A) coordinative interactions of 3.112(3) Å below the sum of van der Waals radii (*ca.* 4.0 Å). This leads to a distorted square pyramidal arrangement around the central metal atom. The axial position is occupied by the carbon atom of the mesityl group bound to bismuth. The four sulfur atoms form the basal plane and the metal atom lies at 0.333 Å above it, inside the pyramid. This is reflected in the magnitude of the C(1)–Bi(1)–S angles (95.7(1)° and 97.9(2)°). Both phosphorus atoms lie also outside the sulfur plane, but on the opposite side with respect to bismuth. The distance between the phosphorus atoms and the plane of the sulfur atoms is 0.63 Å. The Bi(1)–C(1)–C(2) and Bi(1)–C(1)–C(6) angles are different, *viz.* 112.5(7)° and 128.8(9)°, the aromatic ring being bent towards the larger base side formed by the coordinated S(2) and S(2A) atoms. This behaviour could be the result of either steric effects (the S(1)–Bi(1)–S(1A) angle (84.0(1)°) is not much more than half of the S(2)–Bi(1)–S(2A) angle (131.5(1)°)), or packing effects in the crystal. Similar behaviour was observed for the related $PhM[S_2P(O^iPr)_2]_2$ (M = As, Sb) derivatives [13].

The geometry around phosphorus in the dithioligands is distorted tetrahedral with an S–P–S angle larger than the C–P–C angle (112.7(1)° compare with 103.8(3)°). The phosphorus–sulfur bonds are different (2.051(3) and 1.980(3) Å) and might be regarded as single (long) and double (short) bonds. However, the difference between long and short phosphorus–sulfur distances in **2** is only 0.071 Å, significantly less than that in the free acid, Ph_2PS_2H (P–S 2.077(1), P=S 1.954(1) Å [20]; difference 0.123 Å), which is in good agreement with the delocalization of the π-electron system of the double bond as a consequence of the chelate behaviour of the ligand moiety in the complex.

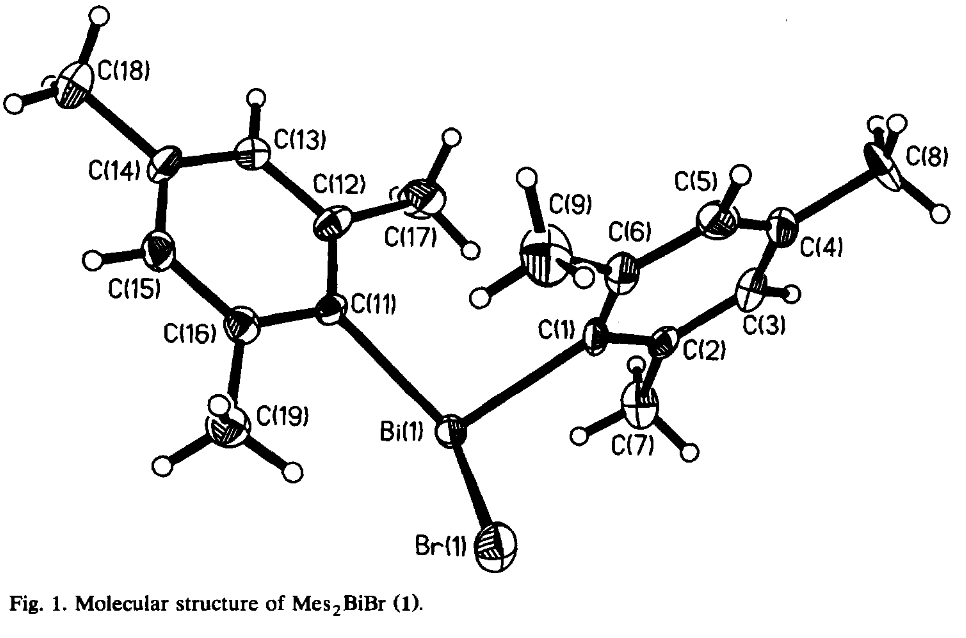

Fig. 1. Molecular structure of Mes_2BiBr (**1**).

3. Experimental details

The infrared spectrum of **2** was recorded for a Nujol mull on a BIO-RAD-FTS7 spectrometer. For the mass spectra a MAT 8222 (Finnigan MAT) (for compound **2**) and a CH7 (A) (MAT) (for compound **1**) instruments were used. ^{1}H NMR spectra were recorded on a Bruker WH 360 instrument at 360 MHz. Details of the X-ray study are given in Table 4.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$)

	x	y	z	U_{eq}[a]
Compound 1				
Bi(1)	4503(1)	2500	4400(1)	18(1)
Br(1)	2578(2)	4470(1)	5035(1)	33(1)
C(1)	5689(13)	4232(11)	3480(11)	20(3)
C(2)	7303(14)	4420(11)	3970(10)	21(3)
C(3)	8116(15)	5441(12)	3472(12)	27(4)
C(4)	7384(16)	6328(12)	2509(12)	29(4)
C(5)	5793(17)	6165(12)	2062(11)	31(4)
C(6)	4950(15)	5122(12)	2514(12)	28(4)
C(7)	8140(14)	3513(13)	5036(13)	31(4)
C(8)	8307(16)	7457(22)	1971(12)	46(4)
C(9)	3222(20)	4995(16)	1887(15)	48(5)
C(11)	3187(14)	1440(10)	2612(10)	18(3)
C(12)	4063(15)	868(11)	1793(11)	24(3)
C(13)	3358(14)	−9(12)	793(11)	23(3)
C(14)	1816(16)	−336(13)	599(11)	30(4)
C(15)	927(14)	252(12)	1406(11)	25(4)
C(16)	1580(14)	1120(11)	2407(11)	22(3)
C(17)	5794(16)	1236(15)	1881(13)	35(4)
C(18)	1072(18)	−1281(15)	−490(13)	40(5)
C(19)	529(15)	1668(13)	3250(12)	28(4)
Compound 2				
Bi(1)	87665(3)	25000	4454(5)	201(1)
S(1)	80148(14)	33256(9)	21259(24)	282(6)
S(2)	94629(14)	38153(10)	−1776(21)	261(6)
C(1)	78673(61)	25000	−14131(123)	178(31)
C(2)	82672(73)	25000	−28253(146)	225(35)
C(3)	77911(80)	25000	−40870(141)	282(37)
C(4)	69471(80)	25000	−39935(140)	265(36)
C(5)	65781(88)	25000	−26544(142)	289(40)
C(6)	70390(77)	25000	−13619(150)	288(38)
C(7)	92015(80)	25000	−30012(137)	309(43)
C(8)	64369(86)	25000	−53896(155)	401(45)
C(9)	65654(90)	25000	435(151)	361(43)
P(1)	88810(12)	39827(9)	16645(21)	193(6)
C(11)	83639(47)	47250(34)	16592(79)	194(22)
C(12)	86625(52)	52081(36)	8388(86)	262(24)
C(13)	82988(55)	57876(41)	9109(101)	320(28)
C(14)	76398(57)	58827(40)	18127(102)	339(29)
C(15)	73388(63)	54152(47)	26288(108)	401(33)
C(16)	76943(59)	48285(41)	25524(99)	324(29)
C(21)	95656(51)	40344(35)	32040(86)	242(24)
C(22)	92553(65)	40885(62)	46038(100)	512(39)
C(23)	97701(78)	41503(58)	57597(104)	545(42)
C(24)	105901(79)	41702(49)	55682(124)	520(39)
C(25)	109044(74)	41329(60)	42003(129)	561(42)
C(26)	104014(60)	40571(48)	30226(109)	416(33)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Important bond distances and angles in compounds **1** and **2**

Compound 1	
Distances (Å)	
Bi(1)–Br(1)	2.696(2)
Bi(1)–C(1)	2.268(12)
Bi(1)–C(11)	2.270(10)
Bond angles (°)	
Br(1)–Bi(1)–C(1)	89.4(3)
Br(1)–Bi(1)–C(11)	106.4(3)
C(1)–Bi(1)–C(11)	98.0(4)
Torsion angles (°)	
Br(1)–Bi(1)–C(1)–C(6)	−57.8(1.0)
Br(1)–Bi(1)–C(11)–C(12)	152.5(0.7)
C(11)–Bi(1)–C(1)–C(2)	−133.0(0.9)
C(1)–Bi(1)–C(11)–C(12)	60.7(0.8)
Intermolecular interactions	
Bi(1b)...Br(1c)	3.795(3)
Br(1c)–Bi(1c) ··· Br(1a)	156.1(1)
Compound 2	
Distances (Å)	
Bi(1)–S(1)	2.662(2)
Bi(1)–S(2)	3.112(3)
Bi(1)–C(1)	2.259(11)
P(1)–S(1)	2.051(3)
P(1)–S(2)	1.980(3)
P(1)–C(11)	1.812(8)
P(1)–C(21)	1.812(8)
Bond angles (°)	
S(1)–Bi(1)–S(1a)	84.0(1)
S(1)–Bi(1)–C(1)	97.9(2)
S(1)–Bi(1)–S(2)	70.6(1)
S(2)–Bi(1)–C(1)	95.7(1)
S(2)–Bi(1)–S(2a)	131.5(1)
Bi(1)–S(1)–P(1)	91.2(1)
Bi(1)–S(2)–P(1)	80.3(1)
Bi(1)–C(1)–C(2)	112.5(7)
Bi(1)–C(1)–C(6)	128.8(9)
S(1)–P(1)–S(2)	112.7(1)
S(1)–P(1)–C(11)	106.7(3)
S(1)–P(1)–C(21)	108.0(3)
S(2)–P(1)–C(11)	112.6(3)
S(2)–P(1)–C(21)	112.5(3)
C(11)–P(1)–C(21)	103.8(3)

3.1. *Preparation of dimesitylbismuth(III) bromide, Mes_2BiBr (1)*

A mixture of 2.02 g (4.5 mmol) of $BiBr_3$ and 100 ml of diethyl ether was added dropwise to 5.10 g (9.0 mmol) of Mes_3Bi [21] in 100 ml of diethyl ether. The mixture was stirred for 2 h and the product **1**, which had separated as a yellow solid, was filtered off, washed with ether, and dried under reduced pressure. Yield

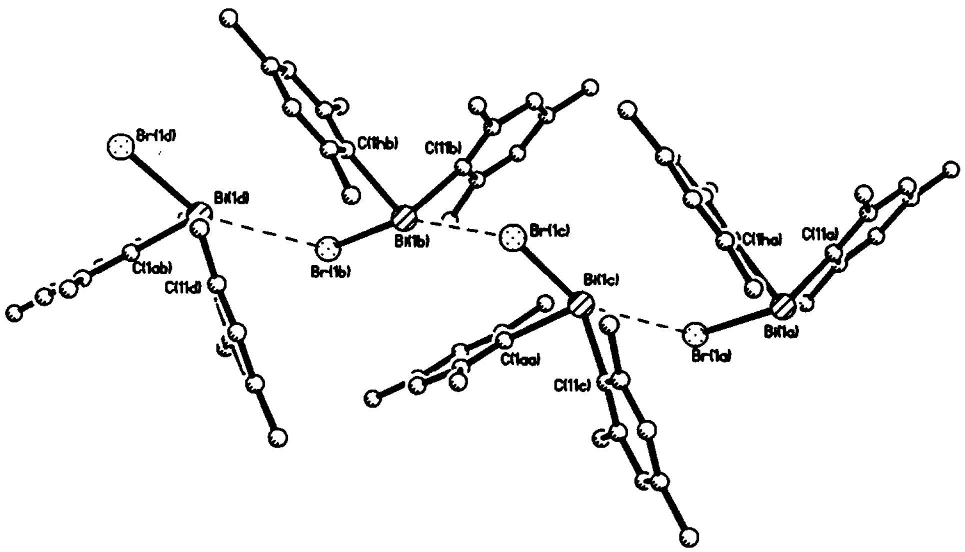

Fig. 2. Association of Mes_2BiBr (1) in the crystal.

6.1 g (81%). Crystals of 1 (m.p. 160°C (dec.)) were obtained by slow evaporation of solutions in diethyl ether.

Elemental analyses: Found C, 39.79; H, 4.24. $C_{18}H_{22}BiBr$ calcd. (527.26): C, 40.98; H, 4.17%. ^1H NMR (C_6D_6): 2.05 (s, 3H, *p*-CH_3); 2.28 (s, 6H, *o*-CH_3);

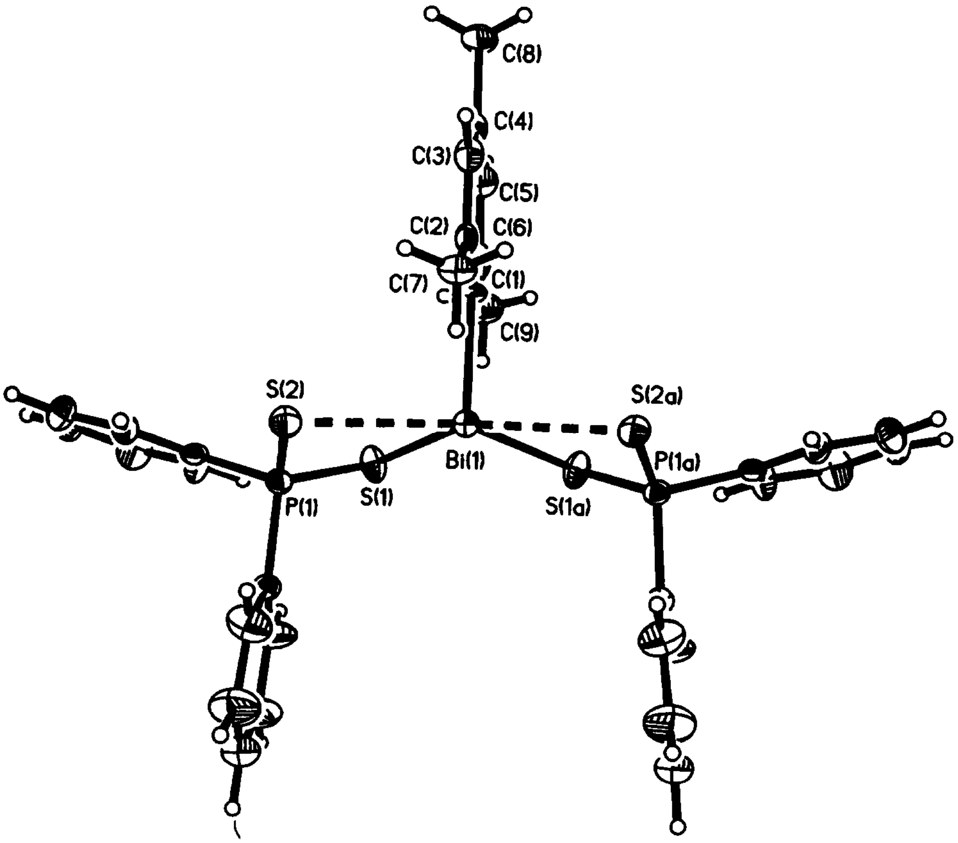

Fig. 3. Molecular structure of $MesBi(S_2PPh_2)_2$ (2).

TABLE 4. Details of the crystal structure determination of compounds **1** and **2** [a]

General: Instrument, Siemens P4; 2θ range, 5.0–55.0°; monochromator, highly orientated graphite crystal; scan type $2\theta-\omega$; 3 standard reflections, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were calculated as a riding model with isotropic U with the SHELXTL PLUS (VMS) program system [23]

Compound **1**: Index ranges, $-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 13$; 4363 reflections were collected; 3984 independent reflections ($R_{int} = 1.93\%$); 3372 reflections used with $F > 6.0\sigma(F)$; absorption correction with Program DIFABS [24]; absorption coefficient, $\mu = 12.362$ mm^{-1}; data to parameter ratio, 18.5:1; max. shift 2.97 e Å^{-3}

Compound **2**: Index ranges, $0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 28$, $0 \leqslant l \leqslant 11$; 4267 reflections were collected; 3824 independent reflections ($R_{int} = 0.65\%$); 2462 reflections used with $F > 6.0\sigma(F)$; absorption correction with program DIFABS [24]; absorption coefficient, $\mu = 5.788$ mm^{-1}; data to parameter ratio, 12.3:1; max. shift 1.76 e Å^{-3}

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[a] Supplementary data: Complete lists of bond lengths and angles, and tables of thermal parameters and hydrogen atom coordinates have been deposited with the Cambridge Crystallographic Data Centre. Additional details of the crystal structure investigations can be ordered from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the journal, authors and the file number CSD-57740.

7.00 (s, 2H, C_6H_2) ppm. MS-EI (70 eV, 50°C): *m/e* (rel.int.) 447 (1), Mes_2Bi^+; 406, 408 (1), $MesBiBr^+$; 328 (20), $MesBi^+$; 209 (40), Bi^+; 120 (100), $MesH^+$.

3.2. Preparation of bis(diphenyldithiophosphinato)mesitylbismuth(III), MesBi(S₂PPh₂)₂ (2)

A stirred mixture of 0.30 g (5.69 mmol) of **1** and 0.15 g (5.62 mmol) of $Ph_2PS_2NH_4$ [22] in anhydrous benzene was refluxed for 2 h during which the colour changed gradually from yellow-green to yellow-orange. The hot mixture was filtered to remove the resulting ammonium bromide and the clear filtrate was allowed to warm to room temperature. Yellow-orange crystals separated from the solution and were filtered off. Yield 0.23 g (100% based on $Ph_2PS_2NH_4$), m.p. 180°C(dec.). Recrystallization from benzene led to well formed crystals suitable for X-ray diffraction studies.

Elemental analyses: Found C, 48.00; H, 3.99. $C_{33}H_{31}BiP_2S_4$ calcd. (826.7): C, 47.94; H, 3.78%. ^1H NMR (C_6D_6): 2.00 (s, 3H, p-CH_3); 2.67 (s, 6H, o-CH_3); 6.8–6.95 (m, 12H, P-C_6H_5); 7.00 (s, 2H, C_6H_2); 7.75–7.90 (m, 8H, P-C_6H_5) ppm. MS-DCI(+) (reactant gas NH_3): m/e (rel.int.) 827 (1), MH^+; 707 (100), $M^+ -$ Mes; 577 (53), $M^+ - Ph_2PS_2$; 458 (2), $M^+ - Ph_2PS_2Mes$.

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft (R.E.S., H.J.B.) and the University of Bremen (C.S.) is gratefully acknowledged.

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