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Structural studies on aryl bismuth halides and halogenoanions. Part 4. Neutral Lewis base adducts of aryl bismuth dibromide and diaryl bismuth bromide compounds [☆]

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Abstract

Structural studies by X-ray crystallography have been carried out for a range of Lewis base ligand complexes of arylbismuth dibromides and diarylbismuth bromides. The complexes $[Bi_2Ph_2Br_4(OPPh_3)_2]$ **17** and $[Bi_2Ph_2Br_4(dmpu)_2]$ **18** (dmpu = N,N'-dimethylpropylene urea) both adopt crystallographically centrosymmetric bromine-bridged dimeric structures, each bismuth centre having a five-coordinate, square-based pyramidal geometry. In both structures a phenyl group occupies the apical site whilst the four basal positions are occupied by three bromine atoms, one terminal and two bridging, and the oxygen atom of the coordinated ligand ($OPPh_3$ in **17** and dmpu in **18**). A bis ligand complex $[BiPhBr_2(dmpu)_2]$ **19** is monomeric, with a similar coordination geometry around the bismuth centre in which the four basal positions are occupied by two *cis* bromine atoms and two *cis* oxygen atoms from the coordinated dmpu ligands. The diarylbismuth halide complexes $[Bi(mes)_2Br(OSPh_2)]$ **20** (mes = $2,4,6-Me_3C_6H_2$) and $[Bi(mes)_2Br(hmpa)]$ **21** (hmpa = hexamethylphosphoramide, $OP(NMe_2)_3$) are both monomeric, each bismuth centre having a four-coordinate, disphenoidal geometry with axial bromine and ligand donor atoms and equatorial mesityl groups. The structures are compared with those of related compounds and some general structural principles are derived and bonding models advanced.

Keywords: Bismuth; Halide; Aryl; Complexes; Structures; Synthesis

1. Introduction

In a series of recent papers [1–3] we have described the results of a number of crystal structure determinations for a range of phenyl bismuth(III) halides and halogenoanions, and a number of structural trends in these and related compounds have become apparent. It is observed, for example, that monoaryl-bismuth or -antimony dihalide compounds have a strong tendency to form additional bonds and assume square-based pyramidal five-coordination around the Group 15 element. For such compounds without additional ligands, this results in polymeric structures in which both halides are involved in bridging interactions, as found for $BiPhBr_2$ (**1**) [3], $SbPhX_2$ (**2**; X = Cl, Br, I) [4], $Sb(4-Me-C_6H_4)X_2$ (**3**; X = Cl, Br) [5], and the related antimony

complexes, $SbBu^tCl_2$ [6] and $SbMeX_2$ (X = Cl, Br, I) [7]; in all cases, the organic group is in an apical site with halides in the basal plane. Alternatively, five-coordination can be achieved by the coordination of one neutral two-electron donor ligand so that only one halide bridges (the other is terminal), as in the complexes $[BiPhX_2(thf)]$ (**4**; X = Cl, Br, I; thf = tetrahydrofuran) [1,2] which are also polymeric. In complexes **2–4**, there are also additional interactions between phenyl rings and the antimony or bismuth centres (as indicated for **2** and **4** in Scheme 1) which result in more two-dimensional structures in the case of **2** and **3**.

Monoaryl-bismuth and -antimony halogeno-anions also exhibit square-based pyramidal five-coordination with apical aryl groups. Thus, for complexes with the empirical formula $[EPhX_3]^-$ (E = Bi, Sb, X = halide), dimeric structures are observed, examples being $[NEt_4]_2[Bi_2Ph_2I_6] \cdot Et_2O$ (**5**) [1], $[NBu^n_4]_2[Bi_2Ph_2Br_6]$ (**6**) [2], $[NMe_4]_2[Sb_2Ph_2Cl_6]$ (**7**) [8], $[NEt_4]_2[Sb_2Ph_2I_6]$ (**8**) [9] and $[C_{10}H_{10}N_2]_2[Sb_2Ph_2Cl_6]$ (**9**) [10]; these are

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[☆] For part 3, see Ref. [3].
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2; X = Cl, Br, I

**4; X = Cl, Br, I**

6, E = Bi, X = Br;   **5, 8, E = Bi, Sb, X = I**
7, 9, E = Sb, X = Cl
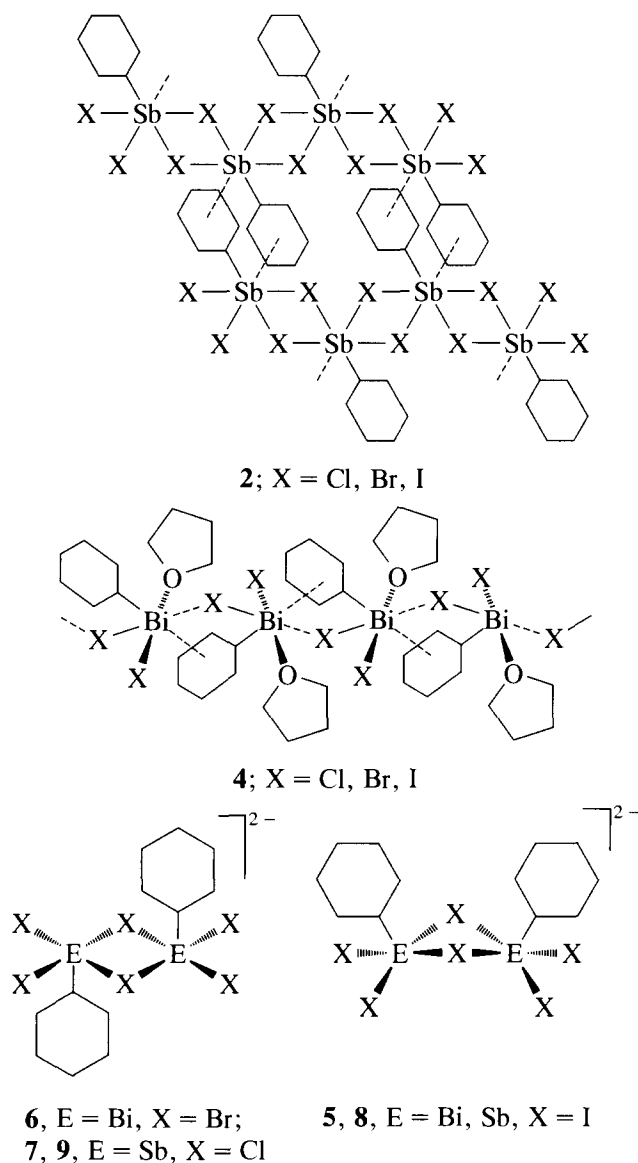
Scheme 1.

of two types as illustrated in Scheme 1. For the general formula $[EPhX_4]^{2-}$, as found in $[C_5H_5NH]_2[SbPhCl_4]$ **(10)** [8], the dianion is monomeric.

In contrast to the above, the structures of diaryl-bismuth or -antimony monohalide compounds tend to have four-coordinate Group 15 element centres, examples of which include $Bi(mes)_2Br$ **(11)** (mes = $2,4,6-Me_3C_6H_2$) [11], and $SbPh_2F$ **(12)** [12] for which a linear polymeric structure is observed as shown in Scheme 2 for **12**. The

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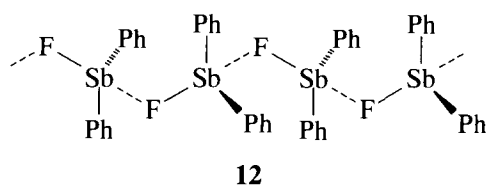
Scheme 2.

coordination geometry around the antimony or bismuth centre may be described as equatorially vacant, trigonal bipyramidal or disphenoidal, with axial halides and equatorial aryl groups, although in the complexes $SbPh_2Br$ [5] and $Bi\{2,4,6-(CF_3)_3C_6H_2\}_2Cl$ [13], monomeric structures without bridging halides are observed.

Four-coordination in diaryl complexes can also be satisfied by the addition of a neutral ligand, as found in the thf adduct $[BiPh_2Br(thf)]$ **(13)** [1] in which the bromine and thf ligand occupy axial sites, or by addition of halide to give halogeno-anions which include $[PPh_4][EPh_2X_2]$ **(14**, E = Bi, X = Br [1]; E = Sb, X = Cl, Br [14]), $[NEt_4][EPh_2X_2]$ **(15**, E = Bi, X = I [2]; E = Sb, X = Cl, I [8,9]) and $[Co(\eta-C_5H_5)_2][SbPh_2Cl_2]$ **(16)** [15]; in $[NEt_4][BiPh_2I_2]$, additional long $Bi \cdots I$ interactions *trans* to one phenyl are also present [4.085(1) Å] resulting in very weakly bound centrosymmetric dimers.

In contrast to the compounds $EArX_2$ and EAr_2X (Ar = aryl), which are generally five- and four-coordinate, respectively, it is found that for the element(III) halides, EX_3 (E = Bi, Sb and X = F, Cl, Br, I) [16], coordination numbers of six (sometimes higher) are commonly observed for the halides themselves, halogenoanions and ligand complexes, whereas triarylbismuth and -antimony complexes [17] show little evidence of Lewis acidity insofar as coordination of halide or neutral ligands is concerned. These observations can be summarised using the general formula $EAr_{3-n}X_n$ where the generally observed coordination number of the E centre is equal to $(3 + n)$ (for similar arguments, see Millington and Sowerby in Ref. [5]). The observed coordination numbers are then consistent with the Lewis acidity of the E centre being associated with the $E-X\sigma^*$-orbitals [18], a concept which allows for a somewhat more rational analysis of the structures than an alternative model employing vacant d-orbitals.

Herein we describe examples of neutral ligand adducts of some aryl- and diaryl-bismuth bromide complexes, the structures of which provide further support for the principles outlined above.

2. Results and discussion

The reaction between $BiPh_2Br$ [19] and one equivalent of $OPPh_3$ in CH_2Cl_2 afforded, after work-up and crystallisation from CH_2Cl_2/hexanes mixtures, colourless crystals, analytical data for which were consistent with the expected formula $[BiPh_2Br(OPPh_3)]$, although these crystals were not of good enough quality for X-ray crystallography. A subsequent recrystallisation from the same solvent system, however, afforded a crop of better quality colourless crystals, but analytical data were consistent with the different formula $[BiPhBr_2-$

Table 1
Selected bond lengths (Å) and angles (°) for **17**

Bi–Br(1)	2.856(2)	Bi–Br(2)	2.694(2)
Bi–Br(1a)	3.143(2)	Bi–O	2.390(9)
Bi–C(1)	2.25(1)	P–O	1.53(1)
Br(1)–Bi–Br(1a)	84.5(1)	Br(1)–Bi–Br(2)	176.0(1)
Br(1)–Bi–O	85.7(2)	Br(1)–Bi–C(1)	92.5(3)
Br(1a)–Bi–Br(2)	97.0(1)	Br(1a)–Bi–O	167.6(2)
Br(1a)–Bi–C(1)	89.2(3)	Br(2)–Bi–O	93.2(2)
Br(2)–Bi–C(1)	91.2(3)	O–Bi–C(1)	83.5(4)
Bi–O–P	125.5(6)	Bi–Br(1)–Bi(a)	95.5(1)

Table 2
Atomic positional parameters ($\times 10^4$) for **17**

	x	y	z
Bi	402.2(4)	−74.2(8)	941.7(2)
Br(1)	1565.5(12)	−778.2(18)	−203.9(6)
Br(2)	−490.9(14)	692.6(20)	1935.9(6)
P	3912(3)	−358(4)	1619(2)
O	2092(8)	−1222(12)	1410(4)
C(1)	−317(11)	−2481(16)	987(5)
C(2)	−669(13)	−3283(18)	485(6)
C(3)	−1022(11)	−4785(19)	521(6)
C(4)	−1117(13)	−5498(17)	1052(6)
C(5)	−780(12)	−4704(19)	1536(6)
C(6)	−336(13)	−3163(18)	1519(6)
C(7)	4407(12)	−1076(16)	1241(5)
C(8)	4191(14)	−1796(18)	733(6)
C(9)	5094(14)	−2336(19)	435(7)
C(10)	6266(14)	−2188(19)	669(7)
C(11)	6461(15)	−1439(19)	1194(7)
C(12)	5542(13)	−892(18)	1483(6)
C(13)	3514(13)	−646(18)	2366(6)
C(14)	2988(12)	−1872(17)	2631(6)
C(15)	3257(13)	−2188(19)	3203(6)
C(16)	4043(14)	−1238(19)	3524(7)
C(17)	4567(13)	−42(23)	3254(6)
C(18)	4291(11)	306(17)	2694(5)
C(19)	3027(12)	1706(16)	1489(5)
C(20)	3225(12)	2282(17)	961(6)
C(21)	2932(14)	3793(20)	824(7)
C(22)	2377(14)	4739(20)	1213(7)
C(23)	2164(14)	4086(19)	1734(7)
C(24)	2474(13)	2621(18)	1878(6)

(OPPh$_3$)] **17**, presumably due to a redistribution reaction having occurred, such reactions being characteristic of aryl-bismuth halide compounds in solution [11b]; crystals of compound **17** can be obtained in higher yield directly from the reaction between BiPhBr$_2$ and one equivalent of OPPh$_3$ in CH$_2$Cl$_2$. The formula for **17** was confirmed by X-ray crystallography (Fig. 1) which revealed the presence of a dimeric (crystallographically centrosymmetric) species [Bi$_2$Ph$_2$Br$_4$(OPPh$_3$)$_2$]; selected bond lengths and angles given in Table 1 and atomic positional parameters are presented in Table 2.

Each bismuth adopts a five-coordinate, square-based pyramidal coordination geometry with the phenyl group in the apical position and the three bromines and OPPh$_3$ oxygen atom in the basal plane. The Bi–C distance [2.25(1) Å] is within the range observed for other Bi(III) phenyl derivatives [1–3] and deserves no special comment. With regard to the Bi–Br distances, that to the terminal bromine Br(2) is the shortest [Bi–Br(2) 2.694(2) Å], with those to the bridging bromine Br(1) somewhat longer [Bi–Br(1) 2.856(2), Bi–Br(1a) 3.143(2) Å]. The difference between the bond lengths to Br(1) and Br(1a) [difference (Δ) = 0.287 Å] reveals a degree of bridge asymmetry which may be compared with that in compound **4** (X = Br) [0.213 Å], a compound with a similar formula to **17** but with a different structure (vide supra). The larger difference in **17** may be attributed in part to the fact that the OPPh$_3$ ligand is

trans to one of the Bi–(μ-Br) bonds (the longer one), whereas in **4** the thf ligand is *trans* to the terminal bromine. In this regard, it is interesting to note the much shorter Bi–OPPh$_3$ distance in **17** [2.390(9) Å] compared with the Bi–O(thf) distance in **4** [2.671(8) Å], indicating that triphenylphosphine oxide is probably a better ligand towards Bi(III) and that the long Bi–Br(1a) bond is the result of this ligand having an appreciable *trans* influence. With regard to the Bi$_2$(μ-Br)$_2$ unit, the phenyl groups may be described as *anti* and the OPPh$_3$ ligands
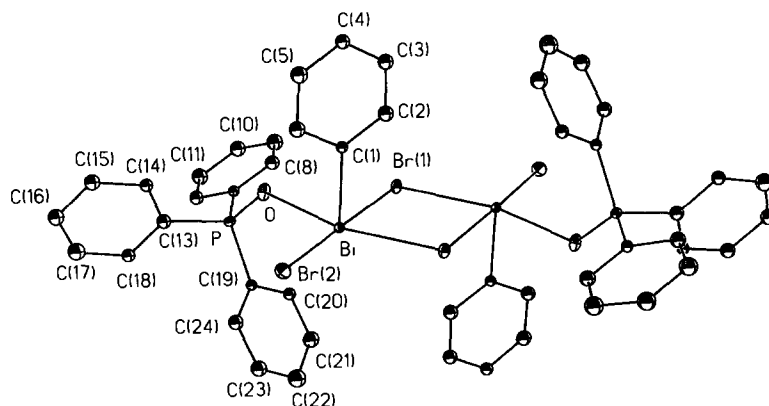

Fig. 1. A view of the molecular structure of **17** showing the atom numbering scheme.
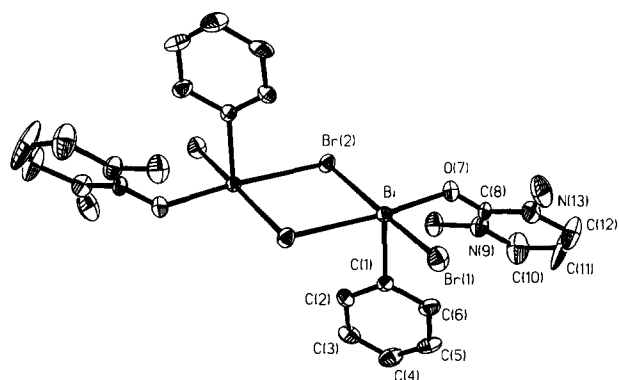
Fig. 2. A view of the molecular structure of **18** showing the atom numbering scheme.

Table 4
Atomic positional parameters ($\times 10^4$) for **18**

	x	y	z
Bi	7446(1)	457(1)	756(1)
Br(1)	9844(3)	1189(1)	−167(2)
Br(2)	4676(3)	−469(1)	1690(2)
C(1)	6287(27)	1419(10)	1360(15)
C(2)	4590(29)	1512(11)	1148(19)
C(3)	3868(30)	2069(12)	1685(24)
C(4)	4804(37)	2544(12)	2491(23)
C(5)	6434(37)	2462(11)	2686(22)
C(6)	7261(32)	1898(10)	2158(17)
O(7)	8597(18)	356(7)	3051(12)
C(8)	9107(28)	743(10)	4006(19)
N(9)	8163(25)	957(10)	4848(15)
C(10)	8779(39)	1423(19)	5904(25)
C(11)	10445(46)	1540(22)	6086(37)
C(12)	11417(41)	1335(18)	5329(28)
N(13)	10752(26)	907(10)	4206(17)
C(14)	6440(30)	780(15)	4573(20)
C(15)	11874(34)	645(16)	3322(25)

as *trans*, a consequence of the crystallographic centre of inversion.

The reaction between BiPhBr$_2$ [1] and an excess of dmpu (dmpu = *N,N'*-dimethylpropylene urea) in toluene afforded, after work-up and crystallisation from CH$_2$Cl$_2$/hexanes mixtures, pale yellow crystals of the complex [Bi$_2$Ph$_2$Br$_4$(dmpu)$_2$] **18**. The structure of **18** was established by X-ray crystallography (Fig. 2, Tables 3 and 4) and is very similar to that of **17** in comprising a bromide-bridged, crystallographically centrosymmetric, dimeric structure with *anti* phenyls [Bi–C(1) 2.21(2) Å] and *trans* dmpu ligands, and with each bismuth centre having a five-coordinate, square-based pyramidal coordination geometry. The terminal Bi–Br bond [Bi–Br(1) 2.700(3) Å] is shorter than those to the bridging bromine [Bi–Br(2) 2.829(2), Bi–Br(2a) 3.146(3) Å], for which the difference Δ is 0.317 Å, somewhat larger than that for **17**, indicating a slightly greater degree of bridge asymmetry. The longer of the Bi–(μ-Br) bonds is *trans* to the dmpu ligand, the Bi–O distance for which [Bi–O(7) 2.34(1) Å] is similar to that found in **17** for the OPPh$_3$ ligand. This observation, taken with the similar length of the long Bi–(μ-Br) bond, indicates that the ligands OPPh$_3$ and dmpu are quite similar in terms of their bonding to the bismuth centre.

A comparison between the dimeric structure of **17** and the polymeric structures of complexes **4** has been

made above and this is also appropriate for **18**. Also noteworthy is the structural similarity between **17/18** and the dianionic compounds **6**, **7** and **9**. The μ-Br asymmetry, however, is much less in **6** [$\Delta = 0.047$ Å], reflecting the *trans* influence of the OPPh$_3$ and dmpu ligands in **17** and **18** (Scheme 3).

A crystalline complex of BiPhBr$_2$ with two dmpu ligands, [BiPhBr$_2$(dmpu)$_2$], **19**, was obtained from the reaction between BiPh$_2$Br and an excess of dmpu in CH$_2$Cl$_2$ (crystallised from CH$_2$Cl$_2$/Et$_2$O mixtures), again as a result of a redistribution reaction similar to that encountered in one of the preparations of **17**. The structure of **19** was established by X-ray crystallography the results of which are shown in Fig. 3; selected bond lengths and angles are given in Table 5 and atomic positional parameters in Table 6. As is evident from Fig. 3, compound **19** is monomeric and involves a five-coordinate, square-based pyramidal bismuth centre with the phenyl group residing in the apical position; the Bi–C distance of 2.25(2) Å is comparable with that found in **17** and **18**. In the basal plane are the oxygen atoms of the coordinated dmpu ligands [Bi–O(7) 2.472(7) and Bi–O(16) 2.564(9) Å] and the two bromine atoms [Bi–Br(1) 2.765(1) and Bi–Br(2) 2.732(2) Å]. Of

Table 3
Selected bond lengths (Å) and angles (°) for **18**

Bi–Br(1)	2.700(3)	Bi–Br(2)	2.829(2)
Bi–Br(2a)	3.146(3)	Bi–O(7)	2.34(1)
Bi–C(1)	2.21(2)	C(8)–O(7)	1.25(2)
Br(1)–Bi–Br(2)	176.3(1)	Br(1)–Bi–Br(2a)	94.8(1)
Br(1)–Bi–O(7)	99.8(4)	Br(1)–Bi–C(1)	91.5(6)
Br(2)–Bi–Br(2a)	83.3(1)	Br(2)–Bi–O(7)	82.3(3)
Br(2)–Bi–C(1)	91.8(6)	Br(2a)–Bi–O(7)	164.8(4)
Br(2a)–Bi–C(1)	89.9(4)	O(7)–Bi–C(1)	85.8(5)
Bi–O(7)–C(8)	139(1)	Bi–Br(2)–Bi(a)	96.7(1)
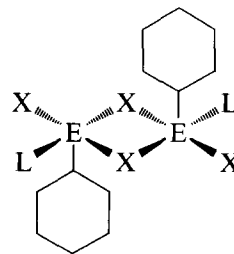
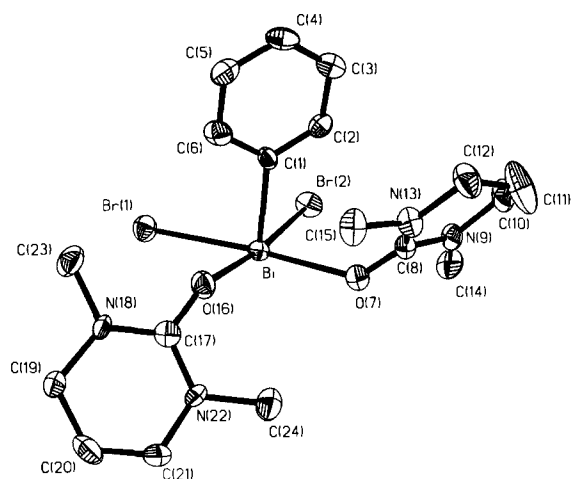**17**, L = OPPh$_3$; **18**, L = dmpu

Scheme 3.

Fig. 3. A view of the molecular structure of **19** showing the atom numbering scheme.

Table 5
Selected bond lengths (Å) and angles (°) for **19**

Bi–Br(1)	2.765(1)	Bi–Br(2)	2.732(2)
Bi–C(1)	2.25(2)	Bi–O(7)	2.472(7)
Bi–O(16)	2.564(9)		
Br(1)–Bi–Br(2)	94.4(1)	Br(1)–Bi–O(7)	169.5(2)
Br(1)–Bi–O(16)	84.5(2)	Br(1)–Bi–C(1)	93.9(3)
Br(2)–Bi–O(7)	96.0(2)	Br(2)–Bi–O(16)	172.0(3)
Br(2)–Bi–C(1)	88.6(3)	O(7)–Bi–O(16)	85.0(3)
O(7)–Bi–C(1)	84.7(4)	O(16)–Bi–C(1)	83.5(4)
Bi–O(7)–C(8)	134(1)	Bi–O(16)–C(17)	135.9(9)

Table 6
Atomic positional parameters ($\times 10^4$) for **19**

|	x	y	z
Bi	953(1)	4942(1)	3027(1)
Br(1)	−955(2)	7776(2)	1849(1)
Br(2)	−1529(2)	4696(2)	4311(1)
C(1)	702(14)	3401(14)	2270(9)
C(2)	453(14)	2089(15)	2782(9)
C(3)	485(16)	1017(16)	2321(11)
C(4)	667(16)	1384(17)	1333(11)
C(5)	874(16)	2714(17)	814(11)
C(6)	920(15)	3715(17)	1260(10)
O(7)	3049(10)	2411(10)	3840(6)
C(8)	3299(14)	961(14)	4061(9)
N(9)	2748(13)	279(12)	4918(7)
C(10)	2879(21)	−1309(18)	5120(11)
C(11)	4164(24)	−2291(19)	4610(14)
C(12)	4497(21)	−1615(16)	3607(11)
N(13)	4157(12)	66(12)	3436(8)
C(14)	1940(18)	1149(18)	5641(9)
C(15)	4669(16)	794(16)	2478(10)
O(16)	3171(10)	5003(10)	1682(6)
C(17)	3983(15)	5807(15)	1367(10)
N(18)	3740(12)	6867(12)	534(7)
C(19)	4669(16)	7813(16)	100(10)
C(20)	5378(19)	7947(18)	864(11)
C(21)	6173(16)	6381(16)	1499(10)
N(22)	5093(12)	5615(12)	1893(7)
C(23)	2584(18)	7068(19)	−75(10)
C(24)	5551(19)	4308(19)	2776(10)
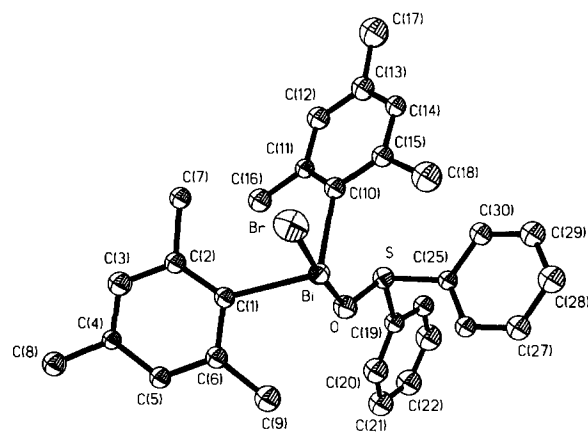
Fig. 4. A view of the molecular structure of **20** showing the atom numbering scheme.
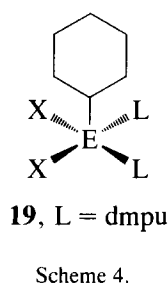
particular note is the fact that the two dmpu ligands are *cis*, and hence each *trans* to one of the bromines. This arrangement is consistent with the acceptor orbitals of the BiPhBr$_2$ unit being the Bi–Br σ*-orbitals, further support for which is evident from the observation that the shorter Bi–O distance [O(7)] is *trans* to the longer Bi–Br distance [Br(1)].

The complexes **1**, **17/18** and **19** provide a good illustration of the effect of adding neutral ligands to the bismuth centre. Thus, in **1**, where no such ligands are present, the bismuth centre is five-coordinate with all bromines bridging, whereas in **17/18**, where one ligand per bismuth is present, the same coordination geometry is retained with only one bridging bromine, whilst in **19**, which has two neutral ligands, both bromines are terminal (Scheme 4).

As described above, reactions using diarylbismuth halides as starting materials can result, via redistribution reactions, in monoarylbismuth dihalide products. In two cases, however, diarylbismuth halide complexes were obtained from reactions involving Bi(mes)$_2$Br (mes = 2,4,6-Me$_3$C$_6$H$_2$) [11]. The complex [Bi(mes)$_2$Br-(OSPh$_2$)] **20** was obtained from the reaction between Bi(mes)$_2$Br and one equivalent of OSPh$_2$ as yellow crystals, suitable for X-ray crystallography, from CH$_2$Cl$_2$/hexanes mixtures. The structure of **20** is shown in Fig. 4, with selected bond lengths and angles given in Table 7 and atomic positional parameters in Table 8. Complex **20** comprises a bismuth atom with a four-co-

Table 7
Selected bond lengths (Å) and angles (°) for **20**

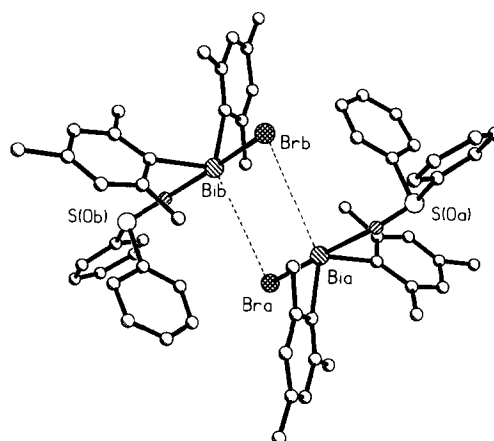| Bi–Br	2.749(3)	Bi–C(1)	2.28(2)
Bi–C(10)	2.25(2)	Bi–O	2.64(1)
Br–Bi–C(1)	91.9(5)	Br–Bi–C(10)	95.1(6)
Br–Bi–O	176.1(3)	C(1)–Bi–C(10)	107.7(8)
C(1)–Bi–O	90.2(6)	C(10)–Bi–O	81.1(7)
Bi–O–S	122.7(8)	O–S–C(19)	104.1(9)
O–S–C(25)	104 (1)	C(19)–Bi–C(25)	101 (1)

19, L = dmpu

Scheme 4.

Fig. 5. A view of centrosymmetrically related pairs of complex **20** showing the long secondary Bi · · · Br interactions.

ordinate, disphenoidal geometry bonded to two mesityl groups, one bromine and one $OSPh_2$ ligand (the latter bonded through the oxygen atom, Bi–O–S 122.7(8)°) with the bromine and the sulfoxide ligand in axial sites. The Bi–C distances [Bi–C(1) 2.28(2) Å and Bi–C(10) 2.25(2) Å] to the equatorial mesityl groups are similar to those in the phenyl complexes described above and in refs. [1–3]. In the axial sites are the oxygen atom of the coordinated $OSPh_2$ ligand, with a Bi–O bond length of 2.64(1) Å, and a bromine atom. The Bi–Br distance [Bi–Br 2.749(3) Å] is comparable with those in **19**, for which similar Bi–O distances to the coordinated ligands

are also observed, but is shorter than the Bi–Br distances *trans* to the O-donor ligands in **17** and **18** which have shorter Bi–O distances. These correlations, and the observed coordination of the sulfoxide ligand *trans* to the Br ligand rather than *trans* to a mesityl group, are consistent with the σ*-orbital bonding model, and is also in accord with previous observations on related structures, for example [$BiPh_2Br(thf)$] **13** described above.

There are no especially short intermolecular contacts in **20**, however pairs of molecules are related by a crystallographic centre of symmetry as shown in Fig. 5, resulting in what may be described as very loosely bound dimers with a Bi · · · Br(b) distance of 5.268 Å. Similar weak association to give centrosymmetric dimers was also observed in the related complex [NEt_4]-[$BiPh_2I_2$] [2] (vide supra).

A similar reaction between $Bi(mes)_2Br$ and an excess of hmpa (hmpa = hexamethylphosphoramide, $OP(NMe_2)_3$), afforded, after work-up and crystallisation from CH_2Cl_2/hexanes mixtures, yellow crystals of the complex [$Bi(mes)_2Br(hmpa)$], **21**, the structure of which was also established by X-ray crystallography. A view of **21** is shown in Fig. 6, with selected bond lengths and angles in Table 9 and atomic positional parameters in Table 10. The structure of **21** is very similar to that of **20** except that the axial $OSPh_2$ ligand in **20** is replaced by a hmpa ligand. Notable features are the Bi–Br bond length [Bi–Br 2.769(2) Å] and the Bi–O distance [Bi–O 2.631(9) Å] both of which are similar to the corresponding distances in **20** (Scheme 5).

In conclusion, the structures described herein provide further support for the general structural principles outlined in the Introduction and are consistent with the view that the Lewis acidity of arylbismuth(III) halide compounds is associated with the Bi–X σ*-orbitals through which the ligands coordinate *trans* to the Bi–X bonds.

Table 8
Atomic positional parameters ($\times 10^4$) for **20**

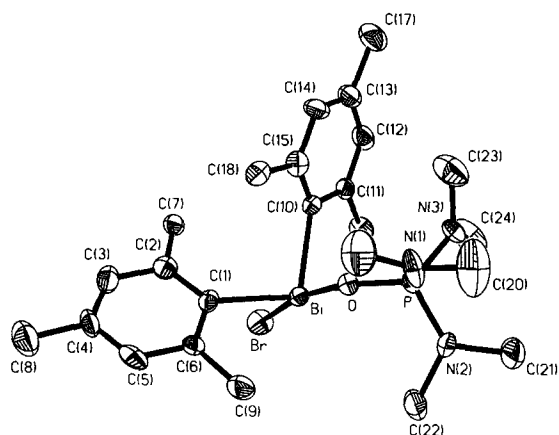|	x	y	z
Bi	9518(1)	181(1)	4049(1)
Br	8971(2)	−1569(2)	4089(2)
S	9393(3)	2662(4)	3953(3)
O	9951(8)	1898(9)	3983(9)
C(1)	10484(13)	−219(14)	3401(10)
C(2)	10423(13)	−749(14)	2885(11)
C(3)	11057(14)	−1033(16)	2560(13)
C(4)	11769(12)	−818(14)	2749(12)
C(5)	11871(12)	−306(14)	3290(11)
C(6)	11234(12)	0(14)	3626(12)
C(7)	9648(11)	−1032(13)	2637(11)
C(8)	12474(13)	−1097(14)	2416(12)
C(9)	11357(14)	584(16)	4192(13)
C(10)	8543(12)	725(15)	3480(12)
C(11)	8614(12)	1131(14)	2897(12)
C(12)	7947(14)	1425(14)	2596(13)
C(13)	7250(14)	1386(16)	2889(14)
C(14)	7179(12)	1036(14)	3460(12)
C(15)	7815(13)	706(15)	3758(12)
C(16)	9377(12)	1268(15)	2575(12)
C(17)	6552(15)	1729(18)	2513(14)
C(18)	7686(16)	366(18)	4417(14)
C(19)	9970(12)	3658(14)	4094(13)
C(20)	10697(14)	3555(18)	4254(13)
C(21)	11193(16)	4306(18)	4334(14)
C(22)	10820(17)	5133(20)	4282(14)
C(23)	10083(18)	5254(20)	4150(15)
C(24)	9629(13)	4489(14)	4064(13)
C(25)	8865(12)	2579(14)	4647(12)
C(26)	9209(12)	2332(14)	5178(12)
C(27)	8773(14)	2229(16)	5700(13)
C(28)	8005(15)	2423(17)	5664(14)
C(29)	7660(14)	2706(17)	5142(13)
C(30)	8078(13)	2792(15)	4614(13)

Fig. 6. A view of the molecular structure of **21** showing the atom numbering scheme.

Table 9
Selected bond lengths (Å) and angles (°) for **21**

Bi–Br	2.769(2)	Bi–C(1)	2.26(1)
Bi–C(10)	2.24(1)	Bi–O	2.631(9)
Br–Bi–C(1)	87.8(4)	Br–Bi–C(10)	102.0(4)
Br–Bi–O	171.7(2)	C(1)–Bi–C(10)	102.5(5)
C(1)–Bi–O	94.5(4)	C(10)–Bi–O	85.3(4)
Bi–O–P	134.2(5)		

Table 10
Atomic positional parameters ($\times 10^4$) for **21**

|	x	y	z
Bi	559(1)	1636(1)	632(1)
Br	−1525(2)	1319(1)	−365(1)
O	2412(10)	1726(6)	1669(5)
P	3587(4)	1163(2)	1895(2)
N(1)	4333(15)	1671(10)	2579(7)
N(2)	3131(13)	130(8)	2074(8)
N(3)	4773(12)	997(8)	1379(6)
C(1)	−657(15)	2825(9)	999(9)
C(2)	−1098(16)	3572(10)	578(9)
C(3)	−2005(18)	4207(11)	840(11)
C(4)	−2465(17)	4138(11)	1500(11)
C(5)	−2008(15)	3410(12)	1916(9)
C(6)	−1125(15)	2754(9)	1652(7)
C(7)	−724(16)	3726(10)	−130(8)
C(8)	−3485(22)	4786(13)	1743(12)
C(9)	−724(19)	1958(12)	2133(9)
C(10)	2096(15)	2330(9)	22(7)
C(11)	2575(17)	1884(10)	−556(8)
C(12)	3703(18)	2184(13)	−870(9)
C(13)	4438(19)	2963(14)	−616(10)
C(14)	3979(17)	3406(12)	−63(9)
C(15)	2843(18)	3101(11)	263(8)
C(16)	1830(18)	1016(11)	−846(8)
C(17)	5727(19)	3259(14)	−940(12)
C(18)	2469(18)	3669(10)	874(8)
C(19)	3974(26)	2513(14)	2795(11)
C(20)	5444(28)	1278(17)	2973(11)
C(21)	4023(22)	−676(12)	2132(15)
C(22)	1796(18)	−74(12)	2343(13)
C(23)	5724(22)	1686(14)	1266(12)
C(24)	4546(20)	420(15)	791(9)

3. Experimental

3.1. General procedures

All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium-benzophenone ketyl for Et_2O, CaH_2 for CH_2Cl_2 and sodium for hexanes and toluene). $BiBr_3$ (99% +), $BiPh_3$, dmpu, hmpa, $OSPh_2$ and $OPPh_3$ were procured commercially and used without further purification; $BiPhBr_2$ and $BiPh_2Br$ were prepared by published methods [8], as was $Bi(mes)_2Br$ [11,20]. Microanalytical data were obtained at the University of Newcastle.

3.2. Preparations

$[Bi_2Ph_2Br_4(OPPh_3)_2]$ **17**: $BiPh_2Br$ (0.100 g, 0.226 mmol) was dissolved in CH_2Cl_2 (5 cm^3) resulting in a pale yellow suspension. A sample of $OPPh_3$ (0.189 g, 0.677 mmol) was then added as a solution in CH_2Cl_2 (5 cm^3), which resulted in a cloudy solution. After stirring for 30 min, hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at −22°C afforded colourless crystals which appeared to lose solvent rapidly and for which analytical data indicated the formula $[BiPh_2Br(OPPh_3)]$ (0.142 g, 87% based on bismuth). $C_{30}H_{25}BiBrOP$ requires C, 49.95; H, 3.50. Found, C, 50.10; H, 3.35. These crystals were redissolved in CH_2Cl_2 (5 cm^3) and hexanes (15 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −22°C afforded colourless crystals of **17** (0.08 g, 49% based on bismuth), one of which was used for X-ray crystallography. $C_{48}H_{40}Bi_2Br_4O_2P_2$ requires C, 39.80; H, 2.80. Found C, 40.05; H, 3.15.

Compound **17** was also prepared in higher yield from the reaction between $BiPhBr_2$ and $OPPh_3$ in CH_2Cl_2 which afforded colourless crystals, analytical data for which were consistent with the expected formula.

$[Bi_2Ph_2Br_4(dmpu)_2]$ **18**: An excess of dmpu (0.2 cm^3, 1.65 mmol) was added dropwise to a yellow suspension of $BiPhBr_2$ (0.100 g, 0.224 mmol) in toluene (5 cm^3) which resulted in a colourless solution. After stirring for 30 min, hexanes (15 cm^3) were added as an overlayer and solvent diffusion over a period of days at −22°C afforded colourless crystals but none were of X-ray quality. The crystals were redissolved in CH_2Cl_2

$$mes_{\prime\prime\prime\prime\prime\prime\prime}\!\!\underset{\underset{Br}{|}}{\overset{\overset{L}{|}}{\underset{mes}{\diagup}Bi}}$$
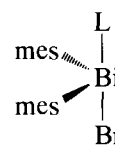
20, L = $OSPh_2$; **21**, L = hmpa

Scheme 5.

(5 cm^3) and hexanes (15 cm^3) were added as an over-layer. Solvent diffusion over a period of days at $-22°C$ afforded pale yellow crystals of **18** (0.104 g, 81% yield based on bismuth), one of which was used for X-ray crystallography. $C_{24}H_{34}Bi_2Br_4N_4O_2$ requires C, 25.10; H, 3.00; N, 4.90. Found C, 24.85; H, 3.05; N, 4.90.

[BiPhBr$_2$(dmpu)$_2$] **19**: An excess of dmpu (0.2 cm^3, 1.65 mmol) was added dropwise to a pale yellow suspension of BiPh$_2$Br (0.100 g, 0.226 mmol) in CH$_2$Cl$_2$ (5 cm^3) resulting in formation of a colourless solution. After stirring for 30 min, hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at $-22°C$ afforded colourless crystals, but none were of X-ray quality. The crystals were redissolved in CH$_2$Cl$_2$ (5 cm^3) and Et$_2$O (15 cm^3) was added as an overlayer. Solvent diffusion over a period of days at $-22°C$ afforded colourless crystals of **19** (0.07 g, 45% based on bismuth), one of which was used

for X-ray crystallography. $C_{18}H_{29}BiBr_2N_4O_2$ requires C, 30.80; H, 4.15; N, 8.00. Found C, 30.80; H, 4.10; N, 7.90.

[Bi(mes)$_2$Br(OSPh$_2$)] **20**: Bi(mes)$_2$Br (0.231 g, 0.566 mmol) was dissolved in CH$_2$Cl$_2$ (5 cm^3) resulting in a yellow solution. A sample of OSPh$_2$ (0.115 g, 0.566 mmol) was then added as a solution in CH$_2$Cl$_2$ (3 cm^3) which resulted in a colourless solution. After stirring for 20 min, hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at $-22°C$ afforded colourless crystals of **20** (0.281 g, 68% based on bismuth). $C_{30}H_{32}BiBrOS$ requires C, 49.40; H, 4.40. Found, C, 49.50; H, 4.30.

[Bi(mes)$_2$Br(hmpa)] **21**: An excess of hmpa (0.2 cm^3, 1.15 mmol) was added dropwise to a yellow solution of Bi(mes)$_2$Br (0.100 g, 0.245 mmol) in CH$_2$Cl$_2$ (5 cm^3). After stirring for 1 h, hexanes (20 cm^3) were added as an overlayer and solvent diffusion

Table 11
Crystallographic and structure solution data for compounds **17–21**

	17	18	19	20	21
Compound formula	$C_{48}H_{40}Bi_2Br_4O_2P_2$	$C_{24}H_{34}Bi_2Br_4N_4O_2$	$C_{18}H_{29}BiBr_2N_4O_2$	$C_{30}H_{32}BiBrOS$	$C_{24}H_{40}BiBrN_3OP$
Cryst. size/mm	$0.10 \times 0.34 \times 0.34$	$0.48 \times 0.51 \times 0.73$	$0.25 \times 0.25 \times 0.35$	$0.22 \times 0.44 \times 0.56$	$0.48 \times 0.51 \times 0.51$
M_r	1448.4	1148.2	702.3	729.5	706.5
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pbca$	$P2_1/n$
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
a (Å)	11.568(6)	8.243(2)	9.499(1)	17.414(3)	9.910(2)
b (Å)	8.649(2)	19.252(6)	9.748(1)	14.725(3)	14.618(2)
c (Å)	23.406(6)	10.148(2)	14.766(2)	21.919(5)	19.412(4)
α (°)			71.58(1)		
β (°)	94.01(3)	98.09(2)	77.19(1)		94.01(3)
γ (°)			62.27(1)		
V (Å^3)	2336(1)	1594.4(8)	1143.7(6)	5620(3)	2805(1)
Z	2	2	2	8	4
D_{calc} (g cm^{-3})	2.059	2.392	2.039	1.724	1.673
$F(000)$	1360	1056	668	2832	1384
μ(Mo-Kα)/cm^{-1}	110.49	160.62	112.21	77.90	77.86
T (K)	173(2)	298(2)	298(2)	300(2)	300(2)
Scan mode	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$
2θ range (°)	4.0–52.5	4.0–50.0	4.0–50.0	4.0–50.0	5.24–50.0
Index ranges	$h, -14–14$; $k, -5–10$; $l, -29–28$	$h, -1–6$; $k, -1–22$; $l, -12–12$	$h, -1–11$; $k, -10–11$; $l, -17–17$	$h, -1–20$; $k, -1–17$; $l, -26–1$	$h, -11–2$; $k, -17–17$; $l, -23–23$
Range of transmission coefficients	0.217–0.513	0.106–0.330	0.079–0.451	0.111–0.571	0.172–0.570
No. of data collected	4943	3079	4816	6610	12238
No. of unique data	4706	2284	4020	4940	4920
R_{merge}	0.0529	0.0445	0.0157	0.0385	0.0631
No. of data in refinement	2677	1582	2818	2052	3273
Observation criterion	$I > 2.0 \sigma(I)$	$I > 2.0 \sigma(I)$	$I > 2.0 \sigma(I)$	$I > 2.0 \sigma(I)$	$I > 2.0 \sigma(I)$
No. of refined parameters	143	165	245	158	282
Final R	0.0466	0.0532	0.0484	0.0687	0.0660
Final R_w	0.0483	0.0631	0.0496	0.0704	0.0730
Goodness of fit, S	1.05	1.15	1.24	1.21	1.36
Largest remaining feature in electron density map (e Å^{-3})	1.85(max), -1.85(min)	1.99(max), -2.00(min)	1.58(max), -0.88(min)	1.23(max), -1.40(min)	2.14(max), -2.46(min)
Largest and mean Δ/σ	0.021, 0.002	0.010, 0.001	0.007, 0.001	0.065, 0.012	0.009, 0.002

over a period of weeks at $-22°C$ afforded pale yellow crystals of **21** (0.132 g, 77% based on bismuth). $C_{24}H_{40}BiBrN_3OP$ requires C, 40.80; H, 5.70; N, 5.95. Found, C, 41.25; H, 5.90; N, 5.90.

3.3. X-ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for all structures are presented in Table 11. The following section deals with the structure of **17** with details for the other structures, where different, given in parentheses. Data were collected on an Enraf-Nonius CAD4 diffractometer [Nicolet P3 for **17**] with graphite monochromated X-radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters were determined by recentering 25 optimal high angle reflections. Three standard reflections were measured every 97 reflections during data collection, and no decrease in intensities was noted. Corrections were applied for Lorentz-polarisation and absorption (SHELXA) effects. The structure was solved for the heavy atoms by direct methods (SHELXTL PLUS) (Patterson for **19**). Subsequent difference syntheses gave all other non-H atomic positions. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter. Refinement was by full matrix least-squares on F using the weighting scheme $w^{-1} = \sigma^2(F) + 0.0005\ F^2$ [0.0015 F^2 for **18**, 0.0005 F^2 for **19**, 0.0010 F^2 for **20** and **21**] and minimising the function $\sum w(|F_o| - |F_c|)^2$. [For **18**, an extinction correction was applied of the form $\chi = 0.00010(4)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$; for **21** a similar correction was applied with $\chi = 0.00006(6)$]. Residual electron density in the final difference Fourier maps was all near the bismuth atoms.

Acknowledgements

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