DALTON

Cationic, arylbismuth(III) complexes of the form $[BiR_2L_2]^+$ and $[BiRL_4]^{2+}$ where L is a neutral two-electron donor ligand

Claire J. Carmalt,[a] **Louis J. Farrugia**[b] **and Nicholas C. Norman** *,†,[a]

[a] *The University of Newcastle upon Tyne, Department of Chemistry, Newcastle upon Tyne NE1 7RU, UK*

[b] *The University of Glasgow, Department of Chemistry, Glasgow G12 8QQ, UK*

Synthetic and structural studies have been made for a range of cationic, ten-electron, four-co-ordinate, diarylbis(ligand)bismuth(III) complexes. Reactions between $BiPh_2Br$, $AgBF_4$ and 2 equivalents of a two-electron donor ligand L afforded the ionic complexes $[BiPh_2L_2][BF_4]$ [L = $OPPh_3$ or pyridine (py)]. The first was characterised by X-ray crystallography and comprises $[BiPh_2(OPPh_3)_2]^+$ cations, tetrafluoroborate anions and CH_2Cl_2 molecules of crystallisation. The bismuth centre is four-co-ordinate with a disphenoidal geometry in which the aryl groups are in equatorial positions with the ligands in axial sites. A long interaction is present between the bismuth centre and one of the fluorines of the BF_4 group. A series of similar reactions were also carried out between BiR_2Br (R = aryl), $TlPF_6$ and 2 equivalents of L affording the ionic complexes $[BiR_2L_2][PF_6]$ [R = Ph, L = $OP(NMe_2)_3$ or py; R = $4\text{-}MeC_6H_4$, L = $OP(NMe_2)_3$; R = $2,4,6\text{-}Me_3C_6H_2$, L = $OP(NMe_2)_3$ or $OPPh_3$]. Two of the complexes have also been characterised by X-ray crystallography, the cations having similar structures to that found in $[BiPh_2(OPPh_3)_2][BF_4]$. The reaction between $BiPhBr_2$, 1 equivalent of $TlPF_6$ and an excess of $OP(NMe_2)_3$ afforded the ionic complex $[BiPh\{OP(NMe_2)_3\}_4][PF_6]_2$. The crystal structure of the dication comprises a square-based pyramidal bismuth centre with an apical phenyl group and four basal $OP(NMe_2)_3$ ligands. Examples of some dihalogenobismuth cations have also been obtained and their structures are described and compared with those of previously reported examples.

An interesting aspect of the chemistry of the heavier Group 15 elements, in terms of both structure and reactivity, which continues to receive significant attention is the area of cationic compounds with low co-ordination numbers. Within this field, the compounds most studied are the phosphenium ions, $[PR_2]^+$, where R is usually a good π-donor group such as dialkylamido.[1] Well characterised examples involving arsenic and particularly antimony and bismuth are less well known, and with these elements there is a marked tendency towards increasing Lewis acidity of the element centre with a concomitant increase in co-ordination number. This is illustrated in the case of arsenic by the dimeric nature of the cation $[cyclo\text{-}AsS_2C_2H_4]^+$ in the solid state,[2] and in the decamethylarsocenium cation $[As(\eta\text{-}C_5Me_5)_2]^+$[3] in which the C_5Me_5 rings are π rather than σ bonded to the arsenic centre. For antimony and bismuth, the few compounds which are known are mostly of the type $[EX_2L_n]^+$ (X = halide, L is a two-electron donor or one such site in a polydentate ligand). Examples include the crown ether complexes (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane), $[BiCl_2(18\text{-crown-}6)]^+$,[4] $[BiBr_2(18\text{-crown-}6)]^+$,[5] $[BiCl_2(MeCN)(18\text{-crown-}6)]^+$,[6] and the related antimony complex $[SbCl_2(18\text{-crown-}6)]^+$,[7] together with the polyether complexes $[BiBr_2L]^+$ {L = 2,2′-[oxybis(ethyleneoxyethyleneoxy)]- or 2,2′-[ethylenebis(oxyethyleneoxy)]-diethanol}[5] in which the crown and polyether ligands are hexa- or penta-dentate. In all of these cations the $EX_2{}^+$ unit is bent, as is also found in the arene complex $[BiCl_2(C_6Me_6)][AlCl_4]$,[8] with X–E–X angles in the range 89.1–94.0°. An example in which a linear $EX_2{}^+$ unit is found is the complex $[BiI_2\{OP(NMe_2)_3\}_4]^+$,[9] and a dimeric dication is present in the complex $[Bi_2(\mu\text{-}Cl)_2Cl_2(tu)_6][BiCl_5(tu)]$ (tu = thiourea). The $[Bi_2(\mu\text{-}Cl)_2Cl_2(tu)_6]^{2+}$ cation has an edge-shared, bioctahedral structure with two bridging chlorides and three ligands in a *fac* configuration on each bismuth centre, the overall structure being centrosymmetric.[10] A somewhat different example for antimony is the octahedral catecholate complex $[Sb(O_2C_6H_4)(phen)_2]^+$ (phen = 1,10-phenanthroline).[11]

In a recent paper[12] we reported the first example of a cationic, four-co-ordinate, ten-electron diarylbismuth(III) complex, namely $[BiPh_2\{OP(NMe_2)_3\}_2][BF_4]$ **1**. In the solid-state complex **1** is ionic and comprises separated $[BiPh_2\{OP(NMe_2)_3\}_2]^+$ cations and tetrafluoroborate anions with no close interionic contacts. The co-ordination geometry around the bismuth centre is of the type anticipated for this electron count which can be described as equatorially vacant, trigonal bipyramidal or disphenoidal with the $OP(NMe_2)_3$ ligands in the axial sites and equatorial phenyl groups; a similar structure has been predicted for the cation in $[BiPh_2(OAsPh_3)_2][ClO_4]$[13] **2** which was characterised by infrared and Raman spectroscopy and analytical data. Both complexes may be viewed as ligand-stabilised $[BiPh_2]^+$ cations. As six-electron species, such cations would have a lone pair and a vacant orbital and would thus be expected to have a bent structure; the two axial ligands may then be viewed as interacting with the vacant Bi 6p orbital in a three-centre, four-electron type interaction. The related cation $[SbPh_2]^+$ is reportedly formed by the electrochemical oxidation of Sb_2Ph_4 in tetrahydrofuran (thf) solution[14] although no structural details are available.

Herein we report more fully on synthetic routes to a range of diarylbismuth cations analogous to **1**[12] together with three representative structures. The first arylbismuth dication is also described together with further examples of dihalogenobismuth cations.

Results and Discussion

The complex $[BiPh_2\{OP(NMe_2)_3\}_2][BF_4]$ **1** was prepared from the reaction between $BiPh_2Br$, 1 equivalent of $AgBF_4$ and 2 equivalents of $OP(NMe_2)_3$ in thf solution as described in ref. 12. A similar reaction involving 2 equivalents of $OPPh_3$

---

† *Present address:* The University of Bristol, School of Chemistry, Bristol BS8 1TS, UK.

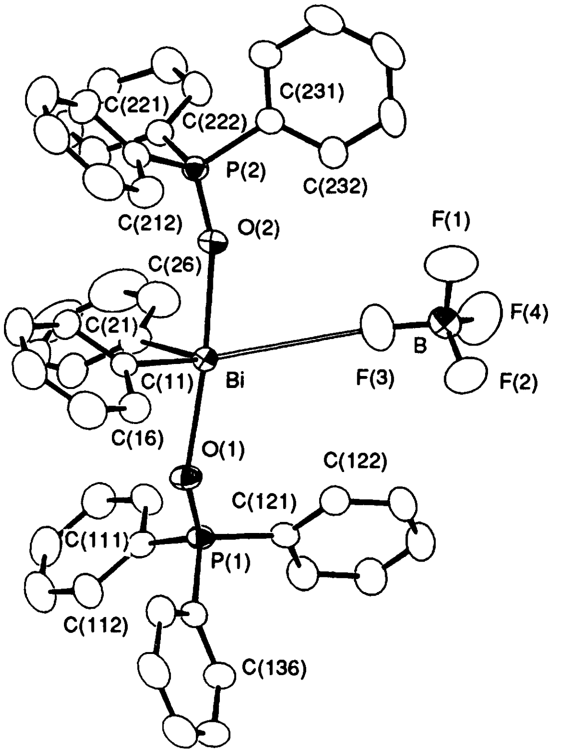


Fig. 1 View of the structure of complex **3** showing the atom numbering scheme. Both cation and anion are shown (but not the CH_2Cl_2 of crystallisation) and the close Bi ··· F contact. Ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted

afforded, after work-up, colourless crystals of the complex $[BiPh_2(OPPh_3)_2][BF_4]$ **3**. Spectroscopic data for **3** (Table 1) were consistent with the expected formula and the structure was confirmed by X-ray crystallography, the results of which are shown in Fig. 1. Selected bond distances and angles are given in Table 2 and atomic positional parameters in Table 3. The structure of **3** is ionic and comprises $[BiPh_2(OPPh_3)_2]^+$ cations, tetrafluoroborate anions and CH_2Cl_2 molecules of crystallisation. In the cation a central bismuth atom is bonded to two phenyl groups [Bi–C(11) 2.223(4) and Bi–C(21) 2.223(5) Å] and two $OPPh_3$ ligands [Bi–O(1) 2.388(3), Bi–O(2) 2.389(3) Å] with a four-co-ordinate disphenoidal geometry in which the phenyl groups are in equatorial positions [C(11)–Bi–C(21) 95.8(3)°] and the $OPPh_3$ ligands in axial sites [O(1)–Bi–O(2) 173.2(2)°]. As such, the structure is very similar to that of the cation $[BiPh_2\{OP(NMe_2)_3\}_2]^+$[12] in **1** with all bond lengths and angles within the usual ranges.[9,12,15–17] However, in addition to the primary co-ordination environment around the bismuth centre and unlike in **1**, there is a weak, secondary interionic interaction involving the bismuth centre and one of the fluorine atoms of the BF_4 group [Bi ··· F(3) 3.533(5) Å] which lies approximately in the equatorial plane [F(3) lies 0.787(5) Å out of the plane defined by Bi, C(11) and C(21)] and subtends angles of 148.1(2) and 113.0(3)° to the phenyl carbons C(11) and C(21) respectively.

A similar reaction between $BiPh_2Br$, $AgBF_4$ and 2 equivalents of dmpu (*N*,*N*′-dimethylpropyleneurea) in thf resulted initially in a colourless semicrystalline material. Crystallisation from pyridine–hexane mixtures resulted in colourless crystals, but none was of a quality suitable for X-ray crystallography. Spectroscopic (Table 1) and analytical data, however, indicated that the ionic species $[BiPh_2(py)_2][BF_4]$ **4** (py = pyridine) had formed, in contrast to the expected dmpu complex, probably *via* a ligand-exchange reaction. Whilst little structural information can be directly deduced from these spectroscopic data, the structure of the cation in **4** is likely to be similar to that in **3** with axial ligands and equatorial phenyls.

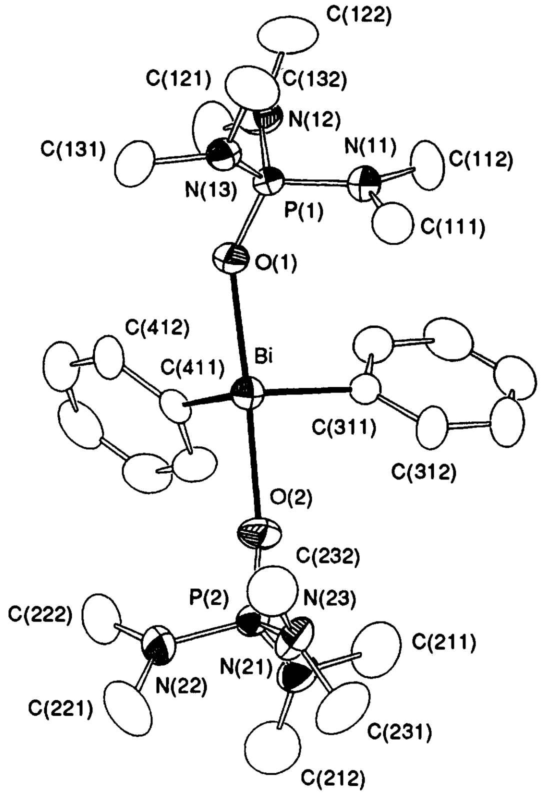


Fig. 2 View of the molecular structure of the cation in complex **5** showing the atom numbering scheme. Ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted

In spite of the results described above, the use of $AgBF_4$ as a halide-abstraction reagent is not ideal due to its hygroscopic nature, and resulting problems with hydrolysis, and also because Ag^+ can potentially compete with the $[BiPh_2]^+$ species for co-ordination of the ligands. Much more satisfactory, in terms of both ease of handling and higher product yields, is the use of $TlPF_6$. Thus, the reaction between $BiPh_2Br$, $TlPF_6$ and 2 equivalents of $OP(NMe_2)_3$ in thf afforded, after work-up, colourless crystals of $[BiPh_2\{OP(NMe_2)_3\}_2][PF_6]$ **5**. Spectroscopic data (Table 1) were consistent with the expected formula, which is similar to that of **1**, and the structure was confirmed by X-ray crystallography, the results of which are shown in Fig. 2. Selected bond distances and angles are given in Table 4 and atomic positional parameters in Table 5. The structure is ionic comprising $[BiPh_2\{OP(NMe_2)_3\}_2]^+$ cations and hexafluorophosphate anions with no close interionic contacts (closest Bi ··· F 6.367 Å). The cations in compounds **5** and **1** have the same formula and are closely similar in structure, both also being similar to that of **3**, described above. Thus, within the disphenoidal geometry around the bismuth centre, the phenyl groups occupy the equatorial positions [average Bi–C 2.211 Å, C(411)–Bi–C(311) 94.3(2)°, *cf.* 2.247 Å and 93.2(5)° for **1**] and the $OP(NMe_2)_3$ ligands are mutually *trans* in the axial sites [average Bi–O 2.336 Å, O(1)–Bi–O(2) 172.4(2)°, *cf.* 2.364 Å and 167.5(3)° for **1**]. The only significant differences between the cations of **1** and **5** are the O–Bi–O angles which differ by almost 5°, and the Bi–O–P angles which for **5** are Bi–O(1)–P(1) 138.8(3) and Bi–O(2)–P(2) 165.2(4)° whereas for **1** they are 131.5(6) and 137.2(5)°. These differences reflect the relatively soft nature of these angles and large changes are to be expected when the nature of the anion and hence the crystal structure and resulting crystal-packing forces are changed.

The analogous reaction between $BiPh_2Br$, $TlPF_6$ and 2 equivalents of pyridine in thf resulted in a white crystalline solid, spectroscopic (Table 1) and analytical data for which were consistent with the formula $[BiPh_2(py)_2][PF_6]$ **6** analogous to **4** although no crystals of X-ray quality were obtained.

Table 1 The NMR data for the complexes[a]

Compound	^{1}H(δ)[b]	^{13}C-{^{1}H}(δ)[b]	^{31}P-{^{1}H}(δ)[c]
3 $[BiPh_2(OPPh_3)_2][BF_4]$[d]	8.09 (d, 4 H, *o*-H of BiPh, J_{HH} = 8) 7.58 and 7.38 (m, 36 H, *m*-, *p*-H of BiPh, $OPPh_3$)		38 (s, $OPPh_3$)
4 $[BiPh_2(py)_2][BF_4]$	8.53 (d, 4 H, *o*-H of py, J_{HH} = 5) 8.21 (d, 4 H, *o*-H of BiPh, J_{HH} = 8) 7.97 (t, 4 H, *m*-H of py, J_{HH} = 5) 7.71 (t, 4 H, *m*-H of BiPh, J_{HH} = 8) 7.50 (t, 2 H, *p*-H of BiPh, J_{HH} = 8) 7.41 (t, 2 H, *p*-H of py, J_{HH} = 5)		
5 $[BiPh_2\{OP(NMe_2)_3\}_2][PF_6]$	8.24 (d, 4 H, *o*-H of BiPh, J_{HH} = 8) 7.69 (t, 4 H, *m*-H of BiPh, J_{HH} = 8) 7.38 (t, 2 H, *p*-H of BiPh, J_{HH} = 8) 2.46 [d, 36 H, $OP(NMe_2)_3$, J_{PH} = 10]	137.1 (s, *o*-C of BiPh) 132.6 (s, *m*-C of BiPh) 129.4 (s, *p*-C of BiPh) 37.3 [s, $OP(NMe_2)_3$]	24 [s, $OP(NMe_2)_3$] −125 (spt, PF_6)
6 $[BiPh_2(py)_2][PF_6]$	8.37 (d, 4 H, *o*-H of py, J_{HH} = 5) 8.13 (d, 4 H, *o*-H of BiPh, J_{HH} = 8) 7.91 (t, 4 H, *m*-H of py, J_{HH} = 5) 7.71 (t, 4 H, *m*-H of BiPh, J_{HH} = 8) 7.48 (t, 2 H, *p*-H of BiPh, J_{HH} = 8) 7.41 (t, 2 H, *p*-H of py, J_{HH} = 5)	183.4 (s, *ipso*-C of BiPh) 148.2, 139.6, 126.1 (py) 137.0 (s, *o*-C of BiPh) 132.4 (s, *m*-C of BiPh) 129.5 (s, *p*-C of BiPh)	−144 (spt, PF_6)
7 $[Bi(C_6H_4Me\text{-}4)_2\{OP(NMe_2)_3\}_2][PF_6]$	8.10 (d, 4 H, *o*-H of C_6H_4, J_{HH} = 8) 7.48 (d, 4 H, *m*-H of C_6H_4, J_{HH} = 8) 2.46 [d, 36 H, $OP(NMe_2)_3$, J_{PH} = 10] 2.32 (s, 3 H, $C_6H_4\mathit{Me}$)	191.4 (s, *ipso*-C of C_6H_4) 139.5 (s, *p*-C of C_6H_4) 137.0 and 133.3 (m, *o*-, *m*-C of C_6H_4) 37.3 [d, $OP(NMe_2)_3$, J_{PC} = 5] 22.3 (s, *p*-$C_6H_4\mathit{Me}$)	25 [s, $OP(NMe_2)_3$] −144 (spt, PF_6)
8 $[Bi(mes)_2\{OP(NMe_2)_3\}_2][PF_6]$	7.26 (s, 4 H, *m*-H of C_6H_2) 2.44 (s, 12 H, $C_6H_2\mathit{Me}$-*o*) 2.41 [d, 36 H, $OP(NMe_2)_3$, J_{PH} = 10] 2.22 (s, 6 H, $C_6H_2\mathit{Me}$-*p*)	196.0 (s, *ipso*-C of C_6H_2) 139.6 (s, *o*-C of C_6H_2) 132.4 (s, *m*-C of C_6H_2) 127.0 (s, *p*-C of C_6H_2) 37.1 [s, $OP(NMe_2)_3$] 26.4 ($C_6H_2\mathit{Me}$-*o*) 21.8 ($C_6H_2\mathit{Me}$-*p*)	25 [s, $OP(NMe_2)_3$] −144 (spt, PF_6)
9 $[Bi(mes)_2(OPPh_3)_2][PF_6]$	7.60 and 7.22 (m, 34 H, *m*-H of C_6H_2, $OPPh_3$) 2.28 (s, 6 H, $C_6H_2\mathit{Me}$-*p*) 2.24 (s, 12 H, $C_6H_2\mathit{Me}$-*o*)		38 (s, $OPPh_3$) −144 (spt, PF_6)
11 $[BiPh\{OP(NMe_2)_3\}_4][PF_6]_2$	8.96 (d, 2 H, *o*-H of Ph, $J_{HH} \approx 8$) 8.10 (t, 2 H, *m*-H of Ph, $J_{HH} \approx 8$) 7.46 (t, 1 H, *p*-H of Ph, $J_{HH} \approx 8$) 2.45 [d, 72 H, $OP(NMe_2)_3$, J_{PH} = 10]		

[a] All spectra obtained in CD_2Cl_2, *J* in Hz. [b] Referenced to $SiMe_4$, positive values to high frequency. [c] Referenced to H_3PO_4. [d] ^{11}B ($BF_3{\cdot}Et_2O$): δ − 2.7.

Additional diaryl complexes $[Bi(C_6H_4Me\text{-}4)_2\{OP(NMe_2)_3\}_2][PF_6]$ **7**, $[Bi(mes)_2\{OP(NMe_2)_3\}_2][PF_6]$ **8** (mes = $2,4,6\text{-}Me_3C_6H_2$) and $[Bi(mes)_2(OPPh_3)_2][PF_6]$ **9** were prepared similarly from either $Bi(C_6H_4Me\text{-}4)_2Br$ or $Bi(mes)_2Br$, spectroscopic data for which (Table 1) were consistent with the expected formulae. The structure of **8** was confirmed by X-ray crystallography, the results of which are shown in Fig. 3 with selected bond distances and angles given in Table 6 and atomic positional parameters in Table 7. The cation in **8** is similar to those of **1** and **5**, the two mesityl groups occupying the equatorial positions [average Bi–C 2.236 Å, C(411)–Bi–C(311) 108.3(5)°] and the $OP(NMe_2)_3$ ligands being *trans* in the axial sites [average Bi–O 2.382 Å, O(1)–Bi–O(2) 177.2(4)°]; the C–Bi–C angle is slightly larger here than in either **1** or **5** due to the more bulky nature of the mesityl groups. For **9** a unit cell was obtained which had the correct volume for the expected formula but the poor quality of the crystal prevented adequate data from being collected and no solution was obtainable.

The structures of the cations of complexes **1**, **3** and **5** may be compared with those of the anionic species $[BiPh_2Br_2]^-$ [15] and $[BiPh_2I_2]^-$ [16] which are also four-co-ordinate, ten-electron bismuth(III) complexes having a similar geometry with equatorial phenyls and axial sites occupied by halides. As mentioned in the Introduction, this disphenoidal geometry is that expected for four-co-ordinate, ten-electron species and the axial site preference for the more electronegative groups or ligands is also in line with previous observations; valence-shell electron-pair repulsion (VSEPR)[18] offers a straightforward rationale for this geometry and site preference. Distortions from this geometry are sometimes observed, however, such as those seen in the complexes $[BiX_2(ML_n)_2]^-$ [X = Cl or Br; ML_n = $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$][19] or $[Bi\{Co(CO)_4\}_4]^-$ (ref. 20) which have distorted-tetrahedral and regular tetrahedral geometries respectively. Possible reasons for these distortions have been addressed in refs. 19 and 20.

It is also worth noting, from a structural point of view, the indium complex $[InPr^i_2(thf)_2][BF_4]$ **10**[21] for which the cation has a similar disphenoidal geometry around the indium centre but in which the positions of the organo groups and the two electron-donor thf ligands are reversed, *i.e.* the thf ligands reside in the equatorial positions and the Pr^i groups in axial sites. The indium centre has eight valence electrons and is essentially a linear $InPr^i_2{}^+$ cation to which two thf ligands are co-ordinated. The distortion from the expected tetrahedral geometry is probably a result both of the apparent preference of $InR_2{}^+$ cations for a linear geometry and also the fact that there are close contacts between the indium centre and the $BF_4{}^-$ fluorines which effectively increase the co-ordination number around the indium. Similar interionic contacts are observed in the complex $[In(mes)_2][BF_4]$,[22] but here there are no other co-ordinated ligands and the structure consists of infinite chains of cations and anions in which the indium centres are co-ordinated

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Bi–O(1)	2.388(3)	Bi–O(2)	2.389(3)
Bi–C(11)	2.223(4)	Bi–C(21)	2.223(5)
Bi ··· F(3)	3.533(5)		
O(1)–Bi–O(2)	173.2(2)	O(1)–Bi–C(11)	85.1(2)
O(1)–Bi–C(21)	89.4(2)	O(2)–Bi–C(11)	88.1(2)
O(2)–Bi–C(21)	90.4(2)	C(11)–Bi–C(21)	95.8(3)
Bi–O(1)–P(1)	143.8(2)	Bi–O(2)–P(2)	162.2(3)
F(3) ··· Bi–C(11)	148.1(2)	F(3) ··· Bi–C(21)	113.0(3)

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

Bi–O(1)	2.317(5)	Bi–O(2)	2.355(5)
Bi–C(311)	2.229(4)	Bi–C(411)	2.192(4)
O(1)–Bi–O(2)	172.4(2)	O(1)–Bi–C(311)	89.7(2)
O(1)–Bi–C(411)	84.4(2)	O(2)–Bi–C(311)	88.7(2)
O(2)–Bi–C(411)	88.3(2)	C(311)–Bi–C(411)	94.3(2)
Bi–O(1)–P(1)	138.8(3)	Bi–O(2)–P(2)	165.2(4)

Table 3 Atomic positional parameters for complex **3**

Atom	*x*	*y*	*z*
Bi	2374.8(2)	3250.8(1)	2777.8(1)
P(1)	2135(1)	3448.7(9)	5111.5(7)
P(2)	2008(1)	2786(1)	271.0(7)
O(1)	2395(3)	3817(3)	4277(2)
O(2)	2353(3)	2887(3)	1249(2)
B	4512(6)	714(5)	2756(4)
F(1)	4854(4)	781(4)	1975(3)
F(2)	5464(3)	1228(3)	3443(2)
F(3)	3579(4)	1143(4)	2714(3)
F(4)	4041(4)	−295(3)	2814(4)
Cl(1)	9747(2)	2087(2)	7257(1)
Cl(2)	9399(3)	−38(2)	6613(2)
C(1)	8725(6)	887(7)	6720(5)
C(11)	2615(4)	4900(2)	2632(4)
C(12)	1804(5)	5181(4)	2009(2)
C(13)	2032(4)	6220(4)	1907(3)
C(14)	3069(4)	6979(2)	2429(3)
C(15)	3879(5)	6698(4)	3052(2)
C(16)	3652(3)	5658(4)	3154(4)
C(21)	334(4)	2749(6)	2477(3)
C(22)	−306(6)	3396(5)	2768(3)
C(23)	−1583(5)	3027(4)	2631(4)
C(24)	−2219(4)	2011(5)	2203(3)
C(25)	−1579(6)	1364(4)	1912(4)
C(26)	−303(5)	1733(4)	2049(5)
C(111)	556(3)	3195(4)	5157(3)
C(112)	170(5)	3908(4)	5647(2)
C(113)	−1078(5)	3724(2)	5622(4)
C(114)	−1939(3)	2828(4)	5107(3)
C(115)	−1553(5)	2115(4)	4617(3)
C(116)	−305(5)	2298(2)	4642(4)
C(121)	2565(4)	2309(4)	5269(4)
C(122)	3501(3)	2143(3)	4885(3)
C(123)	3959(3)	1328(3)	5068(3)
C(124)	3482(4)	679(3)	5634(4)
C(125)	2545(2)	844(2)	6017(2)
C(126)	2087(4)	1659(3)	5835(4)
C(131)	3018(6)	4439(4)	6030(2)
C(132)	3533(4)	5447(4)	5883(2)
C(133)	4198(3)	6239(2)	6590(3)
C(134)	4347(5)	6022(3)	7445(2)
C(135)	3832(3)	5014(3)	7592(2)
C(136)	3167(4)	4222(2)	6885(3)
C(211)	2273(4)	4028(3)	−72(4)
C(212)	3342(4)	4812(5)	374(4)
C(213)	3628(5)	5789(4)	120(2)
C(214)	2846(4)	5981(2)	−582(3)
C(215)	1777(4)	5197(5)	−1029(3)
C(216)	1491(6)	4221(4)	−774(2)
C(221)	434(4)	2042(4)	−176(2)
C(222)	107(3)	1034(4)	−642(4)
C(223)	−1129(5)	454(3)	−943(4)
C(224)	−2038(4)	884(4)	−778(2)
C(225)	−1711(4)	1892(3)	−313(4)
C(226)	−475(5)	2472(3)	−12(3)
C(231)	2956(4)	2176(3)	−225(4)
C(232)	3705(4)	1733(3)	299(2)
C(233)	4480(3)	1279(4)	−65(3)
C(234)	4506(4)	1268(3)	−952(4)
C(235)	3757(4)	1711(4)	−1475(2)
C(236)	2982(3)	2165(5)	−1112(4)

Table 5 Atomic positional parameters for complex **5**

Atom	x	y	z	Atom	x	y	z
Bi	4016(1)	2136(1)	1101(1)	C(122)	6886(6)	2736(14)	2526(5)
P(1)	5700(1)	3217(2)	1837(1)	C(131)	6348(5)	4154(11)	900(3)
P(2)	2099(1)	1691(3)	402(1)	C(132)	6458(6)	5945(11)	1710(4)
P(3)	−1026(1)	3187(3)	1363(1)	C(211)	1407(7)	424(17)	1267(5)
O(1)	5232(3)	2200(6)	1455(2)	C(212)	1022(7)	−557(17)	369(5)
O(2)	2795(3)	1704(8)	745(2)	C(221)	1851(8)	1808(14)	−740(4)
N(11)	5271(4)	4113(9)	2342(3)	C(222)	2775(6)	−114(16)	−363(4)
N(12)	6317(4)	2093(9)	2139(3)	C(231)	932(6)	3776(16)	429(5)
N(13)	6059(3)	4614(7)	1462(3)	C(232)	2158(6)	4799(14)	246(5)
N(21)	1522(4)	460(10)	671(3)	C(311)	3606(3)	1551(6)	1958(2)
N(22)	2280(4)	1203(11)	−240(3)	C(312)	2987(3)	2354(7)	2161(3)
N(23)	1720(4)	3444(10)	398(3)	C(313)	2747(3)	2074(9)	2706(3)
F(1)	−711(6)	4241(19)	956(7)	C(314)	3127(5)	993(10)	3049(2)
F(2)	−1571(5)	4497(12)	1533(4)	C(315)	3746(4)	190(8)	2846(2)
F(3)	−1341(7)	2098(16)	1781(6)	C(316)	3986(3)	469(7)	2300(3)
F(4)	−470(8)	3642(19)	1769(6)	C(411)	4278(3)	−334(5)	888(2)
F(5)	−530(8)	1895(15)	1203(5)	C(412)	4971(3)	−698(6)	664(2)
F(6)	−1614(12)	2846(17)	947(7)	C(413)	5136(3)	−2254(7)	515(2)
C(111)	4778(5)	5447(13)	2229(4)	C(414)	4609(4)	−3445(5)	590(2)
C(112)	5199(6)	3422(13)	2905(4)	C(415)	3916(4)	−3081(6)	814(3)
C(121)	6429(7)	501(13)	1989(4)	C(416)	3750(3)	−1525(7)	963(2)

Table 6 Selected bond lengths (Å) and angles (°) for complex **8**

Bi–O(1)	2.35(1)	Bi–O(2)	2.41(1)
Bi–C(311)	2.26(1)	Bi–C(411)	2.21(1)
O(1)–Bi–O(2)	177.2(4)	O(1)–Bi–C(311)	86.6(6)
O(1)–Bi–C(411)	90.7(9)	O(2)–Bi–C(311)	96.0(5)
O(2)–Bi–C(411)	87.4(6)	C(311)–Bi–C(411)	108.5(5)
Bi–O(1)–P(1)	138.0(2)	Bi–O(2)–P(2)	143.0(2)

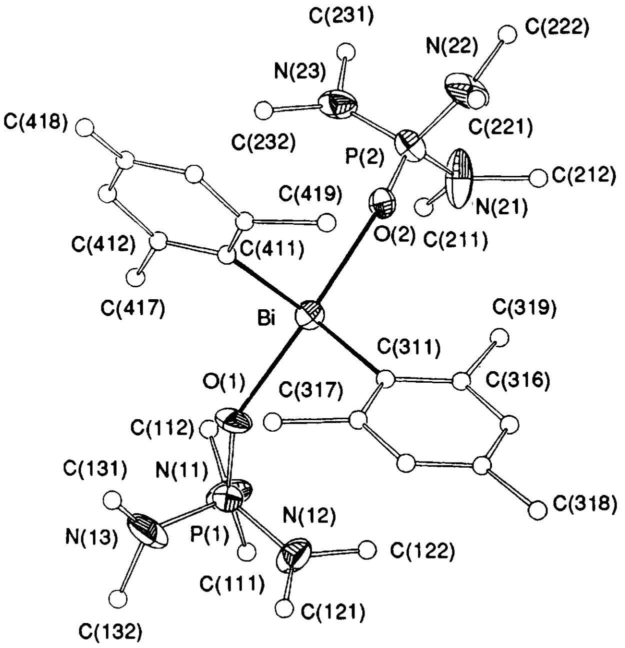
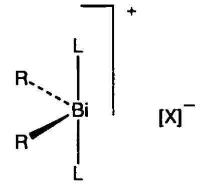
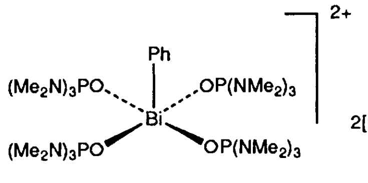


Fig. 3 View of the molecular structure of the cation in complex **8** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted



3 (R = Ph, L = $OPPh_3$, X = BF_4), **4** (R = Ph, L = py, X = BF_4), **5** [R = Ph, L = $OP(NMe_2)_3$, X = PF_6], **6** (R = Ph, L = py, X = PF_6), **7** [R = *p*-tolyl, L = $OP(NMe_2)_3$, X = PF_6], **8** [R = mesityl, L = $OP(NMe_2)_3$, X = PF_6], **9** (R = mesityl, L = $OPPh_3$, X = PF_6)



11

by two BF_4^- anions resulting in a distorted-octahedral geometry.

Chemical shifts and coupling constants in the ^1H, ^{13}C and ^{31}P NMR spectra for the diaryl cations are collected in Table 1, and it is worth mentioning that the resonances due to the phenyl protons in the ^1H spectra, in particular, are characteristically deshielded with the *o*-, *m*- and *p*-protons typically observed at δ 8.2 (d), 7.7 (t) and 7.4 (t) respectively. In some spectra, however, additional signals comprising a doublet at δ ≈9 and, in some cases, when not hidden by signals due to $OPPh_3$ ligands, a pair of triplets at δ ≈8 and ≈7.5 were observed. The deshielded nature of these signals indicated the possible presence of either a monophenyl dication of the form $[BiPhL_x]^{2+}$ or perhaps a monophenylbismuth bromide monocation of the form $[BiPh(Br)L_x]^+$, resulting from two or one halides respectively being abstracted from a phenylbismuth dibromide precursor, $BiPhBr_2$, the presence of which would not be surprising in view of the facile redistribution reactions characteristic of arylbismuth halides in solution. In an attempt to isolate a monocation of the form $[BiPh(Br)L_x]^+$, $BiPhBr_2$ was treated with 1 equivalent of $TlPF_6$ in the presence of an excess of $OP(NMe_2)_3$ in thf solution. After work-up and crystallisation from thf–hexane mixtures, however, colourless crystals of the complex $[BiPh\{OP(NMe_2)_3\}_4][PF_6]_2$ **11**, containing an arylbismuth dication, were isolated, the structure of which was established by X-ray crystallography (Fig. 4); selected bond lengths and angles are given in Table 8 and atomic positional parameters in Table 9.

The structure of complex **11** was not particularly well determined due to problems with solvent loss from the crystal as described in the Experimental section. However, the essential structure is more than adequately elucidated from the data available and consists of $[BiPh\{OP(NMe_2)_3\}_4]^{2+}$ dications

Table 7 Atomic positional parameters for complex **8**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Bi	633(1)	0	1943(1)	C(211)	2000(30)	2092(22)	48(26)
P(1)	−1154(4)	651(3)	4301(4)	C(212)	1312(38)	1638(36)	−1781(32)
P(2)	2450(5)	458(4)	−404(4)	C(221)	2118(29)	−895(21)	−1814(28)
P(3)	−3691(8)	−2078(6)	6833(6)	C(222)	3258(38)	350(30)	−2424(37)
F(1)	−4922(16)	−2213(24)	6419(21)	C(231)	4680(27)	1293(20)	63(25)
F(2)	−3588(42)	−2998(18)	6771(33)	C(232)	4108(22)	164(16)	1367(17)
F(3)	−3125(23)	−1991(24)	5655(17)	C(311)	−1150(10)	−568(9)	1190(10)
F(4)	−4268(38)	−2240(29)	7895(24)	C(312)	−1750(13)	−1218(9)	1711(10)
F(5)	−2367(21)	−2076(41)	7277(28)	C(313)	−2891(14)	−1499(10)	1263(13)
F(6)	−4132(55)	−1162(33)	6784(44)	C(314)	−3432(11)	−1130(11)	292(13)
O(1)	−278(13)	23(29)	3646(11)	C(315)	−2832(13)	−480(11)	−230(11)
O(2)	1664(10)	−27(19)	249(9)	C(316)	−1692(12)	−199(8)	219(11)
N(11)	−750(15)	1677(11)	4428(12)	C(411)	1855(10)	−1051(8)	2553(10)
N(12)	−2577(16)	600(10)	3719(14)	C(412)	2701(12)	−869(7)	3449(10)
N(21)	1900(17)	1433(12)	−718(15)	C(413)	3622(11)	−1452(9)	3768(10)
N(22)	2626(16)	−20(18)	−1587(13)	C(414)	3698(13)	−2215(9)	3191(13)
N(13)	−1141(18)	129(24)	5527(18)	C(415)	2852(14)	−2397(7)	2295(12)
N(23)	3730(16)	604(10)	377(15)	C(416)	1931(11)	−1815(9)	1976(10)
C(111)	−1509(27)	2352(20)	4642(24)	C(317)	−1206(28)	−1634(19)	2839(21)
C(112)	472(24)	1952(19)	4355(23)	C(318)	−4668(33)	−1446(28)	−262(32)
C(121)	−3478(22)	30(26)	4085(20)	C(319)	−1119(29)	487(19)	−462(25)
C(122)	−2922(26)	1118(19)	2759(21)	C(417)	2670(16)	38(16)	4137(14)
C(131)	−637(32)	−575(26)	5712(32)	C(418)	4187(57)	−3201(22)	3398(62)
C(132)	−1761(36)	528(27)	6424(32)	C(419)	1130(26)	−2066(22)	805(20)

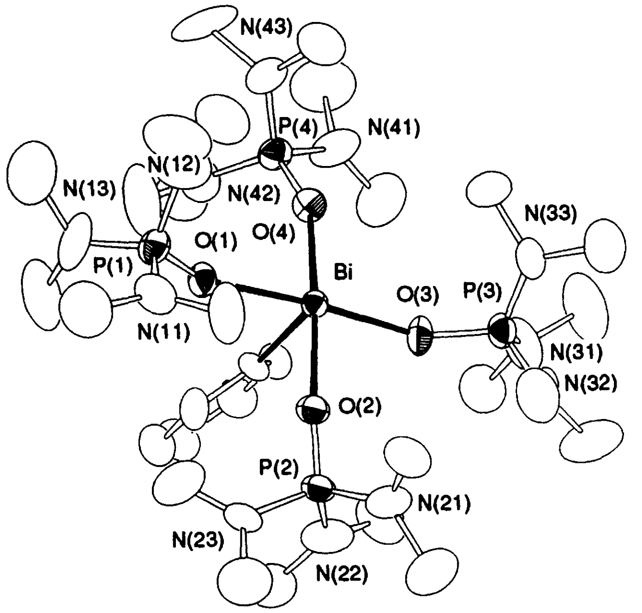


Fig. 4 View of the molecular structure of the dication of complex **11** showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted

Table 8 Selected bond lengths (Å) and angles (°) for complex **11**

Bi–C(111)	2.27(1)	Bi–O(1)	2.35(1)
Bi–O(2)	2.32(1)	Bi–O(3)	2.32(1)
Bi–O(4)	2.36(1)		
C(111)–Bi–O(1)	87.4(5)	C(111)–Bi–O(2)	85.3(5)
C(111)–Bi–O(3)	86.8(5)	C(111)–Bi–O(4)	87.2(5)
O(1)–Bi–O(2)	85.4(5)	O(1)–Bi–O(3)	174.2(5)
O(1)–Bi–O(4)	94.8(5)	O(2)–Bi–O(3)	93.3(5)
O(2)–Bi–O(4)	172.5(5)	O(3)–Bi–O(4)	85.8(5)
Bi–O(1)–P(1)	154.6(9)	Bi–O(2)–P(2)	155.9(9)
Bi–O(3)–P(3)	148.4(9)	Bi–O(4)–P(4)	156.7(9)

and two $[PF_6]^-$ anions. The bismuth centre adopts a square-based pyramidal co-ordination geometry with the phenyl group in the apical position, the Bi–C distance for which is comparable to those observed in **1**, **3**, **5** and **8** [Bi–C(111) 2.27(1) Å]. The four $OP(NMe_2)_3$ ligands lie in the basal plane, with Bi–O distances ranging from 2.32(1) to 2.36(1) Å, the bismuth atom lying 0.135(1) Å below the O_4 mean plane (with respect to the phenyl group). The observed geometry is that expected from VSEPR for an AB_5E system, the lone pair being formally stereochemically active and occupying the site *trans* to the phenyl group. There is, however, a close contact between the bismuth centre and one of the fluorines from one of the PF_6 anions [Bi···F(63) 3.28(3) Å] approximately *trans* to the phenyl [C(111)–Bi–F(63) 162°], which, if considered as part of the bismuth co-ordination sphere, results in a distorted-octahedral geometry.

A ^1H NMR spectrum of complex **11** (Table 1) revealed phenyl resonances close to the chemical shifts mentioned above at around δ 9, 8 and 7.5 indicating that the additional species sometimes observed in spectra of the $[BiPh_2L_2]^+$ monocations are therefore likely to have been dications analogous to that of **11**. Indeed, in the spectrum of **11**, resonances due to **5** were also seen together with aryl resonances due to a third unidentified species suggesting that the solution chemistry of these cationic compounds is complex and prone (not unexpectedly) to redistribution reactions.

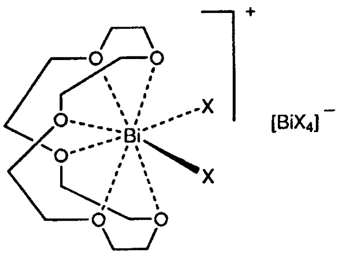
An example of a related bismuth dication is found in the structure of the compound $[BiCl(MeCN)_2(18\text{-crown-}6)][SbCl_6]_2$ (synthesised from $BiCl_3$, 18-crown-6 and $SbCl_5$ in MeCN) which contains a $BiCl^{2+}$ dication in which the bismuth centre is co-ordinated to two MeCN ligands and the six oxygens of an 18-crown-6 ring.[6] The geometry may be loosely described as having the six 18-crown-6 oxygens in a basal plane with the chlorine in an apical site and the nitrogen atoms of the MeCN ligands weakly co-ordinated on the opposite side of the crown ether ring.

An attempt was made to isolate other examples of arylbismuth dications, specifically ones containing a mesityl group derived from $Bi(mes)Br_2$. Reactions between $Bi(mes)Br_2$ and $TlPF_6$ did not afford any isolable products, but $Bi(mes)Br_2$ and 2 equivalents of $SbCl_5$ in the presence of 18-crown-6 afforded, after work-up, a small number of yellow crystals, one of which was examined by X-ray crystallography. The results of this study showed the compound to be $[BiX_2(18\text{-crown-}6)][BiX_4]$ **12** where X was a mixture of chlorine and bromine with the approximate ratio $Br_{3.5}Cl_{2.5}$ presumably resulting from traces of $BiBr_3$ in the reaction mixture. Crystals of **12** are isomorphous with the pure chlorine and bromine com-

Table 9 Atomic positional parameters for complex **11**

Atom	*x*	*y*	*z*
Bi	7 564(1)	8 523(1)	1 492(1)
P(1)	9 850(4)	9 010(3)	2 383(3)
P(2)	6 076(4)	9 689(3)	2 314(3)
P(3)	5 332(4)	7 681(3)	963(3)
P(4)	9 030(4)	7 795(3)	171(3)
P(5)	7 236(6)	8 693(4)	7 423(5)
P(6)	7 276(7)	7 264(4)	3 396(5)
N(11)	9 548(19)	9 295(10)	3 082(11)
N(12)	10 279(23)	8 327(15)	2 503(14)
N(13)	10 643(17)	9 420(16)	2 087(14)
N(21)	5 327(17)	9 381(11)	2 796(12)
N(22)	5 455(19)	9 969(13)	1 688(12)
N(23)	6 646(17)	10 285(9)	2 670(13)
N(31)	4 877(20)	7 674(11)	250(13)
N(32)	4 435(19)	7 848(13)	1 428(16)
N(33)	5 714(17)	7 042(10)	1 218(15)
N(41)	8 374(16)	7 446(12)	−437(10)
N(42)	9 531(20)	8 383(12)	−128(12)
N(43)	9 855(15)	7 328(11)	438(11)
O(1)	8 995(9)	8 971(7)	1 929(7)
O(2)	6 781(10)	9 207(6)	2 160(7)
O(3)	6 132(10)	8 167(7)	994(7)
O(4)	8 341(10)	7 927(6)	707(6)
F(51)	7 355(31)	8 314(20)	6 767(22)
F(52)	7 709(34)	9 176(19)	7 010(16)
F(53)	8 258(22)	8 606(19)	7 733(22)
F(54)	7 097(24)	9 151(15)	7 970(18)
F(55)	6 905(36)	8 180(18)	7 772(22)
F(56)	6 211(17)	8 753(17)	7 142(19)
F(61)	6 158(17)	7 389(15)	3 457(15)
F(62)	7 439(25)	7 797(15)	3 890(15)
F(63)	7 218(27)	7 712(14)	2 819(12)
F(64)	8 310(21)	7 146(18)	3 363(18)
F(65)	6 957(34)	6 781(16)	2 971(2)
F(66)	7 319(25)	6 876(13)	4 001(14)
C(11)	8 719(26)	9 019(18)	3 399(16)
C(12)	10 178(30)	9 771(19)	3 402(19)
C(13)	10 696(34)	8 162(20)	3 194(20)
C(14)	10 210(31)	7 812(18)	2 071(21)
C(15)	11 670(35)	9 212(24)	2 062(28)
C(16)	10 455(34)	9 962(20)	1 745(24)
C(21)	5 622(24)	8 969(13)	3 343(14)
C(22)	4 286(26)	9 600(21)	2 839(24)
C(23)	5 555(27)	10 612(18)	1 461(21)
C(24)	4 980(27)	9 575(15)	1 259(19)
C(25)	7 609(24)	10 414(19)	2 709(17)
C(26)	6 141(29)	10 687(19)	3 065(20)
C(31)	4 819(24)	8 196(15)	−195(17)
C(32)	4 495(36)	7 091(20)	−51(26)
C(33)	4 617(26)	7 875(16)	2 153(15)
C(34)	3 475(28)	7 906(22)	1 034(26)
C(35)	5 130(28)	6 542(17)	1 590(22)
C(36)	6 717(19)	6 825(14)	1 072(14)
C(41)	7 428(24)	7 532(20)	−578(19)
C(42)	8 952(32)	7 118(21)	−959(20)
C(43)	9 442(30)	8 603(17)	−815(18)
C(44)	10 004(34)	8 830(20)	314(20)
C(45)	9 660(26)	6 806(15)	876(17)
C(46)	10 908(23)	7 328(20)	235(19)
C(111)	7 502(11)	9 290(6)	741(6)
C(112)	7 768(12)	9 887(7)	912(7)
C(113)	7 749(13)	10 345(5)	437(10)
C(114)	7 464(14)	10 207(7)	−209(9)
C(115)	7 198(13)	9 611(9)	−380(6)
C(116)	7 217(12)	9 152(6)	95(7)

pounds [$BiCl_2$(18-crown-6)][$BiCl_4$][4] and [$BiBr_2$(18-crown-6)][$BiBr_4$][5] which have been previously described, the essential structure of which comprises *cis*-BiX_2 cations co-ordinated by the six oxygens of the 18-crown-6 ligand and polymeric [BiX_4]$^-$ anions. No further discussion of the structure of **12** is warranted here but crystallographic details are described in the Experimental section and presented in Table 12.



12

Compound **12** is an example of a *cis*-dihalogenobismuth cation, examples of which were mentioned in the Introduction. In an attempt to make other examples by more rational routes the reaction was carried out between BiI_3 and 1 equivalent of $TlPF_6$ in thf in the presence of $OP(NMe_2)_3$. This resulted in a yellow crystalline complex, analytical data for which were consistent with the formula [BiI_2{$OP(NMe_2)_3$}$_4$][PF_6] **13**. An attempted crystal structure determination was unsuccessful, however, due to crystal decay and resulting poor-quality data, but the unit-cell volume was consistent with the above formula. The structure is presumed to be similar to that of the complex [BiI_2{$OP(NMe_2)_3$}$_4$][I_3][9] which comprises an octahedral bismuth cation with *trans* iodines and four coplanar $OP(NMe_2)_3$ ligands.

An example of another *trans*-dihalogenobismuth cation was obtained from the reaction between BiI_3 and $Ph_2P(O)CH_2(O)PPh_2$ (dppom) in thf. The anticipated product was a neutral adduct of BiI_3 and the phosphine oxide, but recrystallisation of the reaction mixture from pyridine afforded crystals of a compound characterised by X-ray crystallography as [$BiI_2(py)_3$(dppom)][$BiI_4(py)_2$]·py **14**. Selected bond lengths and angles are given in Table 10 and atomic positional parameters in Table 11. The cation in **14** shown in Fig. 5 comprises a seven-co-ordinate bismuth atom in a pentagonal-bipyramidal environment with the two iodines *trans* in the axial sites [Bi(1)–I(1) 3.009(2), Bi(1)–I(2) 3.084(3) Å, I(1)–Bi(1)–I(2) 177.66(7)°] and the five equatorial sites occupied by three pyridine ligands and the two oxygens of a chelating dppom ligand, these oxygens having a 1,2 disposition (as opposed to the alternative 1,3) as a result of the chelating nature of this ligand; the Bi–O distances average 2.41 Å and the Bi–N distances 2.61 Å. The regularity of the pentagonal-bipyramidal geometry is notable in that none of the bond angles deviates from idealised values by more than a few degrees and the equatorial atoms O(1), O(2), N(331), N(321) and N(311) are very nearly coplanar [maximum deviation from the mean plane 0.13(2) Å] indicating that the bismuth(III) lone pair has little stereochemical activity. Seven-co-ordinate complexes of this type are not well known for bismuth, but we note that the pentagonal-bipyramidal geometry is that expected for a seven-co-ordinate p-block element complex (in preference to alternative capped-octahedral or capped trigonal-prismatic geometries) as discussed recently by Christie *et al.*[23]

The [$BiI_4(py)_2$]$^-$ anion in **14** shown in Fig. 6 is an example of a [BiX_4L_2]$^-$ anion, previous examples of which are the phosphine complexes [$BiI_4(PMe_2Ph)_2$]$^-$ **15** and [SbI_4(dmpe)]$^-$ **16** [dmpe = 1,2-bis(dimethylphosphino)ethane],[24] in all three of which the co-ordination geometry is approximately octahedral and the ligands are *cis*. In **16** the octahedral co-ordination is significantly distorted such that the P–Sb–P angle is much less than 90° whilst the angle between the

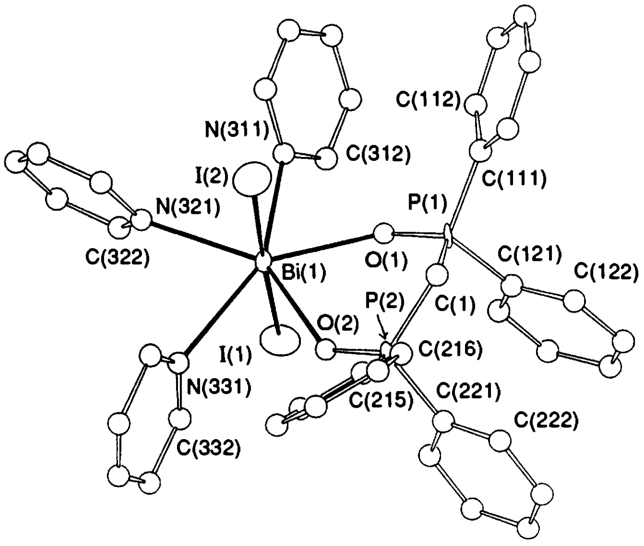


Fig. 5 View of the molecular structure of the $[BiI_2(py)_3(dppom)]^+$ cation in **14** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted

Table 10 Selected bond lengths (Å) and angles (°) for complex **14**

Cation			
Bi(1)–I(1)	3.009(2)	Bi(1)–I(2)	3.084(3)
Bi(1)–O(1)	2.39(2)	Bi(1)–O(2)	2.42(2)
Bi(1)–N(311)	2.56(2)	Bi(1)–N(321)	2.57(2)
Bi(1)–N(331)	2.70(2)		
I(1)–Bi(1)–I(2)	177.66(7)	I(1)–Bi(1)–O(1)	86.7(5)
I(1)–Bi(1)–O(2)	91.7(5)	I(1)–Bi(1)–N(311)	85.8(4)
I(1)–Bi(1)–N(321)	92.5(5)	I(1)–Bi(1)–N(331)	88.5(5)
I(2)–Bi(1)–O(1)	91.0(5)	I(2)–Bi(1)–O(2)	87.8(5)
I(2)–Bi(1)–N(311)	93.2(4)	I(2)–Bi(1)–N(321)	89.3(5)
I(2)–Bi(1)–N(331)	93.4(5)	O(1)–Bi(1)–O(2)	74.0(7)
O(1)–Bi(1)–N(311)	67.4(7)	N(311)–Bi(1)–N(321)	75.1(7)
N(321)–Bi(1)–N(331)	76.0(7)	N(331)–Bi(1)–O(2)	67.9(7)
Anion			
Bi(2)–I(3)	2.951(3)	Bi(2)–I(4)	3.009(3)
Bi(2)–I(5)	3.087(3)	Bi(2)–I(6)	2.955(3)
Bi(2)–N(411)	2.70(2)	Bi(2)–N(421)	2.75(3)
N(421)–Bi(2)–N(411)	79.1(8)	N(421)–Bi(2)–I(4)	90.1(6)
N(421)–Bi(2)–I(5)	85.8(6)	N(421)–Bi(2)–I(6)	94.4(6)
N(421)–Bi(2)–I(3)	168.1(6)	N(411)–Bi(2)–I(3)	89.2(5)
N(411)–Bi(2)–I(4)	88.4(5)	N(411)–Bi(2)–I(5)	88.5(5)
N(411)–Bi(2)–I(6)	173.4(5)	I(3)–Bi(2)–I(4)	91.43(9)
I(3)–Bi(2)–I(5)	92.09(8)	I(3)–Bi(2)–I(6)	97.32(9)
I(4)–Bi(2)–I(5)	175.32(9)	I(4)–Bi(2)–I(6)	92.24(9)
I(5)–Bi(2)–I(6)	90.4(1)		

two *trans* iodines is much greater than 90° [78.59(4) and 123.92(2)° respectively]. In **15** an opposite, although less marked, distortion is observed wherein the P–Bi–P angle is greater than 90° and the related *trans* I–Bi–I angle is (marginally) less than 90° [112.33(6) and 89.86(3)°]. In the anion in **14** a distortion is observed similar to that seen in **16** in that the N(411)–Bi(2)–N(421) angle is 79.1(8)° whilst the related *trans* angle I(3)–Bi(2)–I(6) is 97.32(9)°, the largest of all the *cis* angles in this complex. A discussion of these types of distortions and consequent lone-pair stereochemical activity is given in ref. 24.

As a final point we note that some structures rather similar to that of complex **14** have recently been described in lanthanide chemistry. Thus, for example, crystallisation of $TbCl_3$ from a thf–caprolactone mixture affords crystals of the ionic complex $[TbCl_2(thf)_5][TbCl_4(thf)_2]$[25] and crystallisation of YCl_3 from a thf solution containing *N*-methylimidazole (mim) affords the complex $[YCl_2(mim)_5][YCl_4(mim)_2]$.[26] In both cases the cations are similar to that of **14** in having *trans* axial halides and equatorial ligands, but the anions differ in having more regular octahedral geometries (presumably because the lanthanide element has no lone pair) and ligands which are *trans* rather than *cis*.

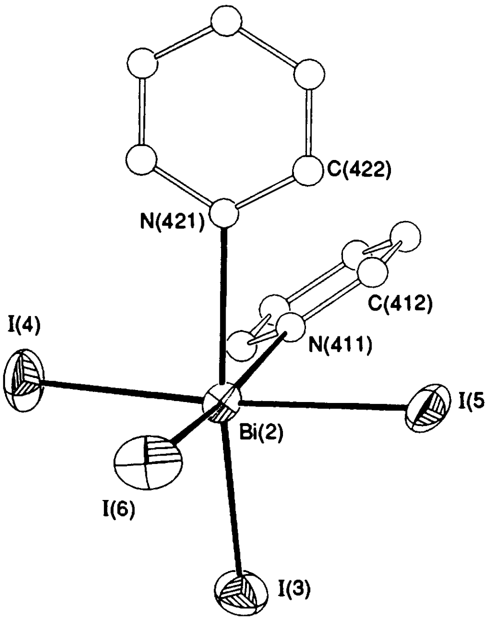


Fig. 6 View of the molecular structure of the $[BiI_4(py)_2]^-$ anion in complex **14** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted

In conclusion, we have shown that ligand-stabilised or complexed diarylbismuth cations are readily synthesised from arylbismuth halide precursors and that these compounds can be isolated as crystalline materials; arylbismuth dications are also available using similar synthetic methods although in lower yields, the chemistry being complicated by facile redistribution reactions.

Experimental

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 for Et_2O and thf, CaH_2 for CH_2Cl_2 and pyridine and sodium for hexanes). The compounds $BiBr_3$ (99%+), BiI_3 (99%+), $BiPh_3$, $OP(NMe_2)_3$, $OPPh_3$, dmpu and $TlPF_6$ were procured commercially and used without further purification; $BiPh_2Br$,[15,27] $Bi(C_6H_4Me\text{-}4)_2Br$,[28] $Bi(mes)_2Br$[28] and $Bi(mes)Br_2$[28] were prepared as described in the literature. The diphosphine dioxide dppom was prepared by treating dppm with a 3% solution of H_2O_2 in acetone. Microanalytical data were obtained at The University of Newcastle. Proton and ^{13}C NMR spectra were recorded on Bruker WP200 and WM500 spectrometers and ^{11}B and ^{19}F spectra on a JEOL FX90Q spectrometer.

Preparations

$[BiPh_2(OPPh_3)_2][BF_4]$ 3. The compound $BiPh_2Br$ (0.112 g, 0.253 mmol) was dissolved in thf (5 cm^3) which gave a pale yellow solution. A sample of $OPPh_3$ (0.141 g, 0.506 mmol) was then added as a solution in thf (5 cm^3) which resulted in a colourless reaction solution. A solution of $AgBF_4$ (0.049 g, 0.253 mmol) in thf (6 cm^3) was then added which led to the

Table 11 Atomic positional parameters for complex **14**

Atom	*x*	*y*	*z*
Bi(1)	−4 630(1)	−3 050(1)	8 041(1)
Bi(2)	695(1)	2 236(1)	6 911(1)
I(1)	−4 593(2)	−5 108(2)	8 993(1)
I(2)	−4 561(2)	−947(2)	7 048(1)
I(3)	−1 374(2)	1 646(2)	6 610(1)
I(4)	856(3)	4 186(2)	5 841(1)
I(5)	743(2)	215(2)	7 970(2)
I(6)	−437(2)	3 333(2)	7 978(1)
P(1)	−1 624(6)	−2 484(6)	7 745(4)
P(2)	−3 144(6)	−1 406(6)	8 756(4)
O(1)	−2 606(17)	−3 166(15)	7 788(10)
O(2)	−4 055(18)	−2 177(16)	8 792(11)
C(1)	−2 031(24)	−1 264(21)	8 001(14)
C(111)	−781(17)	−2 209(15)	6 910(8)
C(112)	−632(17)	−2 982(12)	6 549(10)
C(113)	−12(19)	−2 796(15)	5 886(10)
C(114)	460(19)	−1 836(17)	5 584(8)
C(115)	311(20)	−1 062(14)	5 945(11)
C(116)	−309(20)	−1 249(14)	6 608(11)
C(121)	−788(17)	−3 187(15)	8 294(11)
C(122)	115(18)	−2 718(12)	8 395(11)
C(123)	752(16)	−3 258(16)	8 832(12)
C(124)	486(19)	−4 267(16)	9 167(11)
C(125)	−417(20)	−4 736(13)	9 066(12)
C(126)	−1 054(17)	−4 196(15)	8 629(12)
C(211)	−3 680(16)	−132(12)	8 813(11)
C(212)	−4 814(16)	−46(14)	9 140(12)
C(213)	−5 298(14)	918(17)	9 202(13)
C(214)	−4 649(18)	1 796(13)	8 938(13)
C(215)	−3 516(17)	1 710(12)	8 611(12)
C(216)	−3 031(13)	746(15)	8 549(11)
C(221)	−2 506(19)	−1 870(16)	9 443(10)
C(222)	−1 727(21)	−1 284(15)	9 575(12)
C(223)	−1 270(21)	−1 646(20)	10 129(14)
C(224)	−1 592(24)	−2 594(21)	10 552(12)
C(225)	−2 370(24)	−3 180(16)	10 420(12)
C(226)	−2 828(19)	−2 818(15)	9 866(12)
N(311)	−3 805(16)	−4 032(14)	7 109(9)
C(312)	−3 115(17)	−4 897(14)	7 244(8)
C(313)	−2 473(18)	−5 322(15)	6 722(11)
C(314)	−2 522(21)	−4 883(19)	6 064(9)
C(315)	−3 213(24)	−4 018(20)	5 929(8)
C(316)	−3 855(20)	−3 592(15)	6 452(11)
N(321)	−6 359(18)	−3 515(17)	7 680(12)
C(322)	−6 691(23)	−4 536(16)	7 858(13)
C(323)	−7 541(24)	−4 832(15)	7 609(15)
C(324)	−8 061(22)	−4 105(21)	7 182(15)
C(325)	−7 730(23)	−3 084(19)	7 005(14)
C(326)	−6 879(21)	−2 789(14)	7 254(13)
N(331)	−6 424(16)	−2 480(16)	8 944(9)
C(332)	−6 603(19)	−3 069(14)	9 526(11)
C(333)	−7 388(22)	−2 660(19)	10 105(9)
C(334)	−7 897(19)	−1 769(19)	9 947(11)
C(335)	−7 689(21)	−1 213(15)	9 392(13)
C(336)	−6 876(20)	−1 649(16)	8 789(9)
N(411)	1 956(18)	1 260(16)	5 973(10)
C(412)	2 706(21)	452(18)	6 128(10)
C(413)	3 325(20)	−35(17)	5 629(13)
C(414)	3 194(21)	287(19)	4 976(11)
C(415)	2 444(23)	1 096(20)	4 822(9)
C(416)	1 825(20)	1 582(16)	5 320(11)
N(421)	2 846(22)	2 517(22)	7 024(15)
C(422)	3 392(31)	1 751(21)	7 412(18)
C(423)	4 490(32)	1 895(28)	7 450(21)
C(424)	5 041(24)	2 804(32)	7 101(21)
C(425)	4 494(27)	3 569(24)	6 714(19)
C(426)	3 397(27)	3 425(20)	6 675(16)
N(511)	3 004(41)	−2 946(51)	4 764(34)
C(516)	3 639(54)	−2 096(43)	4 388(29)
C(515)	4 729(50)	−1 998(44)	4 455(32)
C(514)	5 186(49)	−2 750(64)	4 899(42)
C(513)	4 551(74)	−3 601(57)	5 276(41)
C(512)	3 461(67)	−3 698(44)	5 208(35)

immediate formation of a pale yellow precipitate that turned dark grey after a few minutes. The mixture was allowed to stir for 30 min and then filtered through Celite. The colourless filtrate was reduced in volume by vacuum to about 5 cm^3 and hexanes (20 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −22 °C resulted in a white crystalline solid. This was redissolved in CH_2Cl_2 (5 cm^3) and hexanes (20 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −22 °C afforded colourless crystals of complex **3** (0.133 g, 52% based on bismuth) one of which was used for X-ray crystallography (Found: C, 57.40; H, 3.80. $C_{48}H_{40}BBiF_4O_2P_2$ requires C, 57.30; H, 4.00%). Although the crystal structure of **3** shows that a molecule of CH_2Cl_2 is present, this is largely lost on vacuum pumping of the solid so that the analytical results are calculated for the unsolvated solid.

[BiPh$_2$(py)$_2$][BF$_4$] 4. A sample of dmpu (0.1 cm^3, 0.826 mmol) was added dropwise to a stirred solution of $BiPh_2Br$ (0.183 g, 0.413 mmol) in thf (5 cm^3) at room temperature which resulted in a colourless reaction solution. A solution of $AgBF_4$ (0.081 g, 0.413 mmol) in thf (6 cm^3) was then added which led to the immediate formation of a pale yellow precipitate that turned dark grey after a few minutes. The mixture was allowed to stir for 30 min and was then filtered through Celite resulting in a slightly cloudy filtrate which was reduced in volume by vacuum to about 5 cm^3. Hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at −22 °C resulted in a white semicrystalline solid. This was redissolved in pyridine (5 cm^3) and Et_2O (20 cm^3) was added as an overlayer. Solvent diffusion over a period of days at −22 °C afforded colourless crystals of complex **4** (0.08 g, 30%) none of which was of X-ray quality (Found: C, 42.50; H, 3.05; N, 4.35. $C_{22}H_{20}BBiF_4N_2$ requires C, 43.45; H, 3.30; N, 4.60%).

[BiPh$_2${OP(NMe$_2$)$_3$}$_2$][PF$_6$] 5. A sample of $OP(NMe_2)_3$ (0.1 cm^3, 0.575 mmol) was added dropwise to a stirred solution of $BiPh_2Br$ (0.127 g, 0.287 mmol) in thf (5 cm^3) at room temperature which resulted in a colourless reaction solution. A solution of $TlPF_6$ (0.100 g, 0.287 mmol) in thf (6 cm^3) was then added which led to the immediate formation of a pale yellow precipitate. The mixture was stirred for 30 min and then filtered through Celite resulting in a slightly cloudy filtrate which was reduced in volume by vacuum to about 5 cm^3. Hexanes (20 cm^3) were then added as an overlayer and solvent diffusion over a period of days at −22 °C resulted in a white crystalline solid. This was redissolved in CH_2Cl_2 (5 cm^3) and hexanes (9 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −22 °C afforded colourless crystals of complex **5** (0.188 g, 76% based on bismuth) one of which was used for X-ray crystallography (Found: C, 31.40; H, 5.35; N, 9.50. $C_{24}H_{46}BiF_6N_6O_2P_3$ requires C, 33.30; H, 5.35; N, 9.70%).

[BiPh$_2$(py)$_2$][PF$_6$] 6. Pyridine (0.1 cm^3, 0.575 mmol) was added dropwise to a stirred solution of $BiPh_2Br$ (0.127 g, 0.287 mmol) in thf (5 cm^3) at room temperature which resulted in a colourless solution. A solution of $TlPF_6$ (0.100 g, 0.287 mmol) in thf (6 cm^3) was then added which led to the immediate formation of a pale yellow precipitate. Work-up as for complex **5** afforded colourless crystals of **6** (0.188 g, 98% based on bismuth) (Found: C, 40.20; H, 3.55; N, 3.80. $C_{22}H_{20}BiF_6N_2P$ requires C, 39.65; H, 3.05; N, 4.20%).

[Bi(C_6H_4Me-4)$_2${OP(NMe_2)$_3$}$_2$][PF_6] 7. A sample of OP(NMe_2)$_3$ (0.06 cm^3, 0.344 mmol) was added dropwise to a stirred solution of Bi(C_6H_4Me-4)$_2$Br (0.081 g, 0.172 mmol) in thf (10 cm^3) at room temperature which resulted in a yellow solution. A solution of $TlPF_6$ (0.060 g, 0.172 mmol) in thf (6 cm^3) was then added which led to the immediate formation of a pale yellow precipitate. The mixture was allowed to stir for 1 h and then filtered through Celite resulting in a slightly cloudy filtrate which was reduced in volume by vacuum to about 5 cm^3. Hexanes (20 cm^3) were then added as an overlayer and solvent diffusion over a period of days at −30 °C resulted in colourless crystals of complex **7** (0.098 g, 64% based on bismuth) (Found: C, 33.55; H, 5.80; N, 9.90. $C_{26}H_{50}BiF_6N_6O_2P_3$ requires C, 34.90; H, 5.65; N, 9.40%).

The complex [Bi(mes)$_2${OP(NMe_2)$_3$}$_2$][PF_6] **8** was prepared similarly from Bi(mes)$_2$Br (0.127 g, 0.241 mmol) and $TlPF_6$ (0.095 g, 0.241 mmol) in thf (5 cm^3) as a white crystalline solid and some colourless crystals (0.137 g, 60% based on bismuth) one of which was used for X-ray crystallography (Found: C, 32.55; H, 5.75; N, 9.00. $C_{30}H_{58}BiF_6N_6O_2P_3$ requires C, 37.90; H, 6.15; N, 8.85%). The low observed carbon percentage suggests that the sample as isolated is not particularly pure.

[Bi(mes)$_2$($OPPh_3$)$_2$][PF_6] 9. The compound Bi(mes)$_2$Br (0.084 g, 0.159 mmol) was dissolved in thf (5 cm^3) giving a pale yellow solution. A sample of $OPPh_3$ (0.089 g, 0.319 mmol) was then added as a solution in thf (5 cm^3) which resulted in a colourless solution. A solution of $TlPF_6$ (0.056 g, 0.159 mmol) in thf (6 cm^3) was added which led to the immediate formation of a pale yellow precipitate. The mixture was stirred for 1 h and then filtered through Celite giving a colourless filtrate which was reduced in volume by vacuum to about 5 cm^3. Hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at room temperature resulted in pale yellow crystals of complex **9** (0.109 g, 60% based on bismuth) one of which was used for X-ray crystallography to obtain a unit cell (Found: C, 55.40; H, 5.00. $C_{54}H_{52}BiF_6O_2P_3$ requires C, 56.45; H, 4.55%).

[BiPh{OP(NMe_2)$_3$}$_4$][PF_6]$_2$ 11. A sample of OP(NMe_2)$_3$ (0.16 cm^3, 0.924 mmol) was added dropwise to a stirred solution of $BiPhBr_2$ (0.206 g, 0.464 mmol) in thf (5 cm^3) at room temperature which resulted in a colourless reaction solution. A solution of $TlPF_6$ (0.162 g, 0.464 mmol) in thf (6 cm^3) was then added which led to the immediate formation of a pale yellow precipitate. The mixture was stirred for 30 min and then filtered through Celite resulting in a slightly cloudy filtrate which was reduced in volume by vacuum to about 5 cm^3. Hexanes (20 cm^3) were added as an overlayer and solvent diffusion over a period of days at −30 °C resulted in colourless crystals of complex **11** (0.180 g, 30% based on bismuth) one of which was used for X-ray crystallography (Found: C, 28.10; H, 6.00; N, 12.35. $C_{30}H_{77}BiF_{12}N_{12}O_4P_6$ requires C, 27.85; H, 6.00; N, 13.00%).

[BiX_2(18-crown-6)][BiX_4] 12. A sample of $SbCl_5$ (0.05 cm^3, 0.365 mmol) was added dropwise to a stirred solution of Bi(mes)Br_2 (0.089 g, 0.182 mmol) and 18-crown-6 (0.048 g, 0.182 mmol) in MeCN (10 cm^3) at room temperature which resulted in a change from yellow to colourless. After stirring for 2 h the mixture was pumped to dryness in vacuum. The resulting yellow solid was redissolved in hot MeCN (5 cm^3) and Et_2O (20 cm^3) was added as an overlayer. Solvent diffusion over a period of days at room temperature resulted in yellow crystals of complex **12** (0.099 g) one of which was used for X-ray crystallography.

[BiI_2{OP(NMe_2)$_3$}$_4$][PF_6] 13. A solution of $TlPF_6$ (0.040 g, 0.112 mmol) in thf (5 cm^3) was added to a stirred orange solution of BiI_3 (0.067 g, 0.112 mmol) in thf (5 cm^3) at room temperature resulting in no apparent colour change or precipitate. The compound OP(NMe_2)$_3$ (0.1 cm^3, 0.575 mmol) was added dropwise resulting in a darker colour and the formation of a precipitate. The mixture was stirred for 45 min and then filtered through Celite resulting in a yellow solution which was reduced in volume by vacuum to about 8 cm^3 and hexanes (30 cm^3) were added as an overlayer. Solvent diffusion over a period of days at room temperature resulted in an intimate mixture of a yellow crystalline solid and yellow crystals of complex **13** (0.139 g, 40% based on bismuth) one of which was used for X-ray crystallography (Found: C, 22.40; H, 5.45; N, 12.30. $C_{24}H_{72}BiF_6I_2N_{12}O_4P_5$ requires C, 21.75; H, 5.50; N, 12.70%).

[BiI_2(py)$_3$(dppom)][BiI_4(py)$_2$]·py 14. The compound BiI_3 (0.190 g, 0.322 mmol) was dissolved in thf (6 cm^3), affording an orange solution, to which a solution of dppom (0.138 g, 0.322 mmol) in hot thf (6 cm^3) was added at room temperature resulting in a darkening of the orange colour. The mixture was stirred for 1 h during which time a precipitate formed which was then isolated. This solid was redissolved in pyridine (10 cm^3) and hexanes (25 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −22 °C afforded orange crystals of complex **14** (0.048 g, 12% based on bismuth) one of which was used for X-ray crystallography (Found: C, 31.25; H, 2.25; N, 3.85. $C_{50}H_{47}Bi_2I_6N_5O_2P_2 \cdot C_5H_5N$ requires C, 31.90; H, 2.55; N, 4.05%). The low observed nitrogen percentage is probably due to slight loss of pyridine of crystallisation.

All compounds are stable as solids in air for short periods but must be kept under an inert atmosphere for prolonged storage.

X-Ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for all structures are presented in Table 12. The following section deals with the structure of complex **3**; where different, details for the other structures are given in parentheses or separately noted. Data were collected using ω–2θ scans on an Enraf-Nonius Turbo-CAD4 diffractometer, running under CAD4-Express software, and with graphite-monochromated X-radiation (λ = 0.710 73 Å). Accurate unit-cell parameters were determined by refinement of setting angles of 25 optimum high-angle reflections which were flagged during data collection. Standard reflections were measured every 2 h during data collection, and an 8% decrease in intensities was noted and a linear decay correction applied (12% for **5**, 4% for **8**, 36% for **11**, 5% for **12** and 53% for **14** with an interpolated correction applied; for **14**, data collection was stopped after the crystal decay had reached 53% at which point θ_{max} was 18.8°). Corrections were applied for Lorentz-polarisation and absorption (DIFABS[29]) effects (for **11** and **12** the absorption correction was carried out using semi-empirical ψ scans based on nine reflections with χ angles greater than 81°). The structures were solved by direct methods using either SHELXS 86[30] or SIR 92.[31] Subsequent difference syntheses gave all other non-H atomic positions. All non-hydrogen atoms were allowed anisotropic thermal motion. For **8** the Bi, P, N, O and F atoms, except for F(6), were allowed anisotropic thermal motion, while C atoms were refined with isotropic thermal parameters. For **14** the N atom in the pyridine of crystallisation was arbitrarily assigned as the atom with the smallest thermal parameter after all atoms had initially been refined as carbon atoms. The phenyl rings were refined as rigid groups with idealised geometry (C–C 1.395 Å, all angles 120°). Hydrogen atoms were included at calculated positions (C–H 0.96 Å) and assigned isotropic thermal parameters 1.2 times that of their attached carbon atom. For **14** no H atoms were included for the pyridine of crystallisation. For **11** and **12** an extinction correction was applied. Refinement for **3** was by full-

Table 12 Crystallographic and structure solution data for compounds **3**, **5**, **8**, **11**, **12** and **14**

	3	**5**	**8**	**11**	**12**	**14**
Formula	$C_{48}H_{40}BBiF_4O_2P_2\cdot CH_2Cl_2$	$C_{24}H_{46}BiF_6N_6O_2P_3$	$C_{30}H_{58}BiF_6N_6O_2P_3$	$C_{30}H_{77}BiF_{12}N_{12}O_4P_6$	$C_{12}H_{24}Bi_2Br_{3.5}Cl_{2.5}O_6$	$C_{50}H_{47}Bi_2I_6N_5O_2P_2\cdot C_5N_5N$
M_r	1091.51	866.56	950.71	1292.84	1050.58	2070.33
Space group	$P\bar{1}$	$P2_1/n$	$P2_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	11.6469(9)	17.8759(6)	10.9452(9)	13.851(2)	8.3265(3)	12.180(2)
b/Å	13.6055(8)	8.4212(6)	15.6764(9)	21.768(2)	11.1690(6)	13.315(3)
c/Å	15.6846(9)	23.7314(14)	12.0261(13)	20.387(4)	15.0640(11)	21.078(4)
α/°	96.222(5)				109.846(5)	76.82(1)
β/°	100.357(5)	90.935(4)	94.817(7)	92.60(2)	97.841(5)	75.62(1)
γ/°	106.510(5)				103.309(4)	85.48(1)
U/Å^3	2310.4(3)	3572.0(4)	2056.2(3)	6141(2)	1246.6(1)	3223(1)
θ range for cell/°	17.6–20.7	17.6–20.2	17.6–20.8	10.3–19.5	17.5–20.8	11.0–12.0
Z	2	4	2	4	2	2
D_c/g cm^{-3}	1.57	1.611	1.536	1.398	2.799	2.133
$F(000)$	1080	1720	956	2616	950	1908
μ(Mo-Kα)/cm^{-1}	40.41	51.32	44.65	31.03	199.97	84.17
T/K	298	293	293	293	293	293
θ range/°	2.4–25.0	2.3–25.1	2.3–25.0	2.4–23.6	2.6–25.0	2.5–18.8
Crystal size/mm	0.43 × 0.36 × 0.16	0.3 × 0.2 × 0.03	0.3 × 0.23 × 0.23	0.4 × 0.25 × 0.3	0.25 × 0.2 × 0.2	0.4 × 0.3 × 0.3
Range of transmission coefficients	0.87–1.19	0.71–1.34	0.75–1.18	0.404–0.464	0.628–1.00	0.68–1.49
No. data collected	8449	7008	3950	9654	4561	5335
No. unique data	8076	6306	3746	9227	4380	5000
hkl Ranges	−13 to 13, −16 to 0, −18 to 18	0 to −21, −10 to 0, −28 to 28	−12 to 0, −18 to 0, −14 to 14	−15 to 0, 0–24, −22 to 23	−9 to 9, −13 to 12, 0–17	−11 to 0, −12 to 12, −19 to 18
R_{merge}	0.018	0.033	0.032	0.126	0.023	0.071
No. data in refinement (n)	6738	6306	3746	9217	4380	4994
No. refined parameters (p)	454	367	262	598	242	223
Final R	0.031^a	0.043^b	0.062^b	0.096^b	0.040^b	0.098^b
Final R'	0.035^c	0.103^d	0.175^d	0.263^d	0.069^d	0.268^d
Goodness of fit, S	1.46^e	0.928^f	1.026^f	1.022^f	1.015^f	1.029^f
Largest remaining features (maximum, minimum) in electron density map/e Å^{-3}	+0.77, −0.78	+0.71, −0.59	+2.13, −1.53	+1.48, −0.81	+1.08, −0.87	+4.41, −3.52
Shift/e.s.d. (maximum, average) in last cycle	0.015, 0.0012	0.148, 0.004	1.14, 0.09	0.8, 0.005	0.011, 0.001	0.059, 0.003

[a] Based on data with $I > 3\sigma(I)$, $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] Based on data with $F > 4\sigma(F)$, $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [c] Based on data with $I > 3\sigma(I)$, $R' = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma(w|F_o|)^2\}^{\frac{1}{2}}$. [d] Based on data with $F_o > 4\sigma(F_o)$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [e] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]$. [f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]$.

matrix least squares on F_o and with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. Refinement of all other structures was by full-matrix least squares on F^2; for **5** the weighting scheme used was $w = [\sigma^2(F_o)^2 + (0.0737P)^2]^{-1}$ where $P = [(F_o^2/3) + (2F_c^2/3)]$; for **8** $w = [\sigma^2(F_o)^2 + (0.142P)^2 + 6.97P]^{-1}$; for **11** $w = [\sigma^2(F_o)^2 + (0.1382P)^2 + 116.54P]^{-1}$; for **12** $w = [\sigma^2(F_o)^2 + (0.0402P)^2 + 2.106P]^{-1}$, and for **14** $w = [\sigma^2(F_o)^2 + (0.0624P)^2]^{-1}$; $\sigma(F_o)$ or $\sigma(F_o)^2$ was estimated from counting statistics. For **8** refinement did not proceed smoothly and many distance restraints were applied in the final cycles of refinement. The quality of the data as judged by the unit-cell accuracy and internal R factors was not poor. It is possible that pseudo-symmetry is the cause of the poor determination of the light-atom positions. The possibility that the true space group was centrosymmetric $P2_1/m$ was examined, but discounted in view of the fact that (*a*) the E statistics uniformly were consistent with a non-centric space group and more importantly (*b*) the molecule does not possess an internal mirror plane as would be required by the centric space group. In view of these problems the accuracies of the bond distances and angles are low compared with those in structures **3** and **5**. For **11** there was substantial decay in the intensity of the standards during data collection which was undoubtedly due to solvent loss although there were no residuals in the electron-density maps which could be ascribed to any solvent molecule. However, a view of the packing of the ions of **11** in the crystals clearly revealed voids in the structure and calculations using PLATON[32] indicated that the total void volume per unit cell was about 830 Å^3 which is enough to accommodate four small molecules such as thf. These voids are centred around the inversion points 0, 0.5, 0 and 0, 0, 0.5. This solvent problem accounts for the high residuals for this structure. For **12** least-squares refinement of the population parameters for the halogen atoms revealed that each site was partially occupied by a Br atom and a Cl atom. A free refinement of these parameters gave an overall total of 3.5 Br and 2.5 Cl atoms per asymmetric unit, *i.e.* 7 Br and 5 Cl atoms per unit cell. This overall total was then fixed, and the relative proportion of these halogens in each site was allowed to vary. In the figures all the sites are labelled as Br atoms but the overall refined populations were Br(1) 54.6(6)% Br, Br(2) 74.8(5)% Br, Br(3) 56.1(6)% Br, Br(4) 59.5(5)% Br, Br(5) 84.4(6)% Br and Br(6) 20.7(6)% Br, estimated standard deviations on the final significant digit being given in parentheses. Refining these sites as pure Br or Cl atoms gave significantly worse fits.

Neutral atom scattering factors were taken from ref. 33 with corrections for anomalous dispersion. For complex **3** calculations were carried out using the Glasgow GX suite of programs.[34] For all other structures, calculations were carried out using SHELXL 93.[35]

Crystal data for complex **13**: $a = 13.524$, $b = 16.370$, $c = 26.069$ Å, orthorhombic, probable space group *Pbca*, $U = 5771.4$ Å^3, $D_c = 1.524$ g cm^{-3}.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

We thank the SERC for a studentship (to C. J. C.) and N. C. N. thanks the Royal Society for additional supporting funds.

References

1 A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367.
2 N. Burford, B. W. Royan, J. M. Whalen, J. F. Richardson and R. D. Rogers, *J. Chem. Soc., Chem. Commun.*, 1990, 1273; C. Payrastre, Y. Madaule and J. G. Wolf, *Tetrahedron Lett.*, 1990, **31**, 1145.
3 P. Jutzi, T. Wippermann, C. Krüger and H. J. Kraus, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 250.
4 N. W. Alcock, M. Ravindran and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1989, 1063.
5 R. D. Rogers, A. H. Bond, S. Aguinaga and A. Reyes, *J. Am. Chem. Soc.*, 1992, **114**, 2967.
6 M. Schäfer, G. Frenzen, B. Neumüller and K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 334.
7 A. Neuhaus, G. Frenzen, J. Pebler and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1992, **618**, 93.
8 W. Frank, J. Weber and E. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 74.
9 W. Clegg, L. J. Farrugia, A. McCamley, N. C. Norman, A. G. Orpen, N. L. Pickett and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1993, 2579.
10 L. P. Battaglia, A. Bonamartini Corradi, G. Pelizzi and M. E. Vidoni Tani, *Cryst. Struct. Commun.*, 1975, **4**, 399.
11 F. Huber, H. Preut, G. Alonzo and N. Bertazzi, *Inorg. Chim. Acta*, 1985, **102**, 181.
12 C. J. Carmalt, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Organomet. Chem.*, 1993, **460**, C22.
13 T. Allman, R. G. Goel and H. S. Prasad, *J. Organomet. Chem.*, 1979, **166**, 365.
14 Y. Mourad, Y. Mugnier, H. J. Breunig and M. Ates, *J. Organomet. Chem.*, 1990, **388**, C9.
15 W. Clegg, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1992, 1967.
16 W. Clegg, R. J. Errington, G. A. Fisher, R. J. Flynn and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1993, 637.
17 W. Clegg, M. R. J. Elsegood, R. J. Errington, G. A. Fisher and N. C. Norman, *J. Mater. Chem.*, 1994, **4**, 891.
18 *The VSEPR Model of Molecular Geometry*, R. J. Gillespie and I. Hargittai, Allyn and Bacon, Boston, 1991.
19 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, D. C. R. Hockless, N. C. Norman, A. G. Orpen and S. E. Stratford, *J. Chem. Soc., Dalton Trans.*, 1992, 3515; R. J. Errington, G. A. Fisher, N. C. Norman, A. G. Orpen and S. E. Stratford, *Z. Anorg. Allg. Chem.*, 1994, **620**, 457.
20 C. J. Carmalt, L. J. Farrugia and N. C. Norman, *Inorg. Chim. Acta*, 1995, **234**, 189 and refs. therein.
21 B. Neumüller and F. Gahlmann, *J. Organomet. Chem.*, 1991, **414**, 271.
22 F. Gahlmann and B. Neumuller, *Z. Anorg. Allg. Chem.*, 1994, **620**, 847.
23 See, for example, K. O. Christie, E. C. Curtis and D. A. Dixon, *J. Am. Chem. Soc.*, 1993, **115**, 1520; K. O. Christie, D. A. Dixon, J. C. P. Sanders, G. J. Schrobilgen and W. W. Wilson, *J. Am. Chem. Soc.*, 1995, **115**, 9461 and refs. therein.
24 W. Clegg, M. R. J. Elsegood, V. Graham, N. C. Norman and N. L. Pickett, *J. Chem. Soc., Dalton Trans.*, 1993, 997; W. Clegg, M. R. J. Elsegood, N. C. Norman and N. L. Pickett, *J. Chem. Soc., Dalton Trans.*, 1994, 1753.
25 W. J. Evans, J. L. Shreeve, J. W. Ziller and R. J. Doedens, *Inorg. Chem.*, 1995, **34**, 576.
26 W. J. Evans, J. L. Shreeve, T. J. Boyle and J. W. Ziller, *J. Coord. Chem.*, 1995, **34**, 229.
27 H. Gilman and H. L. Yablunky, *J. Am. Chem. Soc.*, 1941, **63**, 207; H. Gilman and H. L. Yale, *Chem. Rev.*, 1942, **30**, 281.
28 K. H. Ebert, R. E. Schulz, H.-J. Breunig, C. Silvestru and I. Haiduc, *J. Organomet. Chem.*, 1994, **470**, 93; L. D. Freeman and G. O. Doak, *Chem. Rev.*, 1982, **82**, 15.
29 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
30 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.
31 SIR 92, a program for automatic solution of crystal structures, A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1994, **27**, 435.
32 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
33 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
34 P. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.
35 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Received 22nd June 1995; Paper 5/04044B