# Structural Studies on Phenyl Bismuth Halides and Halogenoanions. Part 2. X-Ray Crystal Structures of $[BiPhCl_2(thf)]$ (thf = tetrahydrofuran), $[NBu^n{}_4]_2[Bi_2Ph_2Br_6]$ and $[NEt_4][BiPh_2I_2]$†

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Structural studies by X-ray crystallography have been carried out on the complexes $[BiPhCl_2(thf)]$ **1** (thf = tetrahydrofuran), $[NBu^n{}_4]_2[Bi_2Ph_2Br_6]$ **4** and $[NEt_4][BiPh_2I_2]$ **6**. Complex **1** comprises a chloride-bridged polymeric chain with each bismuth centre in a square-based pyramidal co-ordination environment. A phenyl group occupies the apical site whilst the four basal positions are occupied by three chlorine atoms, one terminal and two bridging, and the oxygen of a co-ordinated thf molecule. The chloride bridges are quite asymmetric and a comparison is made with the increasing trend towards symmetric bridges found in the previously characterised bromide and iodide derivatives. The structure of the anionic part of **4** comprises a centrosymmetric $[Bi_2Ph_2Br_6]^{2-}$ dianion with a planar $Bi_2Br_6$ unit and *trans* phenyl groups with each bismuth centre also adopting a square-based pyramidal co-ordination geometry with apical phenyls. Comparisons are made with similar bismuth, antimony and tellurium complexes and the differences discussed. The structure of the anion of **6** can be described as disphenoidal or equatorially vacant, trigonal bipyramidal with axial iodides and equatorial phenyls. This is similar to the previously known bromide complex except that **6** exists in the solid state as a weakly bound centrosymmetric dimer. All of the above structures are compared with those of related compounds and the various trends which are apparent are discussed.

In a recent paper[1] we described the results of structural studies carried out for a range of phenyl bismuth halides and halogenoanions and commented upon the co-ordination geometries around the bismuth centres and the observed trends in bismuth–halogen bond lengths. Herein we describe the structures of three further compounds and discuss these in the context of the arguments put forward previously.[1]

## Results and Discussion

The compound $BiPhCl_2$ was prepared in essentially quantitative yield from the reaction between $BiPh_3$ and two equivalents of $BiCl_3$ in $Et_2O$.[2] As with the preparation of the bromo derivative,[1] both reactants are quite soluble in $Et_2O$ whilst the product is insoluble and precipitates immediately as a white powder. Dissolution in tetrahydrofuran (thf) and crystallisation by solvent diffusion with hexanes at low temperature afforded clear, colourless crystals of the solvated complex $[BiPhCl_2(thf)]$ **1**. The structure of **1** was determined by X-ray crystallography, the results of which are shown in Figs. 1 and 2. Selected bond distances and angles are given in Table 1 and atomic positional parameters in Table 2. The crystals are isomorphous with those of the bromo analogue $[BiPhBr_2(thf)]$ **2**[1] and both structures are very similar to the iodide derivative $[BiPhI_2(thf)]$ **3**.[1] Thus, as with **2** and **3**, compound **1** is polymeric in the solid state and the co-ordination geometry around the bismuth centre may be described as square-based pyramidal with the phenyl group in the apical site and three chlorines and the oxygen of the thf ligand in the basal plane (the Bi atom lies 0.088 Å below the plane). The Bi–C distance [2.266(7) Å] is comparable to those found in **2** and **3** [2.281(9) and 2.239(16), 2.242(16) Å respectively; two independent monomeric units are present in the structure of **3**] but the Bi–O distance [2.608(7) Å] is significantly shorter than the corresponding lengths in **2** [2.671(8) Å] and **3** [2.808(17), 2.813(18) Å]. Previously[1] we commented on Bi–O bond lengths in general noting that all of the distances to the thf oxygens in **2** and **3** are long, but a trend in

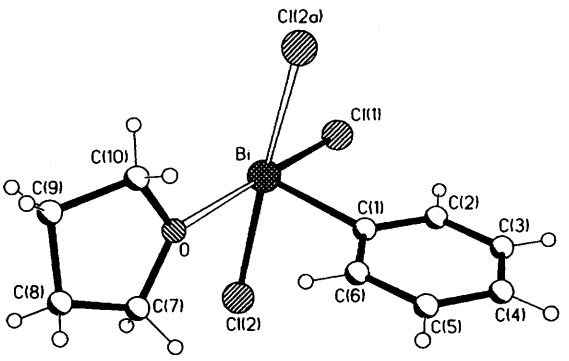

**Fig. 1** A view of the structure of the monomeric unit of **1** showing the atom numbering scheme adopted, including the link to the next unit *via* a chloride bridge

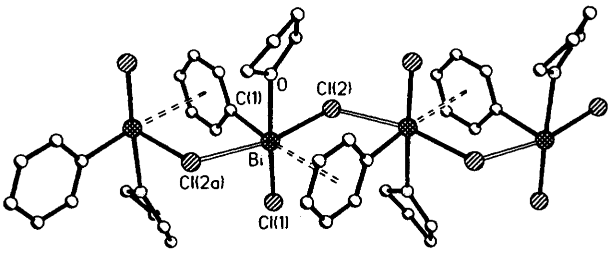

**Fig. 2** A view of part of the chloride-bridged polymeric structure of **1**

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† Ref. 1 may be regarded as Part 1 of the series.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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

| | | | |
|---|---|---|---|
| Bi–Cl(1) | 2.543(3) | Bi–Cl(2) | 2.654(3) |
| Bi–Cl(2a) | 2.934(3) | Bi–O | 2.608(7) |
| Bi–C(1) | 2.266(7) | | |
| C(1)–Bi–Cl(1) | 92.6(2) | C(1)–Bi–O | 88.3(2) |
| Cl(1)–Bi–O | 177.32(12) | C(1)–Bi–Cl(2) | 88.9(2) |
| Cl(1)–Bi–Cl(2) | 93.34(7) | O(1)–Bi–Cl(2) | 84.15(14) |
| C(1)–Bi–Cl(2a) | 82.8(2) | Cl(1)–Bi–Cl(2a) | 95.56(7) |
| O(1)–Bi–Cl(2a) | 87.06(13) | Cl(2)–Bi–Cl(2a) | 168.10(3) |
| Bi–Cl(2)–Bi(b) | 109.15(7) | | |

* Symmetry operators: (a) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (b) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$.

**Table 2** Atomic coordinates ($\times 10^4$) for compound **1**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Bi | 56.7(3) | 1985.2(3) | 2367.4(2) |
| Cl(1) | 1698(3) | 1938(2) | 1126.6(14) |
| Cl(2) | 1720(2) | −267(2) | 3051.9(11) |
| C(1) | 1882(8) | 3543(8) | 3027(5) |
| C(2) | 3170(8) | 4193(8) | 2646(4) |
| C(3) | 4196(8) | 5213(8) | 3042(5) |
| C(4) | 3934(9) | 5630(8) | 3820(5) |
| C(5) | 2650(9) | 4982(8) | 4204(5) |
| C(6) | 1618(9) | 3962(8) | 3813(5) |
| O | −1583(8) | 1907(5) | 3654(4) |
| C(7) | −1322(9) | 1034(8) | 4384(5) |
| C(8) | −2923(13) | 933(13) | 4740(7) |
| C(9) | −4175(11) | 1725(10) | 4172(6) |
| C(10) | −3134(9) | 2654(9) | 3655(5) |

the above values is clearly apparent in that the Bi–O bond lengths decrease in the order **3** > **2** > **1**. We suggest that this trend reflects the change in the electronegativity of the halogen atoms; as the electronegativity increases on going from iodide to chloride, the bismuth centre develops a greater partial positive charge (becomes more Lewis acidic) which leads to the thf ligand being more strongly bound resulting in a shorter Bi–O distance. Alternatively, we could argue that increasing polarisation of the Bi–X (X = halide) bonding electron density towards X as X becomes more electronegative provides more room for the oxygen lone pair at the bismuth centre and thus leads to a shorter bond length. Further trends are also apparent when considering the Bi–Cl bond lengths. The distance to the terminal chlorine atom [Bi–Cl(1) 2.543(3) Å] is slightly longer than that found in the only other aryl bismuth chloride structure of which we are aware, namely $[\mathrm{BiCl\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2}]$[3] [2.463(3) Å], which is monomeric in the solid state. Moreover, in crystalline $\mathrm{BiCl_3}$ the Bi–Cl bond lengths are also shorter and range from 2.468(4) to 2.518(7) Å[4] with no intermolecular contacts shorter than 3.2 Å. The reason for the longer distance in **1** is probably the presence of the *trans* thf ligand. As we have discussed before,[1] the important acceptor orbitals at the bismuth centre for bismuth halide species are likely to be the Bi–X σ* orbitals (X = halide), the consequences of which are a *trans* disposition of a ligand, L, to the Bi–X bond (*i.e.* L ··· Bi–X) and a lengthening of this bond in inverse proportion to the length of the secondary bond. The presence of the weakly bound thf ligand *trans* to Cl(1) is thus the likely cause of the slightly longer Bi–Cl bond length.

The distance to the second chlorine [Bi–Cl(2) 2.654(3) Å] is longer but this is not surprising since it is this chlorine which bridges between the bismuth centres (a matter which we discussed for **2** and **3** in ref. 1), the longer, secondary interaction being 2.934(3) Å. The trend which is apparent here is the increasingly asymmetric nature of the bridging interaction on going from iodide to chloride. We commented on this matter with respect to the structures of **2** and **3** and it is even more obvious when the structure of **1** is considered. The average difference between the primary and secondary Bi–I distances in **3** is 0.152 Å, that between the bromides in **2** is 0.213 Å whilst the corresponding difference for **1** is 0.280 Å. As has been noted by Alcock in his review of secondary bonding,[5] this difference can be taken as a measure of the strength of secondary bonding interactions, and clearly indicates that the secondary bonding is strongest for the iodide and weakest for the chloride. These results are consistent with a more general observation that secondary bonding interactions become stronger, as evidenced by a smaller difference between primary and secondary distances, as the electronegativity of the bridging atom decreases. It is not intuitively obvious why this should be so; it might be thought, for example, that as the electronegativity of the bridging atom increases, the element centre, bismuth in this case, would become more Lewis acidic and secondary bonding would become stronger. Recall that this argument was used to explain the observed trend in the Bi–O distances in **1**–**3**. It is also true, however, that a more electronegative atom is less likely to donate an electron pair, *i.e.* act as a Lewis base, and therefore take part in a strong bridging interaction. The most likely explanation is that on going from chloride to iodide, the orbitals become larger and more diffuse leading to better overlap between the lone pair and the central element σ* orbital. Moreover, on this basis, decreasing electronegativity of the central element would also be expected to lead to an increase in the occurrence of secondary bonding as is observed.[5]

Bismuth–chlorine distances generally span a range from about 2.45 to 3.05 Å as found in $[\{(\mathrm{BiCl_4})^-\}_n]$,[6] $[\mathrm{BiCl_6}]^{3-}$,[7] $[\mathrm{BiCl_5(py)}]^{2-}$ (py = pyridine),[8] $[\mathrm{Bi_4Cl_{16}}]^{4-}$,[9] $[\mathrm{Bi_4Cl_{18}}]^{6-}$,[10] and $[\{(\mathrm{Bi_2Cl_9})^{3-}\}_n]$;[11] the Bi–Cl bond lengths found in **1** clearly fall within this range. In Fig. 8 in ref. 1, we plotted a graph of primary *vs.* secondary Cl ··· Bi–Cl bond lengths derived from data obtained from the Cambridge Crystallographic Database and commented on the appearance of two distinct curves although if we plot the Bi–Cl(2) and Bi–Cl(2a) lengths on this graph, they fall between these curves. We will not reiterate the points made in ref. 1 regarding this graph except to note that **1** is a 'new' type of bismuth chloride complex (according to the criteria given in the caption of Fig. 8, ref. 1) and that a continuum of curves was considered likely once a sufficiently large number of compounds had been reported. Bond distances in bismuth halogen compounds in general will be discussed in a future publication.[12]

Two final points regarding the structure of **1** are noteworthy. First, the structure of one other organobismuth dichloride has been described by Frank,[13] namely the cyclopentadienyl complex $[\{\mathrm{BiCl_2(C_5H_5)}\}_n]$ which is also polymeric with chlorine atoms bridging between adjacent bismuth centres. Secondly, it is apparent from Fig. 2 that there is an interaction between the phenyl rings and adjacent bismuth centres. This interaction is such that the bismuth atom lies close to a line perpendicular to the ring which passes through the ring centroid, although the distance is long [Bi–$\mathrm{C_6}$ (ring centroid) 3.426 Å] implying a rather weak interaction. The same situation is found in the structures of **2** and **3** for which the Bi–$\mathrm{C_6}$ (centroid) distances are 3.472 and 3.541 (av.) Å respectively. We did not comment on these arene–bismuth interactions at the time[1] but it is worth drawing attention to the matter in view of the recent work of Schmidbaur and co-workers[14] on arene bismuth halide complexes. In the structures of the neutral $[\mathrm{BiCl_3(\eta^6\text{-}C_6H_3Me_3\text{-}2,4,6)}]$ and $[\mathrm{Bi_2Cl_6(\eta^6\text{-}C_6Me_6)}]$ the Bi–$\mathrm{C_6}$ (centroid) distances are 3.11(2) and 3.07(2) Å respectively, somewhat shorter and probably stronger than those found in **1**–**3**.

The reaction between **2** and one equivalent of $[\mathrm{NBu^n{}_4}]\mathrm{Br}$ afforded, after work-up and crystallisation, pale yellow crystals of the ionic complex $[\mathrm{NBu^n{}_4}]_2[\mathrm{Bi_2Ph_2Br_6}]$ **4** the structure of which was determined by X-ray crystallography. The results are shown in Fig. 3, selected bond lengths and angles are given in Table 3 and atomic positional parameters in Table 4. There are no short interionic contacts. The structure of the anion of **4** is

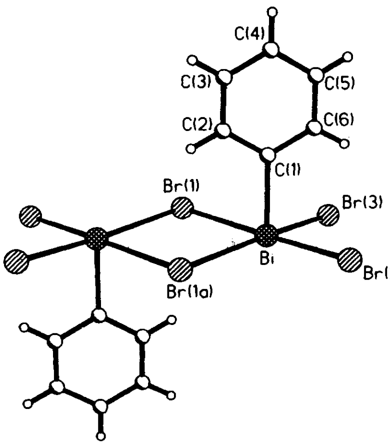

**Fig. 3** A view of the structure of the dianion $[Bi_2Ph_2Br_6]^{2-}$ in **4** showing the atom numbering scheme adopted

**Table 3** Selected bond lengths (Å) and angles (°) for compound **4** *

| | | | |
|---|---|---|---|
| Bi–Br(1) | 3.0072(14) | Bi–Br(2) | 2.7559(14) |
| Bi–Br(3) | 2.7417(14) | Bi–Br(1a) | 3.0545(14) |
| Bi–C(1) | 2.249(9) | | |
| Br(2)–Bi–Br(1) | 176.59(3) | Br(3)–Bi–Br(1) | 90.31(4) |
| Br(3)–Bi–Br(2) | 92.01(4) | Br(1)–Bi–Br(1a) | 84.48(3) |
| Br(2)–Bi–Br(1a) | 93.47(4) | Br(3)–Bi–Br(1a) | 171.85(4) |
| C(1)–Bi–Br(1) | 87.8(2) | C(1)–Bi–Br(2) | 89.6(2) |
| C(1)–Bi–Br(3) | 92.8(2) | C(1)–Bi–Br(1a) | 93.2(2) |
| Bi–Br(1)–Bi(a) | 95.52(3) | | |

* Symmetry operator: (a) $1 - x, 1 - y, 1 - z$.

**Table 4** Atomic coordinates ( × $10^4$) for compound **4**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Bi | 6268.6(3) | 6007.5(2) | 5345.4(2) |
| Br(1) | 5885.3(11) | 4974.9(6) | 3850.1(6) |
| Br(2) | 6459.9(11) | 6970.3(7) | 6714.3(6) |
| Br(3) | 8374.8(11) | 6696.3(7) | 4568.4(7) |
| C(1) | 4800(9) | 6813(5) | 4753(5) |
| C(2) | 3576(10) | 6564(6) | 4475(7) |
| C(3) | 2675(12) | 7076(8) | 4108(7) |
| C(4) | 3003(14) | 7829(8) | 4020(7) |
| C(5) | 4202(11) | 8087(6) | 4306(7) |
| C(6) | 5102(10) | 7589(6) | 4677(6) |
| N | 1531(8) | 7333(5) | 7000(5) |
| C(11) | 340(10) | 7830(6) | 7201(7) |
| C(12) | −335(11) | 8226(6) | 6477(7) |
| C(13) | −1405(11) | 8754(6) | 6794(7) |
| C(14) | −2183(14) | 9132(8) | 6071(9) |
| C(21) | 2065(10) | 7053(6) | 7852(6) |
| C(22) | 3207(11) | 6484(7) | 7800(7) |
| C(23) | 3729(15) | 6323(7) | 8665(8) |
| C(24) | 4807(15) | 5730(9) | 8675(10) |
| C(31) | 1159(10) | 6671(6) | 6438(6) |
| C(32) | 185(11) | 6098(6) | 6789(8) |
| C(33) | 53(13) | 5403(7) | 6217(9) |
| C(34) | −938(15) | 4832(9) | 6510(13) |
| C(41) | 2579(11) | 7797(6) | 6544(6) |
| C(42) | 3093(15) | 8498(9) | 6984(9) |
| C(43) | 3986(17) | 8982(10) | 6438(12) |
| C(44) | 3314(26) | 9493(13) | 5881(15) |

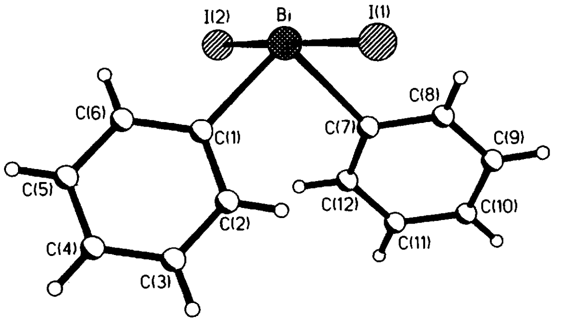

**Fig. 4** A view of the structure of the anion $[BiPh_2I_2]^-$ in **6** showing the atom numbering scheme adopted

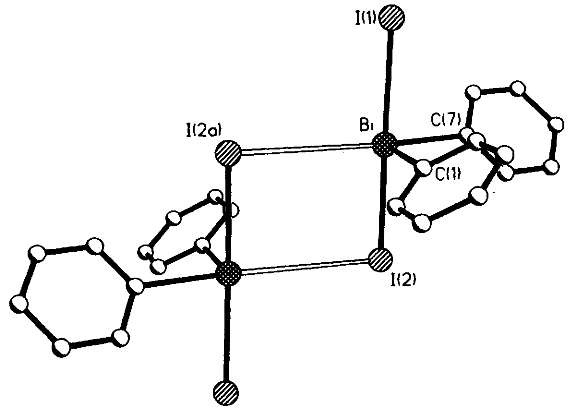

**Fig. 5** A view of the weakly bound dimer $[Bi_2Ph_4I_4]^{2-}$ found in the structure of **6**

**Table 5** Selected bond lengths (Å) and angles (°) for compound **6** *

| | | | |
|---|---|---|---|
| Bi–I(1) | 3.1415(8) | Bi–I(2) | 3.0517(8) |
| Bi–C(1) | 2.251(7) | Bi–C(7) | 2.294(7) |
| Bi–I(2a) | 4.0850(11) | | |
| I(2)–Bi–I(1) | 177.87(2) | C(1)–Bi–I(1) | 89.7(2) |
| C(7)–Bi–I(1) | 88.1(2) | C(1)–Bi–I(2) | 91.7(2) |
| C(7)–Bi–I(2) | 90.2(2) | C(1)–Bi–C(7) | 93.6(3) |
| I(1)–Bi–I(2a) | 88.76(2) | I(2)–Bi–I(2a) | 92.95(2) |
| C(1)–Bi–I(2a) | 85.7(2) | C(7)–Bi–I(2a) | 176.8(2) |
| Bi–I(2)–Bi(a) | 87.05(2) | | |

* Symmetry operator: (a) $1 - x, 1 - y, 1 - z$.

centrosymmetric (the mid-point between the Bi atoms lies on a crystallographic inversion centre) and comprises an essentially planar $Bi_2Br_6$ unit in which each bismuth atom is additionally bonded to a phenyl group such that the co-ordination geometry around the bismuth centres is square-based pyramidal. The phenyls reside in the apical positions and are mutually *trans* with respect to the $Bi_2Br_6$ plane. This structure is the same as that found for the analogous antimony chloride complex $[C_5H_5NH]_2[Sb_2Ph_2Cl_6]$ described by Hall and Sowerby[15] and also to one form of the neutral tellurium(IV) complex $[Te_2Ph_2I_6]$ reported by Alcock and Harrison[16] (the other form has a planar $Te_2I_6$ unit but the phenyls are *cis*). It is in contrast, however, to the structure of the related bismuth iodide complex $[NEt_4]_2[Bi_2Ph_2I_6]$ **5** described in ref. 1, in which the $Bi_2I_6$ unit is not planar but is bent at the central iodines with an interplane angle of 105.2°. It should be borne in mind that the cations are different for **4** and **5** and it is probably this factor, and the resulting differences in crystal packing, that are responsible for the different structures. We suggest that the differences in energies between the bent and planar forms for these structures are likely to be small and, with this in mind, we would draw attention to somewhat similar situations found for the dirhodium complexes $[Rh_2(\mu\text{-}X)_2L_4]$ (X = halide; L = CO, $PR_3$ or other two-electron donors; or $L_2$ = chelating four-electron donors) described by Hoffman[17] and in a series of bis(thiolate)-bridged dinickel(II), dipalladium(II) and diplatinum(II) complexes.[18]

The final compound which is described here is the ionic compound $[NEt_4][BiPh_2I_2]$ **6** obtained as yellow crystals from the reaction between $BiPh_2I$ and $[NEt_4]I$. The structure was established by X-ray crystallography, the results of which are shown in Figs. 4 and 5 and presented in Tables 5 and 6. Crystallographic data for all three structures are collected in Table 7. The structure of **6** contains no short cation–anion contacts and the anion $[BiPh_2I_2]^-$ is very similar in all respects to that of the analogous anion in the structure of $[PPh_4][BiPh_2Br_2]$ **7**[1] (related antimony and tellurium complexes are discussed in ref. 1, see also ref. 19). The co-ordination geometry around the bismuth centre is disphenoidal or equatorially vacant, trigonal bipyramidal with angles I(1)–Bi–I(2) 177.87(2) and C(1)–Bi–C(7) 93.6(3)°, the former such that the iodines are bent slightly towards the phenyl groups. Both of these angles are very similar to the corresponding angles found in **7** the magnitudes of which are discussed in ref. 1. However, an important difference between the structures of **6** and **7** is that whereas the bromide complex is entirely monomeric (the shortest intermolecular Bi • • • Br distances in **7** are 4.898 Å), the iodide analogue exists in the solid state as a weakly bound centrosymmetric dimer as shown in Fig. 5 [Bi–I(2a) 4.085(1) Å]. This observation is consistent with the greater tendency of iodide complexes to form secondary bonding interactions as discussed above although care must be exercised in looking for trends in this case since the counter cations are different for the two structures. Also noteworthy are the angles between I(2a) and the phenyl *ipso* carbons C(1) and C(7) [I(2a)–Bi–C(1) 85.7(2), I(2a)–Bi–C(7) 176.8(2)°]. From these angles it can be seen that the bridging iodide is essentially *trans* to C(7) and that this is reflected in a longer than usual Bi–C bond length [Bi–C(7), 2.294(7) Å].

**Table 6** Atomic coordinates ( × $10^4$) for compound **6**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Bi | 5 498.8(3) | 5 288.8(3) | 5 904.46(9) |
| I(1) | 3 432.9(6) | 4 778.6(6) | 6 708.6(2) |
| I(2) | 7 550.8(7) | 5 882.6(7) | 5 145.7(2) |
| C(1) | 6 026(7) | 2 830(8) | 5 932(2) |
| C(2) | 6 419(8) | 2 142(8) | 6 382(3) |
| C(3) | 6 711(8) | 630(9) | 6 407(3) |
| C(4) | 6 616(8) | −219(9) | 5 992(3) |
| C(5) | 6 225(9) | 414(10) | 5 539(3) |
| C(6) | 5 919(8) | 1 952(9) | 5 515(3) |
| C(7) | 7 135(8) | 5 896(8) | 6 527(2) |
| C(8) | 6 766(8) | 6 859(9) | 6 891(2) |
| C(9) | 7 747(9) | 7 371(10) | 7 255(3) |
| C(10) | 9 085(9) | 6 884(10) | 7 258(3) |
| C(11) | 9 440(9) | 5 919(11) | 6 895(3) |
| C(12) | 8 462(8) | 5 453(9) | 6 529(3) |
| N | 8 480(6) | 9 847(7) | 3 722(2) |
| C(13) | 8 713(8) | 8 588(10) | 4 100(3) |
| C(14) | 10 110(10) | 8 538(12) | 4 381(3) |
| C(15) | 7 047(8) | 9 641(9) | 3 480(3) |
| C(16) | 6 637(9) | 10 670(10) | 3 058(3) |
| C(17) | 9 533(8) | 9 758(10) | 3 352(3) |
| C(18) | 9 557(10) | 8 279(11) | 3 078(3) |
| C(19) | 8 658(9) | 11 381(10) | 3 961(3) |
| C(20) | 7 740(12) | 11 726(13) | 4 360(3) |

## 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 thf, $Et_2O$ and hexanes; $CaH_2$ for $CH_2Cl_2$). Compounds $BiX_3$ (X = Cl, Br or I) and $BiPh_3$ (all 99%+) were procured commercially and used without further purification.

*Preparations.*—The preparations described below are all based on literature methods which are listed in ref. 2. Specific references[20–22] are available for **1**, **4** and **6** respectively.

$[BiPhCl_2(thf)]$ **1**. A sample of $BiCl_3$ (0.141 g, 0.447 mmol) was dissolved in $Et_2O$ (5 $cm^3$) which gave a clear solution. A solution of $BiPh_3$ (0.098 g, 0.223 mmol) in $Et_2O$ (5 $cm^3$) was then added resulting in the precipitation of white solid. The $Et_2O$ was removed by syringe and the white solid, after drying by vacuum, was dissolved in thf (10 $cm^3$) over which hexanes (30 $cm^3$) were layered. Solvent diffusion over a period of days at −30 °C afforded colourless crystals of **1** (89%).

**Table 7** Crystallographic data

| Compound | 1 | 4 | 6 |
|---|---|---|---|
| Formula | $C_{10}H_{13}BiCl_2O$ | $C_{44}H_{82}Bi_2Br_6N_2$ | $C_{20}H_{30}BiI_2N$ |
| *M* | 429.1 | 1536.5 | 747.2 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ |
| *a*/Å | 8.086(4) | 10.103(2) | 9.7748(12) |
| *b*/Å | 9.066(4) | 17.464(3) | 8.9125(9) |
| *c*/Å | 16.679(7) | 15.892(3) | 27.276(3) |
| β/° | 94.38(4) | 90.18(2) | 95.015(12) |
| $U/Å^3$ | 1219.1(10) | 2804.0(8) | 2367.1(5) |
| *Z* | 4 | 2 | 4 |
| $D_c$/ g $cm^{-3}$ | 2.338 | 1.820 | 2.097 |
| $\mu/mm^{-1}$ | 14.87 | 10.57 | 10.06 |
| *F*(000) | 792 | 1472 | 1384 |
| *T*/K | 160 | 240 | 240 |
| Crystal size/mm | 0.50 × 0.47 × 0.28 | 0.40 × 0.28 × 0.28 | 0.24 × 0.20 × 0.08 |
| Maximum indices, *hkl* | 9, 10, 19 | 12, 20, 18 | 11, 10, 32 |
| Transmission | 0.004–0.017 | 0.021–0.043 | 0.091–0.173 |
| Reflections measured | 4175 | 5563 | 5214 |
| Unique reflections | 2143 | 4929 | 4179 |
| $R_{int}$ | 0.025 | 0.025 | 0.048 |
| Weighting parameters, *a*, *b* | 0.0754, 0 | 0.0616, 5.5827 | 0.0323, 3.3435 |
| Extinction coefficient, *x* | 0 | 0.000 50(14) | 0.000 18(5) |
| Number of refined parameters | 127 | 261 | 222 |
| *R′* | 0.101 | 0.128 | 0.081 |
| *R* (observed data) | 0.038 (1941) | 0.043 (3508) | 0.029 (3041) |
| Goodness of fit | 1.07 | 1.12 | 1.10 |
| Maximum shift/e.s.d. | <0.0005 | 0.112 | 0.002 |
| Maximum, minimum $\Delta\rho$/e $Å^{-3}$ | 2.17, −1.38 | 1.42, −1.10 | 0.80, −1.07 |

$[NBu^n_4]_2[Bi_2Ph_2Br_6]$ **4**. The compounds $BiPhBr_2$ (0.149 g, 0.334 mmol) and $[NBu^n_4]Br$ (0.108 g, 0.334 mmol) were dissolved in thf (10 $cm^3$) and stirred for 24 h which resulted in a pale yellow solution and a small amount of white precipitate. The resulting solution was transferred to a separate flask by syringe and hexanes (20 $cm^3$) were layered over it. Solvent diffusion over a period of days at −30 °C afforded a pale yellow powder which was recrystallised by solvent diffusion from MeCN (10 $cm^3$) and $Et_2O$ (25 $cm^3$) affording **6** as pale yellow crystals (70%).

$[NEt_4][BiPh_2I_2]$ **6**. The compounds $BiPh_2I$ (0.178 g, 0.363 mmol) and $[NEt_4]I$ (0.093 g, 0.363 mmol) were dissolved in thf (10 $cm^3$) which afforded a yellow-orange solution. This solution was stirred for 24 h which led to little change in colour but a small amount of an orange precipitate was formed. The resulting solution was transferred to a separate flask by syringe and hexanes (20 $cm^3$) were layered over it. Solvent diffusion over a period of days at −30 °C afforded yellow crystals of **6** (55%).

*X-Ray Crystallography.*—Crystal data are given in Table 7, together with other information on data collection and structure determination. Instrumentation and methods were as previously described,[1] except for structure refinement,[23] which was by full-matrix least-squares techniques based on $F^2$ values for all measured data. The maximum 2θ for data collection was 50°, with Mo-Kα radiation ($\lambda = 0.710\,73$ Å); standard reflections showed no significant intensity variations.

The refinement weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. An isotropic extinction coefficient $x$ was refined, such that $F_c$ was multiplied by $(1 + 0.001xF_c^2\lambda^3/\sin2\theta)^{-\frac{1}{4}}$. Final residuals are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, calculated only for reflections with $F_o^2 > 2\sigma(F_o^2)$ as a comparison with conventional refinements based on $F_o$ values, and $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ calculated for all reflections; the goodness of fit was also based on $F^2$ for all data.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

*Note added at proof.* Since the submission of this paper a report on the related structure of $SbCl_2Ph$ has appeared.[24]

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