

# Phosphorus donor complexes of bismuth(III). Structural characterisation of $[\text{Bi}_2\text{Cl}_6(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ , $[\text{Bi}_2\text{Cl}_6(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ and $[\text{Bi}_2\text{Cl}_6(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_3]$

Gerald R. Willey,<sup>\*a</sup> Leo T. Daly<sup>a</sup> and Michael G. B. Drew<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

<sup>b</sup> Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, UK

The reactions of the diphosphines dppm [bis(diphenylphosphino)methane] and dppe [1,2-bis(diphenylphosphino)ethane] with bismuth(III) chloride in acetonitrile solution have been studied. The resulting complexes  $[\text{Bi}_2\text{Cl}_6(\text{dppm})_2]$  **1** and  $[\text{Bi}_4\text{Cl}_{12}(\text{dppe})_5]$  **2** respectively, have been structurally identified by X-ray diffraction studies. The centrosymmetric structure **1**·2MeCN consists of coplanar halide-bridged  $\text{Bi}_2\text{Cl}_6$  units with each of the two dppm ligand molecules in a bidentate bridging mode between the two metal sites. The overall co-ordination geometry at each bismuth atom is approximately octahedral with four (equatorial) chlorine atoms and two (axial) phosphorus atoms: Bi–Cl (terminal) 2.475(3), 2.530(4), Bi–Cl (bridging) 2.808(4), 2.820(3), Bi–P 2.872(3), 3.090(3) Å. In **2** there are two separate and independent molecules in the asymmetric unit cell identified as  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_2]$  **2a** and  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_3]$  **2b** respectively. For **2a** the centrosymmetric structure is made up of halide-bridged  $\text{Bi}_2\text{Cl}_6$  units with bidentate chelate attachment of a dppe ligand molecule to each bismuth atom giving rise to an overall edge-shared bioctahedral geometry: Bi–Cl (terminal) 2.409(9), 2.470(11), Bi–Cl (bridging) 2.619(9), 2.945(9), Bi–P 2.699(8), 2.956(10) Å. In the case of **2b** the centrosymmetric dimer contains two  $\text{BiCl}_3(\text{dppe})$  moieties connected by a bridging dppe ligand; thus both bidentate chelate and bidentate bridging modes are observed. Each bismuth atom is surrounded by three terminal chlorine atoms, Bi–Cl 2.514(8), 2.521(9), 2.555(9) Å, and three phosphorus atoms, two from the chelating ligand, Bi–P 2.654(8), 2.916(9) Å, and one from the bridging ligand, Bi–P 2.973(9) Å, in an approximately *mer*-octahedral arrangement.

Renewed interest in bismuth(III) halide complexation with phosphorus-donor ligands has provided a fresh insight into the co-ordination geometry variations of this typical p-block metal. Crystal structure determinations of various monophosphine complexes have been reported<sup>1–4</sup> but the only diphosphine derivative that has been structurally characterised is  $[\text{Bi}_2\text{Br}_6(\text{dmpe})_2]$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ).<sup>3</sup> In a recent report<sup>5</sup> from these laboratories we have described the reactions of  $\text{BiCl}_3$  and the potential bidentate chelating ligands dppm ( $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) and dpae ( $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ ). Whereas there was sufficient analytical and spectroscopic evidence to pinpoint initial 1:1 adduct formation, subsequent recrystallisation from acetonitrile in the presence of activated charcoal provided the new compounds  $[\{\text{BiCl}_3[\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PPh}_2]\}_2]$  and  $[\{\text{BiCl}_3[\text{As}(\text{O})\text{MePh}_2][\text{Ph}_2\text{As}(\text{O})\text{CH}_2\text{CH}_2(\text{O})\text{AsPh}_2]\}_n]$  respectively. In addition to an evaluation of the structural details, speculation of the likely pathways leading to the *in situ* ligand oxidations and subsequent formation of such  $\text{E}=\text{O} \rightarrow \text{Bi}$  (E = As or P) linkages is included in that report.<sup>5</sup>

By dint of rigid exclusion of all traces of air oxygen we have now isolated the direct bismuth(III) chloride complexes using dppm and dppe ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ). Herein we describe the crystal and molecular structures of  $[\text{Bi}_2\text{Cl}_6(\text{dppm})_2]$  and  $[\text{Bi}_4\text{Cl}_{12}(\text{dppe})_5]$  which feature both bidentate chelating and bridging bonding modes for these reputable phosphorus(III) donor ligands.

## Experimental

Manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were stored over  $\text{CaH}_2$  and subsequently  $\text{P}_4\text{O}_{10}$  and then distilled under an argon atmosphere immediately prior to use. Bismuth

trichloride and the phosphorus donor ligands dppm and dppe were used directly as supplied commercially (Aldrich). The IR spectra were recorded on a Perkin-Elmer 580B spectrometer with samples as Nujol mulls smeared between CsI plates, <sup>1</sup>H (400 MHz) and <sup>31</sup>P (161.9 MHz) NMR spectra on a Bruker WH400 spectrometer; the NMR solvents  $\text{CDCl}_3$ ,  $\text{CD}_3\text{COCD}_3$  and  $\text{CD}_3\text{CN}$  were dried over 4 Å molecular sieves prior to use. Microanalytical data were obtained using a Leeman Labs Inc., PS 1000 sequential inductively coupled plasma (ICP) spectrometer and a CE440 elemental (C,H,N) analyser.

## Preparation of the complexes

(i)  $[\text{Bi}_2\text{Cl}_6(\text{dppm})_2]$  **1**. A solution of dppm (0.49 g, 1.27 mmol) in acetonitrile (30 cm<sup>3</sup>) was added dropwise to a stirred and chilled (0 °C) solution of  $\text{BiCl}_3$  (0.40 g, 1.27 mmol) in acetonitrile (30 cm<sup>3</sup>) under a blanket of argon. The resulting yellow solution was warmed at 50 °C with constant stirring for 6 h. Gradual removal of solvent *in vacuo* provided a concentrated solution of ca. 10 cm<sup>3</sup> which was layered with hexane and carefully placed in a refrigerator. Solvent diffusion over a period of several days resulted in deposition of the required compound as a mass of light yellow needle crystals. Yield 0.63 g, 71%. M.p. 248–250 °C (decomp.) (Found: C, 43.05; H, 2.85; Cl, 15.10. Calc. for  $\text{C}_{50}\text{H}_{44}\text{Bi}_2\text{Cl}_6\text{P}_4$ : C, 42.90; H, 3.15; Cl, 15.20%). IR:  $\tilde{\nu}/\text{cm}^{-1}$  (Nujol) 1582, 1307, 1272, 1186, 1156, 1092, 1026, 1000, 968, 917, 851, 780, 721, 695, 510, 500, 479, 439, 420 (ligand), 276 (sh) and 248 [ $\nu(\text{BiCl})$ ]. NMR:  $\delta_{\text{H}}$  7.26–7.49 (20 H, m,  $\text{C}_6\text{H}_5$ ) and 3.68 (2 H, t,  $\text{CH}_2$ );  $\delta_{\text{P}}$  –19.90 (2 P, s,  $\text{PPh}_2$ ).

One of the light yellow needle crystals was carefully selected under the microscope and sealed in a Lindemann tube under an atmosphere of argon for the subsequent X-ray diffraction studies.

(ii)  $[\text{Bi}_4\text{Cl}_{12}(\text{dppe})_5] \mathbf{2}$ . A solution of dppe (0.49 g, 1.22 mmol) in acetonitrile ( $25 \text{ cm}^3$ ) was added dropwise to a chilled ( $0^\circ\text{C}$ ) and stirred solution of  $\text{BiCl}_3$  (0.39 g, 1.22 mmol) in acetonitrile ( $25 \text{ cm}^3$ ) under an argon atmosphere. The resulting yellow solution was warmed to  $50^\circ\text{C}$  and stirred for 6 h. Removal of solvent *in vacuo* provided a yellow solid which was washed with hexane ( $4 \times 10 \text{ cm}^3$ ). Recrystallisation from acetonitrile–dichloromethane (50:50) provided the required compound as deep yellow needle crystals. Yield 0.95 g, 63%. M.p.  $241\text{--}244^\circ\text{C}$  (decomp.) (Found: C, 46.90; H, 3.25; Cl, 12.90. Calc. for  $\text{C}_{130}\text{H}_{120}\text{Bi}_4\text{Cl}_{12}\text{P}_{10}$ : C, 48.00; H, 3.70; Cl, 13.10%). IR:  $\tilde{\nu}/\text{cm}^{-1}$  (Nujol) 1585, 1308, 1278, 1183, 1156, 1090, 1023, 1000, 972, 918, 847, 744, 712, 692, 505, 478, 444, 414 (ligand), 288 (sh), 264 and 235 [ $\nu(\text{BiCl})$ ].

One of the deep yellow needle crystals was carefully selected and sealed in a Lindemann tube under an atmosphere of argon for the subsequent X-ray diffraction studies.

### X-Ray crystallography

Crystal data are given in Table 2, together with refinement details. Data for both crystals were collected with Mo– $\text{K}\alpha$  radiation ( $\lambda$  0.710 70 Å) using the MARresearch Image Plate System. The crystals were positioned 75 mm from the image plate. Ninety-five frames were measured at  $2^\circ$  intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.<sup>6</sup> Both structures were solved using direct methods with the SHELXS 86 program<sup>7</sup> and empirical absorption corrections were applied.<sup>8</sup> In both structures some

of the phenyl rings showed signs of disorder. For the ring in complex  $\mathbf{1}\cdot 2\text{MeCN}$  we were unable to find a suitable disordered model and so it was refined as a rigid phenyl ring. In  $\mathbf{2}$  there were two disordered rings. One was refined as a rigid group but the other was refined in two orientations with a similar apex. Each ring was refined with rigid dimensions and with a common thermal parameter. In both structures the non-hydrogen atoms, apart from the disordered atoms, were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and refined with a thermal parameter equal to 1.2 times that of the atom to which they were bonded. Both structures were then refined using SHELXL.<sup>9</sup> All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Complete atom 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.

### Results and Discussion

Direct treatment of bismuth(III) chloride with the chelating diphosphine ligands dpmm and dppe in acetonitrile solution under an argon atmosphere provided the yellow crystalline compounds  $[\text{Bi}_2\text{Cl}_6(\text{dpmm})_2] \mathbf{1}$  and  $[\text{Bi}_4\text{Cl}_{12}(\text{dppe})_5] \mathbf{2}$ , respectively. We can only stress that the greatest care was taken to exclude any traces of air and moisture, *i.e.* all manipulations were carried out under a blanket of argon so as to avoid any repetition of the ligand oxidation witnessed previously.

**Table 1** Selected bond lengths (Å) and angles ( $^\circ$ ) for compounds  $\mathbf{1}\cdot 2\text{MeCN}$  and  $\mathbf{2}$

Compound $\mathbf{1}^a$			
Bi(1)–Cl(12)	2.475(3)	Bi(1)–Cl(11 <sup>1</sup> )	2.820(3)
Bi(1)–Cl(13)	2.530(4)	Bi(1)–P(1)	2.872(3)
Bi(1)–Cl(11)	2.808(4)	Bi(1)–P(3 <sup>1</sup> )	3.090(3)
Cl(12)–Bi(1)–Cl(13)	92.09(13)	Cl(11)–Bi(1)–P(1)	80.42(9)
Cl(12)–Bi(1)–Cl(11)	88.36(11)	Cl(11 <sup>1</sup> )–Bi(1)–P(1)	91.72(9)
Cl(13)–Bi(1)–Cl(11)	170.52(13)	Cl(12)–Bi(1)–P(3 <sup>1</sup> )	95.68(11)
Cl(12)–Bi(1)–Cl(11 <sup>1</sup> )	172.32(10)	Cl(13)–Bi(1)–P(3 <sup>1</sup> )	105.41(13)
Cl(13)–Bi(1)–Cl(11 <sup>1</sup> )	92.62(12)	Cl(11)–Bi(1)–P(3 <sup>1</sup> )	83.96(8)
Cl(11)–Bi(1)–Cl(11 <sup>1</sup> )	88.00(9)	Cl(11 <sup>1</sup> )–Bi(1)–P(3 <sup>1</sup> )	77.21(8)
Cl(12)–Bi(1)–P(1)	94.33(12)	P(1)–Bi(1)–P(3 <sup>1</sup> )	161.17(8)
Cl(13)–Bi(1)–P(1)	90.10(13)	Bi(1)–Cl(11)–Bi(1 <sup>1</sup> )	92.00(9)
Compound $\mathbf{2}$			
Bi(1)–Cl(12)	2.514(8)	Bi(1)–P(14)	2.654(8)
Bi(1)–Cl(11)	2.521(9)	Bi(1)–P(17)	2.916(9)
Bi(1)–Cl(13)	2.555(9)	Bi(1)–P(18)	2.973(9)
Cl(12)–Bi(1)–Cl(11)	96.5(3)	Cl(13)–Bi(1)–P(17)	87.6(3)
Cl(12)–Bi(1)–Cl(13)	96.8(3)	P(14)–Bi(1)–P(17)	71.8(3)
Cl(11)–Bi(1)–Cl(13)	165.1(3)	Cl(12)–Bi(1)–P(18)	80.5(3)
Cl(12)–Bi(1)–P(14)	88.5(3)	Cl(11)–Bi(1)–P(18)	79.5(3)
Cl(11)–Bi(1)–P(14)	87.7(3)	Cl(13)–Bi(1)–P(18)	109.5(3)
Cl(13)–Bi(1)–P(14)	85.8(3)	P(14)–Bi(1)–P(18)	162.0(2)
Cl(12)–Bi(1)–P(17)	159.5(3)	P(17)–Bi(1)–P(18)	117.0(3)
Cl(11)–Bi(1)–P(17)	77.6(3)		
Bi(2)–Cl(22)	2.409(9)	Bi(2)–P(27)	2.699(8)
Bi(2)–Cl(23)	2.470(11)	Bi(2)–Cl(21 <sup>1</sup> )	2.945(9)
Bi(2)–Cl(21)	2.619(9)	Bi(2)–P(24)	2.956(10)
Cl(22)–Bi(2)–Cl(23)	94.5(4)	Cl(21)–Bi(2)–Cl(21 <sup>1</sup> )	84.2(2)
Cl(22)–Bi(2)–Cl(21)	173.1(4)	P(27)–Bi(2)–Cl(21 <sup>1</sup> )	164.3(3)
Cl(23)–Bi(2)–Cl(21)	92.2(4)	Cl(22)–Bi(2)–P(24)	87.1(3)
Cl(22)–Bi(2)–P(27)	78.9(3)	Cl(23)–Bi(2)–P(24)	158.4(3)
Cl(23)–Bi(2)–P(27)	88.7(4)	Cl(21)–Bi(2)–P(24)	87.2(3)
Cl(21)–Bi(2)–P(27)	102.8(3)	P(27)–Bi(2)–P(24)	70.4(3)
Cl(22)–Bi(2)–Cl(21 <sup>1</sup> )	92.5(3)	Cl(21 <sup>1</sup> )–Bi(2)–P(24)	96.2(3)
Cl(23)–Bi(2)–Cl(21 <sup>1</sup> )	105.2(4)	Bi(2)–Cl(21)–Bi(2 <sup>1</sup> )	95.8(2)

<sup>a</sup> Symmetry transformation used to generate equivalent atoms:  $\mathbf{1} - x, -y, -z$ .

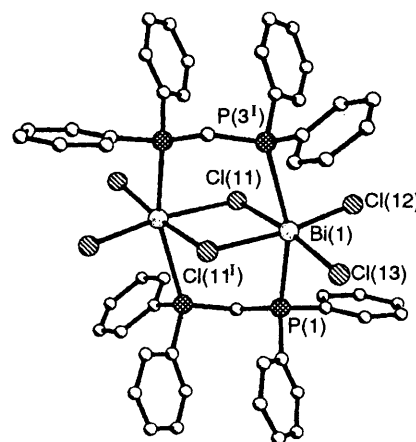
**Table 2** Crystal data and structure refinement for compounds **1**-2MeCN and **2**\*

Formula	[Bi <sub>2</sub> Cl <sub>6</sub> (dppm) <sub>2</sub> ]-2MeCN	[Bi <sub>2</sub> Cl <sub>6</sub> (dpe) <sub>2</sub> ], [Bi <sub>2</sub> Cl <sub>6</sub> (dpe) <sub>3</sub> ]
Empirical formula	C <sub>54</sub> H <sub>50</sub> Bi <sub>2</sub> Cl <sub>6</sub> N <sub>2</sub> P <sub>4</sub>	C <sub>130</sub> H <sub>120</sub> Bi <sub>4</sub> Cl <sub>12</sub> P <sub>10</sub>
<i>M</i>	1481.5	3253.3
<i>a</i> /Å	10.558(7)	10.895(7)
<i>b</i> /Å	12.130(7)	14.500(7)
<i>c</i> /Å	12.783(7)	20.832(7)
$\alpha$ /°	112.93(1)	105.16(1)
$\beta$ /°	100.51(1)	98.25(1)
$\gamma$ /°	105.77(1)	108.08(1)
<i>U</i> /Å <sup>3</sup>	1372	2928
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.793	1.845
$\mu$ /mm <sup>-1</sup>	6.851	6.456
<i>F</i> (000)	716	1586
Crystal size/mm	0.25 × 0.30 × 0.16	0.20 × 0.14 × 0.10
$\theta$ Range for data collection	4.33–24.99	3.01–25.62
<i>hkl</i> Index ranges	–12 to 12, –13 to 13, 0–15	0–13, –15 to 15, –24 to 23
Independent reflections	4136	8558
Data, parameters	4136, 297	8558, 622
Goodness of fit on <i>F</i> <sup>2</sup>	0.691	1.092
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0524, 0.1522	0.0889, 0.1850
(all data)	0.0657, 0.1713	0.1350, 0.2381
Weighting scheme parameters <i>a, b</i>	0.20, 10.87	0.09, 200.89
Largest difference peak and hole/e Å <sup>-3</sup>	1.516, –2.227	1.066, –1.704

\* Details in common: 293(2) K; triclinic, space group *P* $\bar{1}$ ; *Z* = 1;  $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .

**Table 3** Atomic coordinates ( $\times 10^4$ ) for compound **1**-2MeCN

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Bi(1)	1441(1)	1818(1)	1039(1)
Cl(11)	1382(3)	–694(3)	396(3)
Cl(12)	3981(3)	2652(3)	2048(3)
Cl(13)	1403(4)	4069(4)	1920(5)
P(1)	727(3)	1485(3)	2989(2)
C(2)	–30(11)	–153(11)	2776(10)
P(3)	–1616(3)	–1220(3)	1500(2)
C(11)	2318(10)	2180(10)	4176(9)
C(12)	2962(13)	1451(13)	4483(12)
C(13)	4260(15)	2126(17)	5371(15)
C(14)	4900(14)	3451(18)	5939(11)
C(15)	4255(21)	4126(18)	5605(14)
C(16)	2962(19)	3499(14)	4748(14)
C(21)	–337(13)	2330(12)	3606(12)
C(22)	–1273(17)	2478(18)	2865(16)
C(23)	–2176(21)	3012(21)	3265(24)
C(24)	–2029(27)	3464(21)	4478(26)
C(25)	–1087(24)	3340(18)	5218(18)
C(26)	–214(18)	2740(18)	4774(15)
C(31)	–1962(12)	–2695(9)	1580(10)
C(32)	–3267(17)	–3367(14)	1567(24)
C(33)	–3545(29)	–4554(15)	1569(27)
C(34)	–2520(33)	–5068(13)	1584(18)
C(35)	–1216(24)	–4397(16)	1597(23)
C(36)	–937(12)	–3210(14)	1595(21)
C(41)	–2913(11)	–653(12)	1947(10)
C(42)	–2985(14)	–226(14)	3089(12)
C(43)	–3969(16)	206(16)	3390(14)
C(44)	–4973(19)	144(22)	2489(21)
C(45)	–4964(18)	–290(24)	1339(18)
C(46)	–3939(15)	–706(19)	1067(14)
N(100)	2469(20)	–1780(24)	3165(25)
C(101)	2649(29)	–2372(27)	2403(28)
C(102)	2786(49)	–3163(29)	1343(35)

**Fig. 1** View of the centrosymmetric dimeric structure of [Bi<sub>2</sub>Cl<sub>6</sub>(dppm)<sub>2</sub>] **1**

### Compound 1

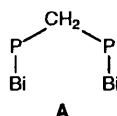
The structure of compound **1** is shown in Fig. 1 with the atom notation used. The gross molecular geometry can be described as centrosymmetric edge-shared bioctahedral in which all the halogens lie in an equatorial plane. Within this coplanar Bi<sub>2</sub>Cl<sub>6</sub> framework the terminal Bi–Cl bond distances are 2.475(3), 2.530(4) Å and the bridging Bi–Cl distances 2.808(4), 2.820(3) Å; the core Bi<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> unit is symmetrical, Bi–Cl–Bi 92.00(9)°. Each Bi has a six-co-ordinate environment comprising the four equatorial halogen atoms and two phosphorus atoms (from separate ligands) mutually *trans* and occupying axial positions. There is little distortion from the ideal octahedral geometry with only two *cis* angles [both involving P(3<sup>1</sup>)] differing by more than 6° from the ideal 90°. The Bi–P bond distances, 2.872(3), 3.090(3) Å, are significantly longer than those in [Bi<sub>2</sub>Br<sub>6</sub>(dmpe)<sub>2</sub>],<sup>3</sup> 2.678(8), 2.791(7) Å. Bonding arrangements for structures of the type [E<sub>2</sub>X<sub>6</sub>L<sub>4</sub>] (E = Sb or Bi, X = halide, L = phosphine) have been considered previously in some detail by Clegg *et al.*<sup>3</sup> and four possible structural types, *viz.* A–D, have been identified. With only a single CH<sub>2</sub> unit in the dppm backbone the structure adopted by compound **1** (referred to as type D), in which the ligand takes up a bidentate bridging mode between the separate bismuth centres is surprising and

The analytical and spectroscopic data for the compounds are in the Experimental section and do not warrant any further discussion; specifically there is no evidence for P=O bond formation either in the IR [ $\nu$ (P=O) bands are normally found in the range 1280–1120 cm<sup>-1</sup><sup>10</sup>] or in the <sup>31</sup>P NMR spectra ( $\delta_p$  based on P<sup>*v*</sup>Ph, *ca.* 30–80<sup>11</sup>). Identification of the resulting structure and ligand-binding type for each of these new compounds was established by X-ray diffraction studies.

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

Atom	x	y	z	Atom	x	y	z
Bi(1)	292(1)	1 397(1)	3 495(1)	C(163)	4 266(34)	4 101(40)	2 764(20)
Cl(11)	-553(9)	2 231(8)	4 466(5)	C(164)	4 180(56)	4 657(33)	2 398(22)
Cl(12)	-1 344(10)	-396(6)	3 225(5)	C(165)	3 116(48)	4 883(38)	2 364(25)
Cl(13)	1 333(9)	1 017(8)	2 480(5)	C(166)	2 293(32)	4 582(27)	2 723(20)
P(18)	1 537(9)	826(8)	4 622(5)	Bi(2)	49(1)	5 694(1)	1 011(1)
C(19)	545(34)	494(32)	5 161(20)	Cl(21)	-1 814(8)	4 779(8)	-1 135(5)
C(111)	2 840(28)	1 833(27)	5 195(16)	Cl(22)	1 886(9)	6 682(9)	2 000(5)
C(112)	3 972(42)	2 204(33)	4 950(24)	Cl(23)	-726(14)	4 207(9)	1 416(7)
C(113)	5 016(37)	3 035(26)	5 371(23)	P(24)	219(9)	7 656(7)	786(5)
C(114)	4 928(41)	3 401(35)	5 993(27)	C(25)	-541(39)	8 258(28)	1 422(18)
C(115)	3 881(29)	3 108(32)	6 186(31)	C(26)	-314(34)	7 937(24)	2 057(17)
C(116)	2 850(38)	2 337(35)	5 830(22)	P(27)	-1 136(8)	6 659(7)	1 867(4)
C(121)	2 257(33)	-82(26)	4 393(19)	C(231)	1 744(24)	8 419(21)	915(15)
C(122)	2 379(32)	-411(27)	3 767(24)	C(232)	2 713(35)	7 990(19)	833(17)
C(123)	2 884(44)	-1 091(42)	3 539(30)	C(233)	4 039(30)	8 621(28)	970(20)
C(124)	3 431(40)	-1 440(33)	4 018(38)	C(234)	4 398(22)	9 681(27)	1 188(18)
C(125)	3 394(73)	-1 074(43)	4 713(37)	C(235)	3 430(30)	10 110(18)	1 270(15)
C(126)	2 770(42)	-457(35)	4 841(21)	C(236)	2 103(26)	9 479(22)	1 133(15)
P(14)	-1 475(8)	1 720(7)	2 650(5)	C(241a)*	-579(42)	7 710(35)	68(18)
C(15)	-737(30)	3 012(27)	2 603(19)	C(242a)*	-1 914(43)	7 077(32)	-183(21)
C(16)	-114(30)	3 731(23)	3 260(19)	C(243a)*	-2 639(32)	7 065(31)	-793(22)
P(17)	1 322(8)	3 550(7)	3 586(5)	C(244a)*	-2 030(41)	7 686(35)	-1 152(19)
C(131)	-2 832(34)	1 709(30)	2 899(19)	C(245a)*	-695(42)	8 320(32)	-900(22)
C(132)	-3 260(30)	1 168(29)	3 295(21)	C(246a)*	30(33)	8 331(32)	-290(22)
C(133)	-4 479(50)	1 005(45)	3 491(35)	C(241b)*	-389(67)	7 915(54)	114(28)
C(134)	-5 159(38)	1 360(39)	3 217(21)	C(242b)*	-731(68)	8 768(47)	138(28)
C(135)	-4 884(33)	1 813(29)	2 813(25)	C(243b)*	-1 288(66)	8 884(43)	-466(36)
C(136)	-3 658(41)	2 024(28)	2 650(21)	C(244b)*	-1 505(66)	8 146(53)	-1 093(28)
C(141)	-2 014(31)	911(27)	1 816(16)	C(245b)*	-1 163(67)	7 292(46)	-1 116(28)
C(142)	-2 426(55)	-97(39)	1 713(19)	C(246b)*	-606(67)	7 177(44)	-513(36)
C(143)	-2 907(75)	-850(53)	1 078(46)	C(251)	-1 078(32)	6 425(29)	2 661(16)
C(144)	-2 846(61)	-330(73)	661(53)	C(252)	-1 930(38)	5 611(27)	2 702(20)
C(145)	-2 503(92)	620(63)	651(25)	C(253)	-1 885(44)	5 371(33)	3 292(20)
C(146)	-2 211(51)	1 313(47)	1 276(30)	C(254)	-1 074(38)	5 942(38)	3 823(28)
C(151)	2 020(30)	4 445(24)	4 397(16)	C(255)	-180(36)	6 780(41)	3 775(15)
C(152)	1 619(39)	5 327(32)	4 627(23)	C(256)	-233(32)	7 085(30)	3 217(20)
C(153)	2 213(46)	5 928(26)	5 272(21)	C(261)	-2 789(26)	6 503(24)	1 644(14)
C(154)	3 237(49)	5 729(57)	5 570(25)	C(262)	-3 141(37)	7 156(33)	2 030(19)
C(155)	3 536(62)	5 006(49)	5 388(39)	C(263)	-4 485(42)	6 996(37)	1 843(26)
C(156)	2 914(37)	4 353(27)	4 766(19)	C(264)	-5 186(43)	6 291(44)	1 284(26)
C(161)	2 353(30)	4 008(21)	3 092(15)	C(265)	-4 826(53)	5 759(44)	900(27)
C(162)	3 385(31)	3 687(29)	3 103(22)	C(266)	-3 517(35)	5 852(31)	1 068(20)

\* Occupation factor 0.5.



completely unexpected. The resulting interligand angle *trans* P(1)–Bi(1)–P(3<sup>l</sup>) 161.2(1)° and the fact that all angles in the sector **A** are significantly greater than the expected tetrahedral values, Bi–P–C 117.9(4), 117.8(4) and P–C–P 115.9(6)°, would seem to signify a certain degree of ligand ‘discomfort’ in order to fit across the central Bi<sub>2</sub>(μ-Cl)<sub>2</sub> sector; the observed octahedral metal geometry, however, refutes any stereochemical involvement of the formal lone pair associated with each bismuth(III) centre. What is clear is that some restraint must be placed on the argument<sup>3</sup> that any ligand (L) will in general prefer to bond in a position *trans* to a halide (X) rather than another ligand (L), *i.e.* it is a vacant Bi–Cl(σ\*) orbital that acts as the most likely acceptor orbital for an incoming ligand (L). Examples of molecules that adopt the particular configuration whereby both P-donor centres (bidentate chelate) from the one and the same ligand are located *trans* to halogen atoms (typifying structural type **A**) include [Bi<sub>2</sub>Br<sub>6</sub>(dmpe)<sub>2</sub>],<sup>3</sup> [Bi<sub>2</sub>Cl<sub>6</sub>{Ph<sub>2</sub>P(O)CH<sub>2</sub>(O)PPh<sub>2</sub>}<sub>2</sub>]<sup>5</sup> where the oxidised form of dppm is featured, Bi–Cl<sub>terminal</sub> 2.472(10), 2.503(12), Bi–Cl<sub>bridging</sub>

2.587(10), 3.045(12) Å with ligand ‘bite’ angle O–Bi–O 80.5(9)° and, as we shall see shortly, both **2a** and **2b**. The same arrangement is observed for [Bi<sub>2</sub>Br<sub>6</sub>(PMe<sub>3</sub>)<sub>4</sub>],<sup>3</sup> Bi–P 2.716(3), 2.865(3) Å, where the monodentate ligand trimethylphosphine is involved.

### Compound **2**

The structure of [Bi<sub>4</sub>Cl<sub>12</sub>(dppe)<sub>5</sub>] consists of two separate and quite different molecules, *viz.* the dinuclear halide-bridged [Bi<sub>2</sub>Cl<sub>6</sub>(dppe)<sub>2</sub>] **2a** depicted in Fig. 2 with atom notation and the dinuclear ligand-bridged [Bi<sub>2</sub>Cl<sub>6</sub>(dppe)<sub>3</sub>] **2b** depicted in Fig. 3.

For [Bi<sub>2</sub>Cl<sub>6</sub>(dppe)<sub>2</sub>] the centrosymmetric edge-shared bioctahedral arrangement (representative of structural type **A**) has each bismuth atom bonded to two terminal chlorine atoms, *cis* Bi–Cl 2.409(9), 2.470(11) Å, two bridging chlorine atoms, *cis* Bi–Cl 2.619(9), 2.945(9) Å and two phosphorus atoms *cis* Bi–P 2.699(8), 2.956(10) Å arising from bidentate chelate binding of the dppe ligand molecules. The terminal and bridging Bi–Cl bond distances are comparable to those noted above for **1** and the co-ordination geometry of the six-co-ordinate bismuth centres is distorted octahedral with *cis* angles varying up to 20° from the ideal 90°. In our view the dppe molecule with its more flexible backbone of two CH<sub>2</sub> ‘hinge’ units would seem at first sight a more reasonable candidate than dppm for bridging

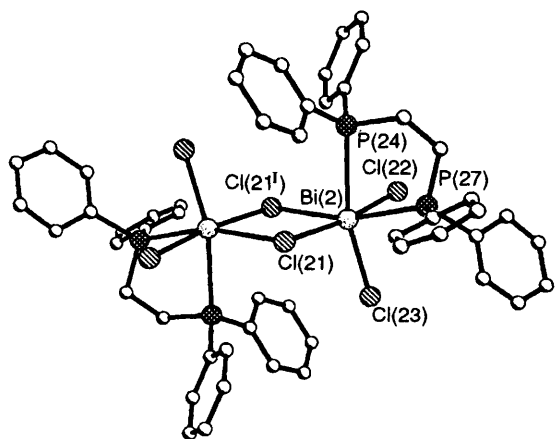


Fig. 2 View of the centrosymmetric dimeric structure of  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_2]$  **2a**

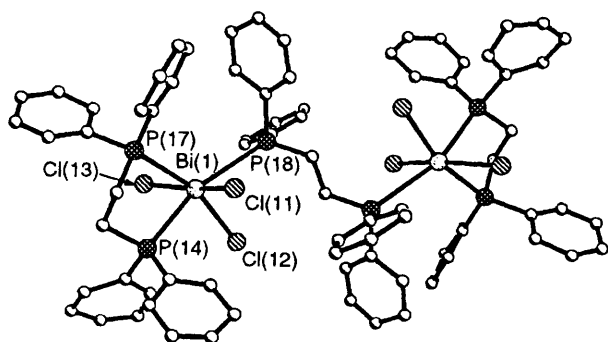


Fig. 3 View of the centrosymmetric structure of  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_3]$  **2b**

attachment between metal centres but this is not the case; the observed bidentate ligand attachment results in the formation of five-membered chelate rings  $\overline{\text{Bi-P-C-C-P}}$  with internal ligand angles  $\text{Bi-P-C}$  108.7(12), 102.0(10)°,  $\text{P-C-C}$  111(3), 109(2) and a ligand 'bite' angle  $\text{P-Bi-P}$  70.4(3)°. For direct comparison,  $[\text{Bi}_2\text{Br}_6(\text{dmpe})_2]$ , which is similarly of structure type A, shows a corresponding 'bite' angle of  $\text{P-Bi-P}$  76.3(2)°.

In the case of  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_3]$  **2b** the centrosymmetric structure consists of two separate  $\text{BiCl}_3(\text{dppe})$  moieties, in which the ligand binding is bidentate chelate, linked together by a single dppe molecule acting as a floppy bridge. Each bismuth centre is six-co-ordinate with an immediate environment of

three terminal chlorine atoms (*mer*)  $\text{Bi-Cl}$  2.514(8), 2.521(9), 2.555(9) Å and three phosphorus atoms  $\text{Bi-P}_{\text{chelate}}$  2.654(8), 2.916(9) Å,  $\text{Bi-P}_{\text{bridge}}$  2.973(9) Å in a geometry approaching ideal octahedral but with  $\text{Cl-Bi-Cl} > 90^\circ$  and  $\text{P-Bi-Cl} < 90^\circ$ . The resulting 'bite' angle  $\text{P-Bi-P}$  71.8(3)° associated with the  $\overline{\text{Bi-P-C-C-P}}$  ring formation is closely similar to that observed in **2a** as indeed are all the remaining angles in the ring. What is puzzling here, bearing in mind the ability of bismuth(III) to assume high co-ordination geometries, is the apparent antipathy toward formation of the seven-co-ordinate mononuclear species  $\text{BiCl}_3(\text{dppe})_2$  as opposed to the observed six-co-ordinate dinuclear species  $[\text{Bi}_2\text{Cl}_6(\text{dppe})_3]$  invoking a bridging ligand.

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