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Cationic, four-co-ordinate, bis(organotransition metal)bismuth(III) complexes

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The ionic complex $[Bi\{OP(NMe_2)_3\}_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$ has been prepared and its crystal structure determined and compared with that of the valence isoelectronic anion $[BiCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^-$. Both structures have a four-co-ordinate bismuth centre with a geometry best described as equatorially vacant, trigonal bipyramidal in which the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments are in the equatorial positions. The structure of $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}_2]$ has also been determined and is compared with that of $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$.

Organotransition-metal complexes incorporating bismuth have received significant attention in recent years as attested by a number of review articles which have appeared dealing either exclusively or significantly with this subject,[1] some of the motivation for these studies being the importance of mixed transition metal–bismuth compounds as heterogeneous catalysts[2] and magneto-optic materials.[3] Part of our own work in this field has centred on organotransition metal–bismuth(III) complexes of the form $[BiX(ML_n)_2]$, where X = halide and ML_n is a 17-electron organotransition-metal fragment such as $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$ or $Mn(CO)_5$, with a view to understanding certain solid-state structural features such as the extent of secondary intermolecular bonding of the form X–Bi ··· X and the co-ordination geometry associated with the bismuth(III) centre.[4–8] Thus, with regard to the latter point, it was found that anionic four-co-ordinate, ten-valence-electron bismuth(III) species of the type $[BiX_2(ML_n)_2]^-$,[9,10] derived from reactions between $[BiX(ML_n)_2]$ and a source of halide anion, adopt structures which are significantly distorted towards a tetrahedral geometry in contrast to those of the valence isoelectronic organo-compounds $[BiX_2Ph_2]^-$[11,12] which have the expected equatorially vacant, trigonal-bipyramidal or disphenoidal structure; in the latter, the formal bismuth(III) lone pair is stereochemically active whereas in the transition-metal complexes this stereochemical activity is becoming less marked. Lone-pair stereochemical inactivity for four-co-ordination is extremely uncommon, the only previous example being found in the anion $[Bi\{Co(CO)_4\}_4]^-$ which has a regular tetrahedral geometry.[13]

In the preceding paper[14] we described the synthesis of a range of organobismuth(III) cations of the form $[BiR_2L_2]^+$,[15] where R = aryl and L is a neutral two-electron donor ligand, which were found to be structurally similar to the anionic compounds $[BiX_2Ph_2]^-$ such that, for both the anions and the cations, the aryl groups occupy equatorial sites and the X groups or L ligands reside in the axial positions with similar X–Bi–X and L–Bi–L angles. Herein we describe related work carried out to prepare cationic organotransition-metal compounds of the form $[BiL_2(ML_n)_2]^+$, which are isoelectronic with the anionic species $[BiX_2(ML_n)_2]^-$, and comment on the similarities and differences between the structures of these two types of compound.

Results and Discussion

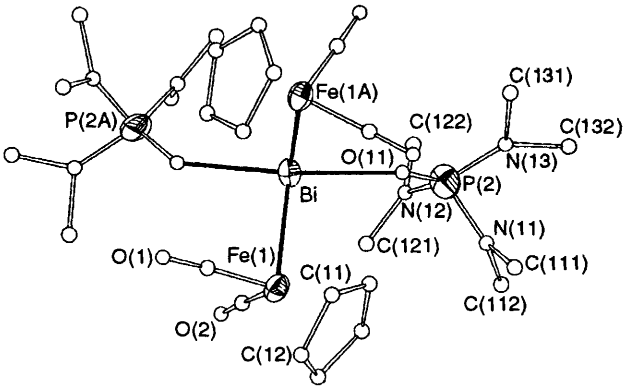

Fig. 1 View of the molecular structure of the cation of complex **2** showing the atom numbering scheme. Ellipsoids for the Bi, Fe and P atoms are drawn at the 30% probability level, C, O and N atoms are drawn as spheres of arbitrary radius. Atoms marked A are related to unmarked atoms by the two-fold symmetry operation $-x, -y, z$

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Bi–Fe(1)	2.675(2)	Bi–O(11)	2.502(8)
O(11)–Bi–O(11A)	160.7(5)	Fe(1)–Bi–Fe(1A)	110.14(8)
Fe(1)–Bi–O(11)	99.2(3)	Fe(1)–Bi–O(11A)	91.8(2)
Bi–O(11)–P(2)	137.8(6)		

Atoms labelled A are related by the symmetry operation $-x, -y, z$.

The reaction between $[BiCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **1**,[4] $TlPF_6$ and 2 equivalents of $OP(NMe_2)_3$ in thf (thf = tetrahydrofuran) afforded, after work-up, dark green crystals of the complex $[Bi\{OP(NMe_2)_3\}_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$ **2**. Spectroscopic and analytical data were consistent with the anticipated 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 1 and atomic positional parameters in Table 2. The structure is ionic comprising $[Bi\{OP(NMe_2)_3\}_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ cations and hexafluorophosphate anions with no close interionic contacts [shortest Bi ··· F 5.80(1) Å]; both the cation and anion reside on crystallographic two-fold axes. In the cation the

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‡ The resonance in the ^1H NMR spectrum for the $OP(NMe_2)_3$ protons was very broad and the corresponding resonance for the carbon atoms in the $^{13}C\text{-}\{^1H\}$ spectrum was not observed, both features probably being due to facile dissociation of the $OP(NMe_2)_3$ ligands in solution.

Table 2 Atomic positional parameters (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Bi	0	0	9 981(1)
Fe(1)	−382(1)	719(1)	11 053(1)
P(1)	0	0	4 793(5)
P(2)	−1 667(2)	−347(2)	8 951(3)
F(1)	−432(20)	−356(13)	5 392(15)
F(2)	−563(9)	362(7)	4 875(29)
F(3)	−300(12)	−251(7)	3 988(12)
N(11)	−2 373(11)	−108(8)	9 327(20)
N(12)	−1 397(20)	−8(8)	8 030(27)
N(13)	−2 084(18)	−834(11)	9 060(19)
N(13′)	−1 742(11)	−839(8)	8 454(19)
O(1)	964(6)	806(5)	11 833(11)
O(2)	−101(6)	1 304(5)	9 449(11)
C(1)	441(8)	768(5)	11 484(10)
C(2)	−199(6)	1 071(5)	10 089(12)
O(11)	−1 137(5)	−360(3)	9 687(8)
C(11)	−865(8)	423(10)	12 220(13)
C(12)	−865(9)	947(10)	12 266(12)
C(13)	−1 207(9)	1 132(7)	11 564(19)
C(14)	−1 449(6)	734(5)	10 980(13)
C(15)	−1 246(7)	321(5)	11 411(12)
C(111)	−2 683(42)	−156(21)	10 259(35)
C(111′)	−2 561(61)	−235(36)	10 336(42)
C(112)	−2 783(15)	205(14)	8 685(32)
C(121)	−1 280(16)	470(12)	8 166(24)
C(122)	−1 374(59)	−416(66)	7 237(189)
C(131)	−1 788(27)	−1 276(15)	9 437(36)
C(132)	−2 762(27)	−997(23)	8 867(49)
C(131′)	−1 403(27)	−1 250(14)	8 810(40)
C(132′)	−2 205(26)	−870(22)	7 549(38)

bismuth centre is four-co-ordinate with an equatorially vacant, trigonal-bipyramidal or disphenoidal geometry, being bonded to two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments [Bi–Fe 2.675(2) Å] and two $OP(NMe_2)_3$ ligands [Bi–O 2.502(8) Å], the former occupying the equatorial positions [Fe(1)–Bi–Fe(1A) 110.14(8)°] and the latter residing in the axial sites [O(11)–Bi–O(11A) 160.7(5)°]; the oxygen atoms of the $OP(NMe_2)_3$ ligands bend away from rather than towards the two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments.

It is interesting to compare the structure of complex **2** with that of the valence isoelectronic anion $[BiCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^-$ present in the compound $[N(PPh_3)_2][BiCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **3**.[9] In $[BiCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^-$ the co-ordination geometry around the bismuth centre is quite similar to that found in the cation of **2** with the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments in the equatorial positions and the chlorine atoms in axial sites. The only significant structural differences are the Cl–Bi–Cl angle in **3** [155.6(2)°], which is about 5° smaller than the O–Bi–O angle in **2**, and the orientations of the two $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragments (conformations about the Bi–Fe bonds), the latter feature being evident from a comparison of Fig. 1 with Fig. 2 in ref. 9, although the Fe–Bi–Fe angles are similar [110.14(8)° for **2**, 111.4(1)° for **3**]. In both structures it is therefore not unreasonable, in terms of valence-shell electron-pair repulsion (VSEPR) arguments, to state that the formal bismuth(III) lone pair resides primarily in the third equatorial site, although the Cl–Bi–Cl angle in **3** is almost 25° less than the idealised value of 180°. Even more distorted structures for other anions related to that in **3** have been observed, in which the lone-pair stereochemical activity is correspondingly less pronounced as discussed in more detail in ref. 9.

A comparison of the structure of complex **2** with those of arylbismuth cations of the general form $[BiR_2L_2]^+$ [14,15] reveals that the structures are broadly similar with the exception that the axial–Bi–axial angle is much closer to 180° in the aryl cations whilst the equatorial–Bi–equatorial angle is about 10° larger for **2**. The latter feature is probably steric in origin whereas the former reflects a formally more stereochemically active lone pair in the aryl compounds. Similar differences are observed between the structure of **3** and related anions, and the structures of the aryl anions $[BiX_2R_2]^-$.

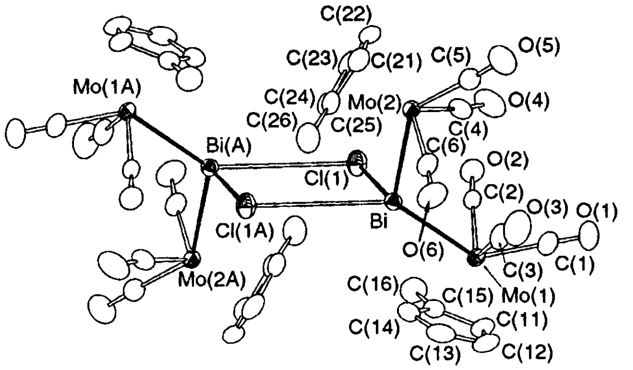

Fig. 2 View of a centrosymmetrically related pair of molecules of complex **10** showing the intermolecular Bi ⋯ Cl interactions and the atom numbering scheme. Ellipsoids are drawn at the 30% probability level. Atoms labelled A are related by the symmetry operation 0, 0.5, 0

Other compounds of interest in relation to **2** are the silicon complex $[Si\{OP(NMe_2)_3\}_2\{Fe(CO)_4\}_2]$ **4** described by Zybill *et al.*,[16] the Group 14 species $[E(bipy)\{Mn(CO)_2(\eta\text{-}C_5H_4Me)\}_2]$ **5** (bipy = 2,2′-bipyridyl; E = Ge, Sn or Pb) characterised by Huttner and co-workers[17] and the bismuth complexes $[BiPh_2\{M(CO)_5\}_2]^-$ **6** (M = Cr, Mo or W) and $[BiPh_2\{Fe(CO)_4\}_2]^-$ **7** reported by Bachman and Whitmire.[18] In compound **4** which has the same phosphine ligands as **2** the angles around the silicon centre are all close to the tetrahedral angle except for Fe–Si–Fe [122.6(1)°] and O–Si–O [92.1(1)°]. Comparison with the Fe–Bi–Fe and O–Bi–O angles in **2** shows that the former is larger and the latter smaller for the silicon compound, but overall the geometry around silicon in **4** is much closer to tetrahedral in line with the presence of only four valence-electron pairs as opposed to five around the bismuth centre in **2** and **3**; in **5**–**7** the geometries are also closer to tetrahedral since there is no formal lone pair present.

The analogous reaction between $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **8**,[5] $TlPF_6$ and 2 equivalents of $OP(NMe_2)_3$ also afforded a dark green crystalline compound for which spectroscopic and analytical data were consistent with the formula $[Bi\{OP(NMe_2)_3\}_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2][PF_6]$ **9**. Crystals of **9** were examined by X-ray crystallography but problems during refinement prevented an accurate structure from being obtained. Nevertheless, the unit-cell volume and the atomic positions which were approximately determined [Bi, Mo, $OP(NMe_2)_3$ and PF_6 groups] were consistent with the expected structure.

Additional reactions involving complex **8**, $TlPF_6$ and using either $OPPh_3$ or dmpu (*N*,*N*′-dimethylpropyleneurea) as ligands afforded dark green compounds for which ^1H NMR and infrared spectroscopic data were consistent with the formulae $[Bi(OPPh_3)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2][PF_6]$ and $[Bi(dmpu)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2][PF_6]$ but only oily rather than crystalline samples were isolated with the result that satisfactory analytical data were not obtained.

An attempted preparation of the complex $[Bi(tmen)\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}_2][PF_6]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylenediamine) from $[BiCl\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}_2]$ **10**, $TlPF_6$ and tmen did not result in the expected product but after work-up a small quantity of dark green crystals was isolated. One crystal was examined by X-ray crystallography and found to be unreacted **10**, the structure of which is reported here (Fig. 2 and Tables 3 and 4). The molecular structure is very similar to that of **8**[5] in that the primary co-ordination geometry around the bismuth centre is trigonal pyramidal, being bonded to two $Mo(CO)_3(\eta\text{-}C_5H_4Me)$ fragments and one chlorine atom. For the two crystallographically independent molecules in the

Table 3 Selected bond lengths (Å) and angles (°) for complex **10**

Bi–Mo(1)	2.9331(5)	Bi–Mo(2)	2.9443(5)
Bi–Cl(1)	2.570(1)	Bi ••• Cl(1A)	3.979(2)
Mo(1)–Bi–Mo(2)	120.29(1)	Mo(1)–Bi–Cl(1)	100.83(4)
Mo(2)–Bi–Cl(1)	97.12(4)	Cl(1)–Bi ••• Cl(1A)	68.6(1)
Bi–Cl ••• Bi(A)	111.4(1)		

Atoms labelled A are related by the symmetry operation 0, 0.5, 0.

Table 4 Atomic positional parameters (× 10^4) for complex **10**

Atom	*x*	*y*	*z*
Bi	1293(1)	3088(1)	1952(1)
Mo(1)	2721(1)	595(1)	2296(1)
Mo(2)	3004(1)	4213(1)	3064(1)
Cl(1)	2468(2)	4170(1)	−113(1)
O(1)	6301(7)	−1257(5)	3255(5)
O(2)	5729(6)	1775(4)	629(4)
O(3)	2799(10)	477(5)	4794(4)
O(4)	6387(7)	2617(7)	2393(7)
O(5)	5576(10)	3316(6)	5117(5)
O(6)	461(8)	2717(5)	4906(4)
C(1)	4988(9)	−581(5)	2923(5)
C(2)	4620(7)	1417(5)	1273(5)
C(3)	2765(10)	590(6)	3853(5)
C(4)	5068(8)	3164(6)	2617(6)
C(5)	4627(10)	3615(6)	4385(6)
C(6)	1473(9)	3200(5)	4237(5)
C(11)	2088(9)	−650(5)	1518(5)
C(12)	1046(10)	−827(6)	2575(6)
C(13)	−189(9)	225(7)	2420(6)
C(14)	40(8)	1064(6)	1283(6)
C(15)	1428(8)	532(5)	715(5)
C(16)	2065(11)	1078(7)	−512(5)
C(21)	2102(10)	6039(5)	3197(6)
C(22)	3621(10)	6090(6)	2421(7)
C(23)	3115(10)	5980(6)	1450(6)
C(24)	1299(8)	5873(5)	1612(5)
C(25)	644(8)	5916(5)	2686(5)
C(26)	−1255(10)	5917(7)	3152(7)

structure of **8** the average Bi–Mo distance is 2.951 Å which compares with the slightly shorter value of 2.939 Å for **10**, and the average Mo–Bi–Mo angle in **8** is 117.4° which is a little smaller than the Mo(1)–Bi–Mo(2) angle of 120.29(1)° for **10**. The conformations about the two Bi–Mo bonds in **10** are also similar to those found in both molecules of **8**. One of the interesting features about the structure of **8** is the intermolecular Bi ••• Cl interactions which are present.[8] The important features relating to the Cl–Bi ••• Cl interactions are the primary and secondary Bi–Cl bond distances and the Cl–Bi ••• Cl angle which for the two independent molecules of **8** are, respectively, 2.746(2), 3.039(3) Å, 151.6(1)° and 2.612(3), 3.596(4) Å, 141.6(1)°. In **10** the Bi–Cl distances are 2.570(1) and 3.979(2) Å which reveal that the secondary Bi ••• Cl bonding is considerably less in the crystal structure of **10** which is further reflected in the much more acute Cl–Bi ••• Cl angle of 68.6°; the more obtuse angles observed in **8** are an expected consequence of the increased extent of secondary bonding interactions, angles closer to 180° being associated with shorter Bi ••• Cl interactions.[8] In fact the weakly associated molecules of **10** are arranged in the crystal structure as centrosymmetric pairs as shown in Fig. 2, and a similar arrangement was also found in the structure of the iodide compound [BiI{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **11**[8] for which the Bi–I, Bi ••• I and I–Bi ••• I parameters are 2.949(1), 4.152(1) Å and 95.2(1)°.

An interesting pair of structures for comparison with those of complexes **8** and **10** are those of the manganese–bismuth complexes [BiCl{Mn(CO)$_2$(η-C$_5$H$_5$)}$_2$] **12** and [BiCl{Mn(CO)$_2$(η-C$_5$H$_4$Me)}$_2$] **13** described by Huttner and co-workers.[19] Compound **12** exists in the solid state as centrosymmetric dimers akin to **10**, notable differences between the two structures being the much more symmetric nature of the Cl–Bi ••• Cl bridges in **12** [2.798(9) and 2.895(8) Å] and the significantly larger M–Bi–M angle [141.0(2)°]. The former feature reflects the fact that the bismuth centre in **12** has four valence-electron pairs as opposed to the five formally present in **10** (if the secondary Bi ••• Cl bond is included); the large M–Bi–M angle in **12** is in common with other 'inidene' complexes as shown in the extensive studies of Huttner and co-workers.[20] In contrast to **12**, however, the structure of **13** reveals a polymeric arrangement somewhat similar to that found in **8**. In **13** the Cl–Bi ••• Cl and M–Bi–M angles are similar to those found in **12** but the Bi–Cl distances are more different [2.63(1) and 3.14(1) Å].

Such marked differences in the extent of secondary Bi ••• Cl bonding between the two independent molecules in complex **8** and in **10** and between the structures of **12** and **13** reflect the weakness of such bonding interactions and indicate that their magnitude is probably of the same order as typical crystal-packing forces. Such a conclusion is also probably valid concerning the extent of any distortion towards a tetrahedral structure in compounds such as **2** and **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 Et$_2$O and thf, CaH$_2$ for CH$_2$Cl$_2$ and pyridine and sodium for hexanes). The compound OP(NMe$_2$)$_3$ was procured commercially and used without further purification; **1**, **8** and **10** were prepared as described in the literature.[4,5] Microanalytical data were obtained at The University of Newcastle. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer in thf solution using CaF$_2$ solution cells, ^{1}H and ^{13}C NMR spectra on a Bruker 200 MHz instrument and referenced to SiMe$_4$ and ^{31}P NMR spectra on a JEOL FX90Q instrument and referenced to 85% H$_3$PO$_4$.

Preparations

[Bi{OP(NMe$_2$)$_3$}$_2${Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$][PF$_6$] 2. A sample of OP(NMe$_2$)$_3$ (0.040 cm^3, 0.224 mmol) was added dropwise to a stirred, dark green solution of complex **1** (0.067 g, 0.112 mmol) in thf (5 cm^3) at room temperature which resulted in no colour change. A solution of TlPF$_6$ (0.044 g, 0.112 mmol) in thf (6 cm^3) was then added and the resulting mixture stirred for 1 h. All volatiles were then removed by vacuum and CH$_2$Cl$_2$ (15 cm^3) was added to the resultant dark green oil giving a dark green solution which was filtered through Celite. The resulting dark green filtrate was reduced in volume by vacuum to about 7 cm^3 and hexanes (20 cm^3) were added as an overlayer. Solvent diffusion over a period of days at −30 °C resulted in dark green crystals of complex **2** (0.083 g, 70% based on bismuth) one of which was used for X-ray crystallography (Found: C, 29.20; H, 4.20; N, 7.85. C$_{26}$H$_{46}$BiF$_6$Fe$_2$N$_6$O$_6$P$_3$ requires C, 29.30; H, 4.35; N, 7.90%). NMR (CD$_2$Cl$_2$); ^{1}H, δ 4.96 (s, 10 H, C$_5$H$_5$) and 2.9 [vbr s, 36 H, OP(NMe$_2$)$_3$]; ^{13}C-{^{1}H}, δ 199.4 (s, CO), 85.8 (s, C$_5$H$_5$), OP(NMe$_2$)$_3$ resonance not observed; ^{31}P-{^{1}H}, δ 34.3 [br s, OP(NMe$_2$)$_3$] and −144 (spt, PF$_6$). IR (thf): ν(C≡O) 2010s, 1979s and 1950s cm^{-1}.

[Bi{OP(NMe$_2$)$_3$}$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$][PF$_6$] 9. Compound **9** was prepared in a similar manner to that of **2** using OP(NMe$_2$)$_3$ (0.065 cm^3, 0.373 mmol), TlPF$_6$ (0.056 g, 0.186 mmol) and **8** (0.137 g, 0.186 mmol). This afforded dark green crystals (0.184 g, 82% based on bismuth) one of which was used

Table 5 Crystallographic and structure solution data for compounds **2** and **10**

	2	**10**
Formula	$C_{26}H_{46}BiF_6Fe_2N_6O_6P_3$	$C_{18}H_{14}BiClMo_2O_6$
M_r	1066.28	762.6
Space group	*Fdd*2	$P\bar{1}$
Crystal system	Orthorhombic	Triclinic
a/Å	19.722(4)	7.5698(3)
b/Å	28.633(6)	12.5989(8)
c/Å	14.289(3)	12.7413(7)
α/°		65.577(5)
β/°		82.971(4)
γ/°		76.380(4)
U/Å^3	8069(3)	1074.9(1)
θ Range for cell/°	17.5–20.9	17.6–20.6
Z	8	2
D_c/g cm^{-3}	1.755	2.356
F(000)	4208	708
μ(Mo-Kα)/cm^{-1}	52.51	94.69
T/K	298	294
Scan mode	ω–2θ	ω–2θ
ω Scan angle/°	0.69 + 0.47 tan θ	0.62 + 0.45 tan θ
θ Range/°	2.51–24.96	2.77–24.97
Crystal size/mm	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.2
Range of transmission coefficients	0.960–0.696	0.301–0.101
No. data collected	2009	4059
No. unique data	1846	3749
hkl Ranges	0–23, −34 to 0, 0–16	−8 to 0, −14 to 14, −15 to 15
R_{sigma}	0.0481	0.0070
No. data in refinement	1846	3747
No. refined parameters	214	256
Final R for all data [for $I > 2\sigma(I)$]	0.055 [0.034]	0.026 [0.025]
Final R' for all data [for $I > 2\sigma(I)$]	0.093 [0.086]	0.072 [0.069]
Goodness of fit, S	1.076	1.103
Largest remaining features (maximum, minimum) in electron-density map/e Å^{-3}	+0.65, −0.42	+1.24, −1.03
Shift/e.s.d. (maximum, average) in last cycle	0.001, 0.0001	0.001, 0.0005

for X-ray crystallography (Found: C, 27.60; H, 3.60; N, 6.70. $C_{28}H_{46}BiF_6Mo_2N_6O_8P_3$ requires C, 28.00; H, 3.85; N, 7.00%). NMR (CD_3CN): ^1H, δ 5.58 (s, 10 H, C_5H_5) and 2.59 [d, 36 H, $OP(NMe_2)_3$, J_{PH} = 9.5 Hz]; ^{13}C-{^1H}, δ 93.1 (s, C_5H_5) and 36.0 [s, $OP(NMe_2)_3$]; ^{31}P-{^1H}, δ 21.7 [s, $OP(NMe_2)_3$] and −144 (spt, PF_6). IR (thf): ν(C≡O) 2011s, 1987s and 1917s (br) cm^{-1}

X-Ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for the structures are presented in Table 5. Full X-ray experimental details are given in ref. 14; where different, details for the structures of **2** and **10** are noted here separately. Standard reflections measured every 2 h during data collection showed a 4% decrease in intensities for **2** and a 2% decrease for **10**. Corrections were applied for Lorentz-polarisation and absorption effects (semiempirical ψ scans based on nine reflections with χ angles greater than 81°). Systematic absences and the E statistics for **2** indicated the non-centrosymmetric F-centred space group *Fdd*2. This choice was confirmed by successful solution and refinement of the structure. The structures were solved for the heavy atoms by direct methods (SHELXS[21]). Subsequent difference syntheses gave all other non-H atomic positions. Several atoms in the $OP(NMe_2)_3$ ligands in **2** were found to be disordered in two sites in a 50:50 ratio. These were refined with isotropic thermal parameters while all other non-H atoms were allowed anisotropic thermal motion. All non-hydrogen atoms in **10** were refined anisotropically. In view of the disorder present in **2** no hydrogen atoms were included. Hydrogen atoms for **10** were included at calculated positions with C–H 0.96 Å. An extinction correction was also applied. Refinement was by full-matrix least squares on F^2 using the weighting scheme $w = [\sigma^2(F_o)^2 + (0.0578P)^2 + 7.708P]^{-1}$ where $P = [(F_o^2/3) + (2F_c^2/3)]$ for **2** and $[\sigma^2(F_o)^2 + (0.0432P)^2 + 2.91P]^{-1}$ for **10**; $\sigma(F_o)^2$ was estimated from counting statistics. Neutral atom scattering factors in the program SHELXL 93[22] were used with corrections applied for anomalous dispersion.

For complex **9** the data set was of good quality and appears to be in the space group $P2_1$ but since it could not be properly solved ($R \approx 0.13$) this was not confirmed by successful refinement. From a preliminary refinement it was clear that both the Mo atoms and both of the $OP(NMe_2)_3$ ligands were disordered over two sites. This disorder could not be satisfactorily resolved, and in view of the likely very poor accuracy of the resulting structural analysis no further work was carried out on this structure. However, the atoms which were found and the unit-cell volume and space group are consistent with the expected formula. The unit-cell dimensions are a = 9.052(1), b = 16.282(1), c = 14.681(1) Å, β = 95.881(6)°, U = 2152.29 Å^3, M_r = 1202.48, D_c = 1.855 g cm^{-3} for Z = 2.

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.

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