Systematics of BX_3 and BX_2^+ Complexes (X= F, Cl, Br, I) with Neutral Diphosphine and Diarsine Ligands

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Abstract

The coordination chemistry of the neutral diphosphines, $R_2P(CH_2)_2PR_2$ (R = Me or Et) and o-$C_6H_4(PR'_2)_2$ (R' = Me or Ph), and the diarsine, o-$C_6H_4(AsMe_2)_2$ towards the Lewis acidic BX_3 (X = F, Cl, Br and I) fragments is reported, including several rare complexes incorporating BF_3 and BF_2^+. The studies have revealed that the flexible dimethylene linked diphosphines form $[(BX_3)_2\{\mu\text{-}R_2P(CH_2)_2PR_2\}]$ exclusively, confirmed by multinuclear NMR (^1H, ^{11}B, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$) and IR spectroscopy and microanalytical data. Crystallographic determinations of the four BX_3 complexes with $Et_2P(CH_2)_2PEt_2$ confirm the 2:1 stoichiometry and, taken together with the spectroscopic data, reveal that the Lewis acid behavior of the BX_3 fragment towards phosphine ligands increases in the order F << Cl ~ Br < I. The first diphosphine and diarsine-coordinated dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}]^+$ (E = P, As), are obtained using the rigid, pre-organized o-phenylene linkages. These complexes are characterized similarly, and the data indicate that the complexes with o-$C_6H_4(AsMe_2)_2$ are much more labile and readily decomposed than the phosphine analogs. X-ray crystallographic studies on $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}][BX_4]$ (X = Cl, Br), $[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}][I_3]$ and $[BCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][BCl_4]$ confirm the presence of distorted tetrahedral coordination at boron through a chelating diphosphine or diarsine and two X ligands, with d(B–P) revealing a similar increase in Lewis acidity down Group 17, whilst comparison of d(B–P) and d(B–As) reveals an increase of *ca*. 0.08 Å from P to As. Reaction of BCl_3 with the diphosphine dioxide $Ph_2P(O)CH_2P(O)Ph_2$ gives the ligand-bridged dimer $[(BCl_3)_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$, whilst using either BF_3 gas or $[BF_3(SMe_2)]$ gives a mixture containing both $[(BF_3)_2\{\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2\}]$ and the unexpected difluoroboronium salt, $[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}][B_2F_7]$ containing a chelating phosphine oxide. The structure of the latter was confirmed crystallographically.

Introduction

The boron(III) halides are good Lewis acids whose acidity is generally stated as increasing $BF_3 < BCl_3 < BBr_3 < BI_3$, and there has been much work (a lot of it computational) over the past fifteen years devoted to exploring the factors involved, the results of which are often subtle. This is a very active area of both experimental and theoretical research and the issues are discussed in detail in several recent articles and reviews. [1,2,3,4,5,6] It is important to note that the properties of both the Lewis acid and Lewis base in a complex must be taken in consideration, and that calculations deal with gas phase species, meaning solvation or solid state effects may mask Lewis acidity trends in solution or in the solid state. Whilst the majority of complexes of BX_3 with neutral or anionic ligands, L, form $[BX_3(L)]^{0/-}$, fluoroboron cations with more flexible neutral ligands (e.g. $[BF_2\{Me_2N(CH_2)_2NMe_2\}]^+$) have been obtained through displacement reactions from mixed BX_3 adducts of monodentate ligands (such as $[BF_nCl_{(3-n)}(py)]$), or by the stepwise displacement of pyridine from $[BF_2(py)_2]^+$ (which itself is made by the displacement of the heavier halide in $[BF_nX_{(3-n)}(py)]$, X = Cl or Br, using excess pyridine).[7] Recent work has developed boron fluoride compounds towards fluoride sensing and PET imaging using ^{18}F.[8]

Due to their innate Lewis acidity, boron(III) halides have found widespread use in organic syntheses and catalysis.[9,10,11] There is also much current interest in the chemistry of boron-based frustrated Lewis pairs.[12]

Early studies on coordination complexes of BX_3 (X = F, Cl, Br or I) with monodentate PR_3 and AsR_3 (R = alkyl or aryl) were mainly via IR, Raman and multinuclear NMR spectroscopy, with some crystallographic data; although complexes of BF_3 are few, with only one structurally characterized example.[1] PR_3-BX_3 complexes, e.g. $[BF_3(PMe_3)]$, have also been identified as by-products from other reactions involving B(III) species and phosphine ligands,[13] whilst various $[BCl_3(PR_3)]$ (R_3 = Me_3, Et_3, Me_2Ph, $^tBu_3$, Cy_3, $MePh_2$, Ph_3) were obtained at different rates as rearrangement products from the reaction of the phosphines with 2-chloro-1,3,2-benzodioxaborole (ClBcat).[14] $[(BCl_3)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ is the only reported example of a diphosphine ligand complex of BX_3, isolated from the reaction of $[Pt_2(Ph_2PCH_2PPh_2)_3]$ and BCl_3, while spirocyclic tetraphosphine complexes have been reported, but without structural data.[15]

We report here a systematic study of the coordination chemistry of the neutral diphosphines, $R_2P(CH_2)_2PR_2$ (R = Me or Et) and o-$C_6H_4(PR'_2)_2$ (R' = Me or Ph), and the diarsine, o-$C_6H_4(AsMe_2)_2$ towards BX_3 (X = F, Cl, Br and I). The studies have revealed the first diphosphine and diarsine dihaloboronium cations, $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}]^+$ (E = P, As), characterized by IR and multinuclear NMR spectroscopy (^1H, ^{11}B, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$) and crystallographic studies.

Results and Discussion

The phosphine complexes were synthesized by two general routes: reaction of the phosphine with $[BX_3(SMe_2)]$ (X = F or Cl) or BX'_3 (X' = Br or I) in anhydrous CH_2Cl_2 solution, or reaction of the BX_3 (X= F, Cl, Br or I) with the phosphine in anhydrous n-hexane. In many cases either route was successful, giving high yields of the same complex, but as detailed below pure samples of some BF_3 adducts were only obtained by the second route. The use of $[BX_3(SMe_2)]$ was generally unsuccessful with arsine ligands and here the second route was used. All preparations and manipulations were carried out in anhydrous solvents under a dinitrogen atmosphere; the fluoride complexes are much more sensitive to moisture than those of the heavier boron halides, which reflects the weaker B–P bonds in the former.

Neutral BX_3 complexes with diphosphine and diarsine ligands

[$BF_3(EMe_3)$] (E = P or As): These two complexes serve as useful models for the bidentate diphosphine and diarsine complexes described below. [$BF_3(PMe_3)$] has been studied on several occasions[13.16] and our spectroscopic data are in good agreement, however, its structure has not been reported previously. Colorless crystals of [$BF_3(PMe_3)$] [1], which decomposed rapidly in air, were obtained by layering a CH_2Cl_2 solution containing [$BF_3(SMe_2)$] and PMe_3 in a 1:1 molar ratio with *n*-hexane. The structure (Fig. 1) reveals the expected C_{3v} geometry; it adopts the same space group ($P2_1/m$) as [$BX_3(PMe_3)$] (X = Cl, Br), [17] but unlike the staggered conformation of the chloro and bromo complexes, [$BF_3(PMe_3)$] has an eclipsed conformation. An *ab initio* study of the structure of [$BF_3(PMe_3)$] found that the staggered conformer is preferred,[18] suggesting that the observed eclipsed arrangement is a result of crystal packing effects. The *d*(B–P) and *d*(B–F) are in good agreement (within 0.02 Å) with predicted values.[19] The B–P bond length in [$BF_3(PMe_3)$] (2.029(10) Å) is significantly longer than in [$BCl_3(PMe_3)$] (1.957(5) Å),[17] consistent with the order of Lewis acidity being $BCl_3 > BF_3$, in agreement with theoretical predictions.[18] The *d*(B–P) and *d*(B–F) are identical to those in [$BF_3(PEt_3)$],[20] the only other reported structure of a BF_3-phosphine complex.

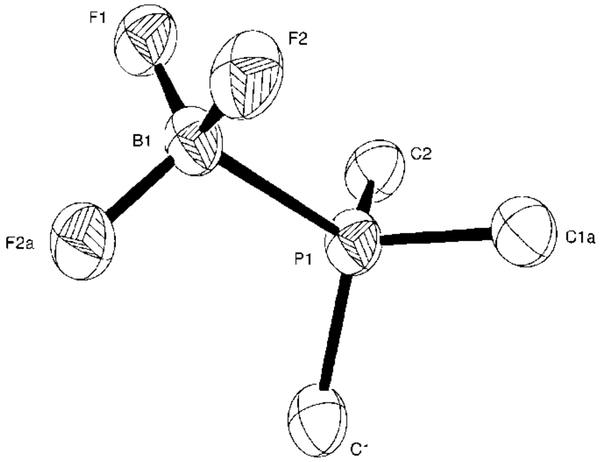
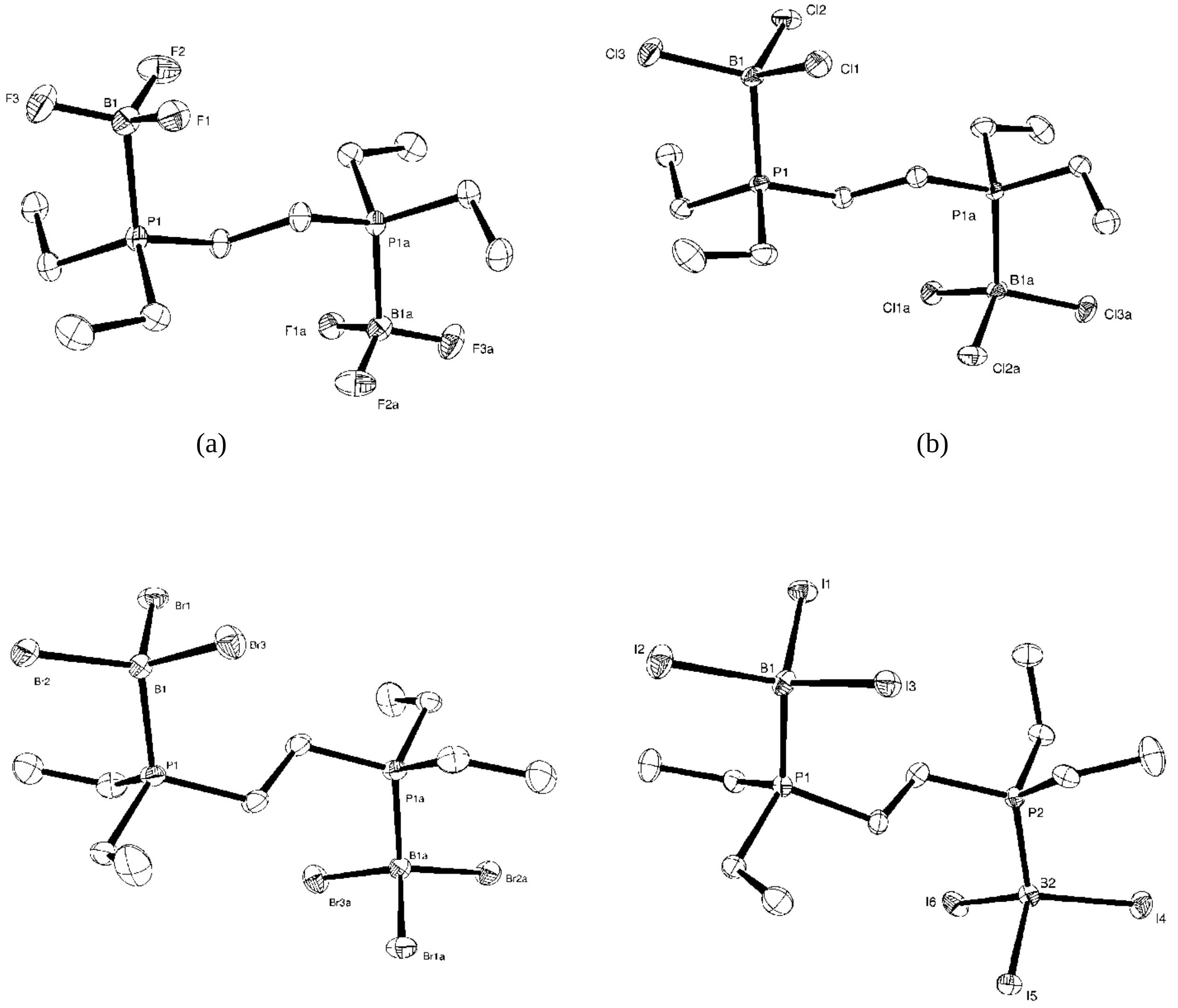


Figure 1: The structure of [$BF_3(PMe_3)$] showing the atom labelling scheme. The molecule lies on a mirror plane going through C2, P1, B1 and F1. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = x, ½ – y, z. Selected bond lengths (Å) and angles (°): B1–F1 = 1.376(11), B1–F2 = 1.396(7), B1–P1 = 2.029(10), F1–B1–F2 = 110.3(5), F2–B1–F2a = 110.5(7), F1–B1–P1 = 108.4(6), F2–B1–P1 = 108.6(5).

Although [$BF_3(AsMe_3)$] [2] has been briefly mentioned,[21] details are scarce. Passing BF_3 into a solution of $AsMe_3$ in *n*-hexane immediately precipitated a white powder, which was isolated by filtration and briefly dried *in vacuo*. The complex has a significant vapor pressure at ambient temperature, readily pumps away *in vacuo*, and a satisfactory microanalysis could not be obtained. However, the spectroscopic properties support the formulation, with a singlet $^{19}F\{^1H\}$ NMR resonance (CD_2Cl_2, 295 K) observed at δ –148.4 and an ^{11}B NMR resonance at δ +0.06. Neither showed any B–F coupling, consistent with fast exchange in solution; the spectra were unchanged at 180 K. The instability prevented growth of crystals for an X-ray study, although structures are known for the other three [$BX_3(AsMe_3)$] (X = Cl, Br or I).[22]

[$BX_3\{\mu$-$R_2P(CH_2)_2PR_2\}$] (R = Me, Et): The reaction of two molar equivalents of [$BX_3(SMe_2)$] (X = F, Cl) or BX_3 (X = Br, I) with one equivalent of $Et_2P(CH_2)_2PEt_2$ in CH_2Cl_2 layered with n-hexane, yielded colorless crystals of [$(BX_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] in each case. X-ray structure determinations (Figs. 2(a)-(d), Table 1) revealed that the [$(BX_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (X = F, Cl, Br) are all centrosymmetric and adopt the monoclinic space group $P2_1/c$, with the isomorphous chloro and bromo complexes having almost identical unit cell dimensions. There are two similar, but crystallographically independent, molecules in the asymmetric unit of [$(BI_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (Fig. 2(d)).



(a) (b)

(c) (d)

Figure 2 The structures of the centrosymmetric (a) [$(BF_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (symmetry operation: a = 2 – x, –y, 1 – z); (b) [$(BCl_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (symmetry operation: a = 1 – x, –y, –z); (c) [$(BBr_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (symmetry operation: a = 1 – x, 1 – y, –z); (d) the structure of the B1/B2-centred molecule of [$(BI_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (the other molecule is similar). In each case the atom labelling scheme is shown. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for $[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (X = F, Cl, Br, I)

	X = F	Cl	Br	I
d(B–X)	1.388(2), 1.385(2), 1.373(2)	1.8536(18), 1.8470(19), 1.834(2)	2.013(3), 2.007(3), 2.017(4)	2.224(3)– 2.239(3)
d(B–P)	2.028(2)	1.9701(18)	1.967(3)	1.966(4), 1.950(4)
X–B–X	111.68(15), 110.96(14), 110.57(15)	111.03(8), 110.55(9), 111.15(10)	110.84(16), 110.25(15), 111.25(16)	109.14(15)– 113.06(13)
X–B–P	108.55(13), 107.89(12), 107.00(12)	109.21(8), 107.30(9), 107.47(8)	108.62(16), 107.21(15), 108.55(16)	105.76(15) – 111.29(16)

All four complexes feature pseudo-tetrahedral boron(III) centres with the staggered diphosphine bridging and similar <X–B–X. The *d*(B–P) is longest in the fluoride complex (Table 1), but for the other three the differences in bond length are not statistically significant. DFT calculations have shown that for strongly bonded BX_3 complexes, the bond length does not always correlate with bond strength, and that bond strength does not always correlate with the intrinsic interaction energy (i.e. donor-acceptor strength).[6(b),18] Moreover, it also clear that in some systems intermolecular interactions, solvation and packing effects in the solids complicate the interpretations.[1,23] While the d(B–P) of $[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ and $[BX_3(PMe_3)]$ are identical when X = F, and similar when X = Cl (1.9701(18) and 1.957(5) Å, respectively[19]), the d(B–P) when X = Br and I are considerably shorter for $[BX_3(PMe_3)]$ (1.967(3) *vs.* 1.924(12) Å for X = Br; 1.950(4)–1.966(4) *vs.*1.918(15) Å for X = I).[19] This can be attributed to the greater steric bulk of the diphosphine ligand, which prevents $Et_2P(CH_2)_2PEt_2$ approaching the boron centre as closely as PMe_3 does when the halide involved is large. The *d*(B–X) are comparable in $[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ and $[BX_3(PMe_3)]$ (X = F, Cl, Br and I).[19]

Despite several attempts, a bulk sample of $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ could not be isolated from the reaction of $[BF_3(SMe_2)]$ with the diphosphine, the reactions producing oils with significant amounts of phosphonium tetrafluoroborate present. However, bubbling BF_3 gas into a solution of the ligand in *n*-hexane readily produced a high yield of $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ as a white powder. This complex is extremely readily hydrolysed both in the solid state and solution with release of ‘free’ phosphine, and a solution in anhydrous CH_2Cl_2 after 12 h in glass tubes shows ^{19}F NMR resonances of $[SiF_5]^-$ and $[SiF_6]^{2-}$; the

$[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (X = Cl, Br, I) were obtained as white powders and are much less readily hydrolysed. The complex, $[(BF_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$, was obtained from BF_3 and $Me_2P(CH_2)_2PMe_2$ in *n*-hexane, and in an impure form from $[BF_3(SMe_2)]$ and $Me_2P(CH_2)_2PMe_2$ in a 2:1 molar ratio in anhydrous CH_2Cl_2. The complex is also extremely sensitive to moisture and dioxygen and in CH_2Cl_2 solution it decomposes rapidly, generating $[BF_4]^-$. The chloro analog, $[(BCl_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$, was obtained from $[BCl_3(SMe_2)]$ and ligand in a 2:1 molar ratio, and appears to be stable in solution in the absence of moisture. The IR spectra of both series of complexes show the expected ν(BX) stretches for complexes possessing C_{3v} symmetry at boron.[24] None of these complexes showed evidence in the multinuclear NMR spectra for the presence of ionic species $[BX_2(L\text{–}L)][BX_4]$.

Multinuclear NMR spectroscopic data are given in Table 2; in each case there was a single species present in solution, identified as the neutral ligand-bridged complex on the basis of the coupling patterns and the absence of a $[BX_4]^-$ resonance in the ^{11}B NMR spectrum.

Table 02 Selected NMR spectroscopic data for $[(BX_3)_2\{\mu\text{-}R_2P(CH_2)_2PR_2\}]$ (R = Et, X = F, Cl, Br, I; R = Me, X = F, Cl)

Complex	$\delta(^1H)$ / 295 K^a	$\delta(^{31}P\{^1H\})$ / 295 K^a	$\delta(^{11}B)$ / 295 K^b	$^1J_{PB}$ / Hz
$[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$	1.12 (t) 1.84 (br) 1.91 (br)	–3.8 (br)	+2.09 (dq) $^1J_{BF}$ = 53 Hz,	176
$[(BCl_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$	1.30 (dt) 2.02-2.17 (m) 2.36 (d)	+3.0 ^{c}	+3.39 (d)	155
$[(BBr_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$	1.34 (dt) 2.13-2.28 (m) 2.55 (d)	–0.8 ^{c}	–14.82 (d)	146
$[(BI_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$	1.41 (dt) 2.29-2.45 (m) 2.82 (d)	–11.6 ^{c}	–72.11 (d)	129
$[(BF_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$	1.37 (br), 1.84(br)	–17.7 (br)	+2.08 (br)	not resolved
$[(BCl_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$	1.63 (d), 2.36 (d)	–4.5 ^{c}	+3.42 (d)	160

[a] CD_2Cl_2; [b] CH_2Cl_2/CD_2Cl_2; [c] the expected quartet shows further splitting due to AA'XX' spin system (*vide infra*).

As observed for $[BX_3(PMe_3)]$ (X = F, Cl, Br, I),[25] the resonances in the ^1H NMR spectra of $[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ move to successively higher frequencies as the halogen group is descended. The resonances in the $^{31}P\{^1H\}$ NMR spectra are all to high frequency of $Et_2P(CH_2)_2PEt_2$ ($\delta = -18$); for X = Cl, Br, I, the coordination shift (Δ) becomes smaller down the group, trends that have also been reported for $[BX_3\{P(CH{=}CH_2)_3\}]$.[20] The $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ is anomalous, with $\Delta = +14.2$, possibly reflecting the weaker coordination of the phosphine to BF_3. A similar trend is seen for the corresponding $Me_2P(CH_2)_2PMe_2$ complexes (Table 2), and we reported a similar pattern for $[TiX_4(\text{diphosphine})]$ (X = F, Cl, Br, I).[26]

The increased shielding of the boron centre upon ligand coordination is evident in the ^{11}B NMR spectra, with $[(BI_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ showing the greatest degree of shielding ($\delta(BI_3) = -7.9$, $\Delta = -64.2$; $\delta(BBr_3) = 38.7$, $\Delta = -53.5$; $\delta(BCl_3) = 46.5$, $\Delta = -43.1$; $\delta(BF_3) = +12.0$, $\Delta = -9.9$),[27] parallel to the generally accepted order of Lewis acidity. Each ^{11}B NMR spectrum consists of a doublet, with the $^1J_{PB}$ coupling constant decreasing as the halide gets heavier, which has been attributed to a decrease in the *s*-character of the P–B bond with decreasing electronegativity of X.[20]

The resonances in the $^{31}P\{^1H\}$ NMR spectra of $[(BX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (X = Cl, Br I) are not simple four line patterns as expected (from coupling to the quadrupolar ^{11}B, I = 3/2 nucleus), but display eight lines. Although the complex is less soluble, the $^{31}P\{^1H\}$ NMR spectrum of $[(BCl_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$ was also an eight line pattern (Fig. 3(a)).

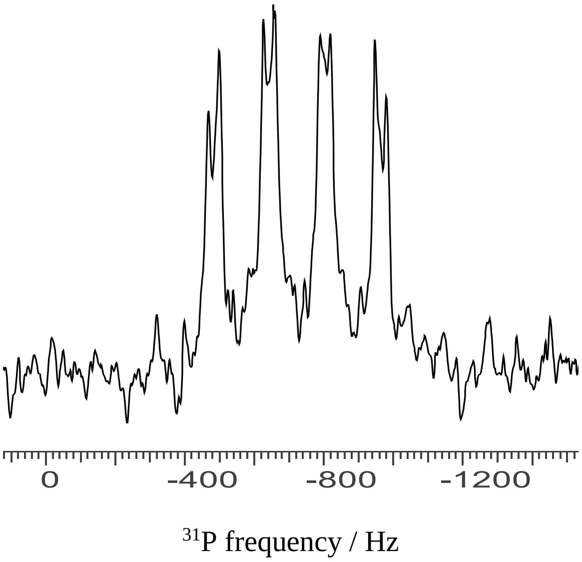


Figure 03(a) $^{31}P\{^1H\}$ NMR spectrum of $[(BCl_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$ in CD_2Cl_2 at 295 K. Coupling to ^{10}B **I=** 3; 19.6% abundant, $Q = 8.5 \times 10^{-30}$ m^2) is not resolved.

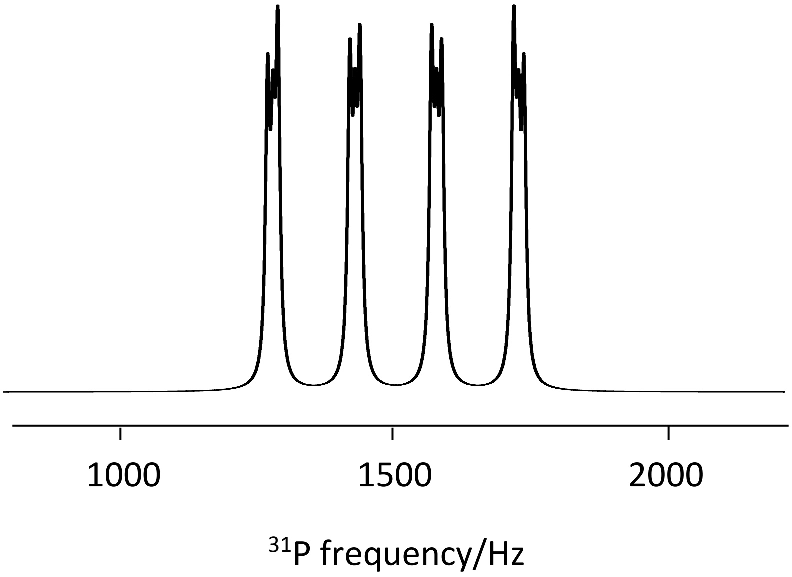
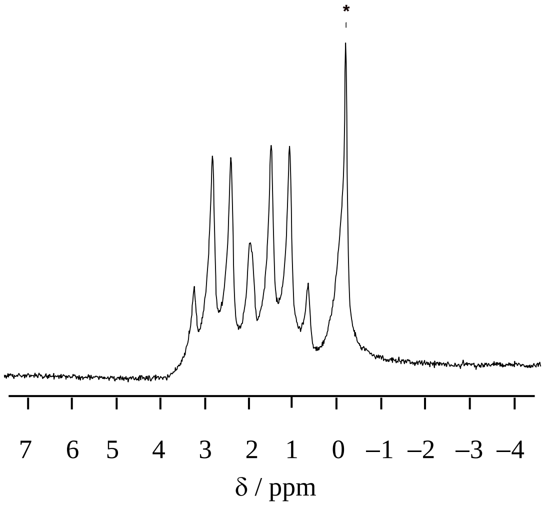


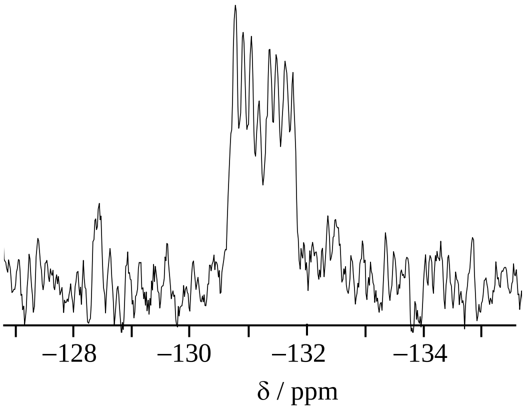
Figure 3(b) Simulated ^{31}P NMR spectrum for an AA'XX' spin system where A = ^{31}P and X = ^{11}B with J_{AX} = $J_{A'X'}$ = 160 Hz and $J_{AA'}$ = 30 Hz.

The two phosphorus nuclei are symmetrically equivalent, but because $J_{AX} \neq J_{AX'}$, they are not magnetically equivalent and so the spectrum is that of an AA′XX′ spin system with A = ^{31}P and X = ^{11}B, in which J_{PP} affects the spectrum. To test this interpretation the ^{31}P NMR spectrum was simulated using Spinach.[28] The predicted spectrum with J_{AX} = $J_{A'X'}$ = 160 Hz, $J_{AA'}$ = 30 Hz (to match the experimentally observed coupling constants) and all other couplings at zero can be seen in Fig. 3(b).

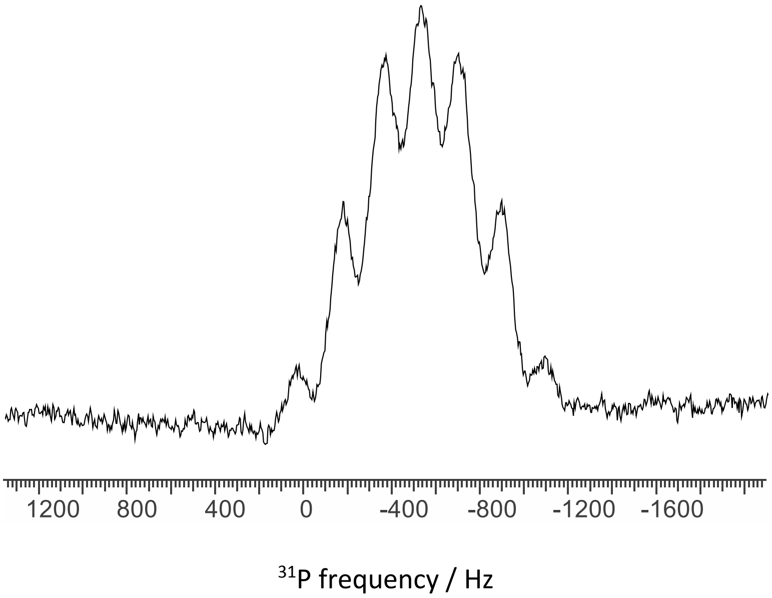
The solution NMR spectra (CH_2Cl_2) of $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ are shown in Fig 4. The ^{11}B NMR spectrum (Fig. 4a) shows a doublet of quartets for the neutral species and a resonance close to 0 ppm, which increases in relative intensity over time, indicative of the formation of $[BF_4]^-$ by decomposition. The ^{19}F NMR spectrum (Fig. 4b) is also a doublet of quartets due to coupling to ^{31}P and ^{11}B, respectively. Both of these spectra were satisfactorily analyzed as first order. The ^{31}P{^{1}H} NMR spectrum (Fig. 4c) shows seven lines and this was satisfactorily simulated (also 1st order) using the coupling constants determined from the ^{11}B and ^{19}F NMR spectra (Fig. 4d).



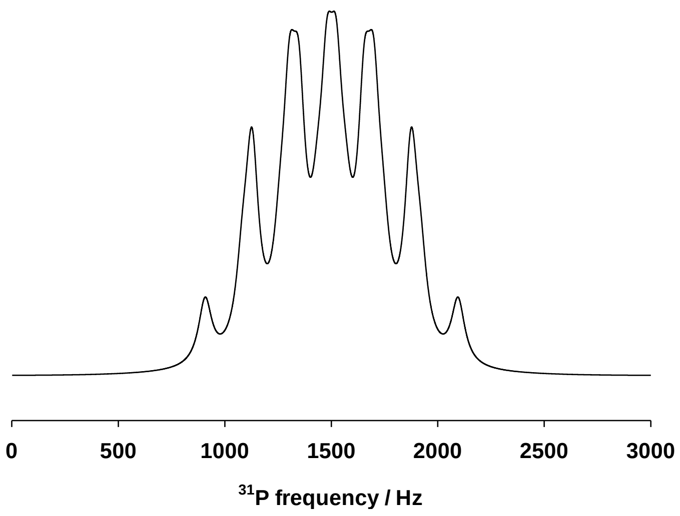
(a)


−128
−130
−132
−134
δ / ppm

(b)


1200
800
400
0
-400
-800
-1200
-1600
31P frequency / Hz

(c)



(d)

Figure 4 (a) ^{11}B (* = $[BF_4]^-$ from hydrolysis – see text), (b) ^{19}F and (c) ^{31}P{^{1}H} NMR spectrum of $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ in CD_2Cl_2 at 295 K; (d) simulation of the ^{31}P NMR spectrum with the coupling constants $^2J_{PF}$ = 220 Hz, $^1J_{PB}$ = 176 Hz.

The analogous $[(BF_3)_2\{\mu\text{-}Me_2P(CH_2)_2PMe_2\}]$ is less soluble, and more strongly coordinating solvents caused decomposition. At room temperature in CD_2Cl_2 the peaks were broad and unresolved, but upon cooling below 273 K, coupling could clearly be seen in the ^{19}F and ^{11}B NMR spectra, and was partially resolved in the ^{31}P{^{1}H} NMR spectrum. Full details of the low temperature spectra are included in the Experimental and parallel the behavior of the $[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$.

Cationic complexes with the diphosphine ligand *o*-$C_6H_4(PMe_2)_2$

The reaction of the $[BCl_3(SMe_2)]$ in anhydrous CH_2Cl_2 and BBr_3 or BI_3 in n-hexane solution with the diphosphine *o*-$C_6H_4(PMe_2)_2$ in a 2:1 molar ratio produced $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}][BX_4]$ (X = Cl or Br) and $[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}]I$ respectively. The diphosphine is pre-organized for chelation, and the same products were obtained irrespective of the ratio of reagents used. This ligand also chelates to the other Group 13 metal ions, forming six-coordinate cations with Al(III)[23(d)] and Ga(III)[29] of type *trans*-$[MX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][MX_4]$ (M = Al, Ga, X = Cl, Br or I) (although AlF_3 and GaF_3 complexes with phosphines do not form),[30] whilst with In(III)[31] four-coordinate $[InX_2\{o\text{-}C_6H_4(PMe_2)_2\}][InX_4]$, six-coordinate *trans*-$[InX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][InX_4]$ and halide-bridged dimers $[In_2X_4(\mu\text{-}X)_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ are known. Crystals containing the three cations were grown from CH_2Cl_2-n-hexane (Figs. 5a-c), those of the iodide as a triiodide(1-) salt. While there are numerous crystal structures containing $[BCl_4]^-$, and several with $[BBr_4]^-$, there is only one crystallographically authenticated example of $[BI_4]^-$ in $[Ph_3PCH_2P(OBI_3)Ph_2][BI_4]$,[32] suggesting that it does not readily form. The complexes are the first crystallographically authenticated examples of BX_2^+ cations with a neutral diphosphine ligand. A small number of mixed halo/hydrido and hydrido boronium cations have been described.[33]

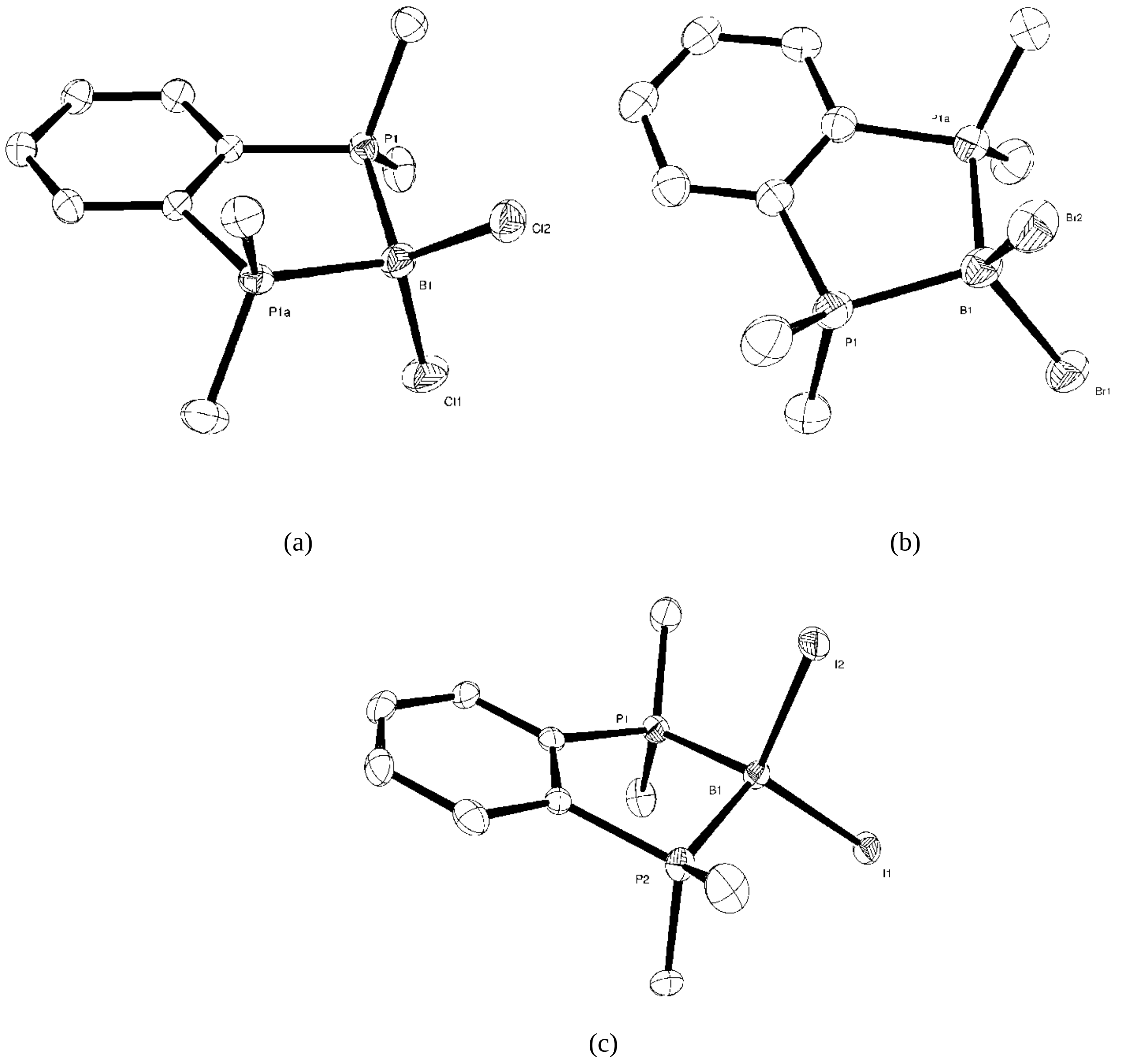


Figure 5 The structure of the cation in (a) [BCl_2{o-$C_6H_4(PMe_2)_2$}][BCl_4] (symmetry operation: a = – x, y, z); (b) [BBr_2{o-$C_6H_4(PMe_2)_2$}][BBr_4] (symmetry operation: a = x, 1/2 – y, z); (c) [BI_2{o-$C_6H_4(PMe_2)_2$}][I_3]. In each case the atom labelling scheme is shown, ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for the [BX_2{o-$C_6H_4(PMe_2)_2$}]$^+$ cations (X = Cl, Br, I)

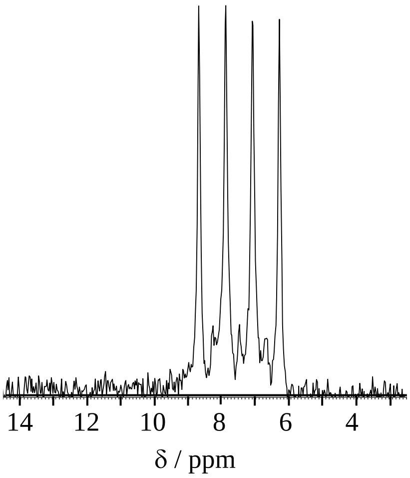
	X = Cl	X = Br	X = 1
B1–X	1.836(5), 1.832(5)	2.003(6), 2.007(6)	2.197(6), 2.224(6)
B1–P	1.990(3)	1.974(4)	1.961(6), 1.930(7)
P1–B1–P1a	99.8(2)	101.1(3)	99.4(3) (P1–B–P2)

X–B1–X	115.0(3)	114.8(3)	114.1(3)

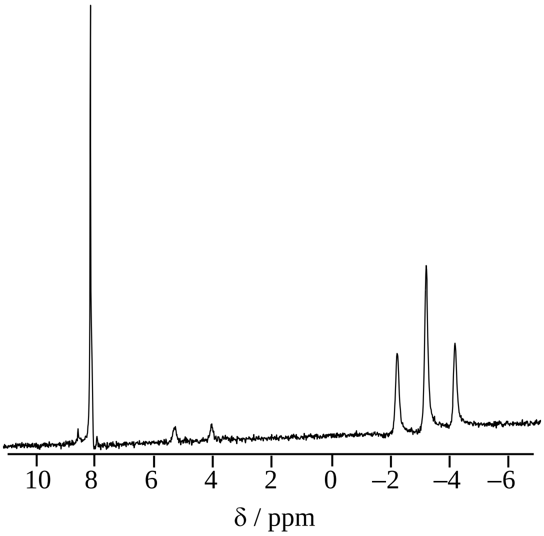
All three $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ cations have pseudo-tetrahedral boron centres, distorted by the chelate bite angle of $o\text{-}C_6H_4(PMe_2)_2$ (<P–B–P = ~100°). The angles around the boron are little affected by the halide present. Unlike the symmetric chelation seen in the chloro and bromo complexes, in $[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ the diphosphine is asymmetrically chelated, with *d*(B–P) = 1.961(6) and 1.930(7) Å. As the halide gets heavier there is a decrease in the *d*(B–P). The *d*(B–X) are ~0.02 Å shorter in the $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ cations compared to the corresponding neutral $[BX_3(PMe_3)]$ (X = Cl, Br, I) complexes,[17] whilst the $[BCl_4]^-$ and $[BBr_4]^-$ anions have slightly longer *d*(B–X) than the cations.

The reaction of $o\text{-}C_6H_4(PMe_2)_2$ with $[BF_3(SMe_2)]$ in CH_2Cl_2 or BF_3 gas in *n*-hexane immediately precipitated a fine white powder, identified as $[BF_2\{o\text{-}C_6H_4(PMe_2)_2\}][BF_4]$. The complex is insoluble in CH_2Cl_2 and acetone and is decomposed by MeCN, dmf or dmso. It dissolves in nitromethane, allowing spectroscopic measurements, but this solution also decomposes over time and was not suitable for crystal growth. A powder was also produced on allowing BF_3 gas to diffuse into a solution of $o\text{-}C_6H_4(PMe_2)_2$ in *n*-hexane and thus crystals of the fluoride complex could not be obtained. The reaction of $[BCl_3(SMe_2)]$ with $o\text{-}C_6H_4(PPh_2)_2$ in a 2:1 molar ratio in CH_2Cl_2 resulted only in the recovery of $o\text{-}C_6H_4(PPh_2)_{2,}$ which suggests that although pre-organized for chelation, its much greater steric bulk (and weak σ-donor power) prevents it from chelating to the small boron centre. We note that PPh_3, a monodentate phosphine with a similar *σ*-donor strength, readily forms the complexes $[BX_3(PPh_3)]$.[34]

The IR spectra of the $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}][BX_4]$ (X = F, Cl, Br) show the expected vibrations of the anions,[35] and in addition, each shows two bands which can be assigned as the a_1 and b_1 vibrations of the BX_2^+ cations. Multinuclear NMR spectroscopic data for the $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ (X = Cl, Br, I) cations are given in Table 4, Fig. 6, and the ^{11}B NMR spectra show the expected resonances for the $[BX_4]^-$ anions (X = Cl or Br).[36] The coupling patterns seen in the $^{31}P\{^1H\}$ and ^{11}B NMR spectra are consistent with a BX_2 moiety coordinated to a chelating diphosphine ligand. The resonances in the $^{31}P\{^1H\}$ NMR spectra have shifted to a much higher frequency from free $o\text{-}C_6H_4(PMe_2)_2$ (δ = –55) and differ very little with X, whilst the $^1J_{PB}$ coupling decreases Cl > Br > I. There is however no clear trend in the shielding of the boron centre when moving from a $[BX_3L]$ to a $[BX_2(L\text{–}L)]^+$ complex, as the resonance in the ^{11}B NMR spectrum of $[BCl_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ is to low frequency of that in $[(BCl_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$, whereas $[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ is at a much higher frequency than $[(BI_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$.



(a)



(b)

Figure 6 (a) $^{31}P\{^1H\}$ NMR spectrum and (b) ^{11}B NMR spectrum of $[BCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][BCl_4]$ (CH_2Cl_2/CD_2Cl_2, 295 K).

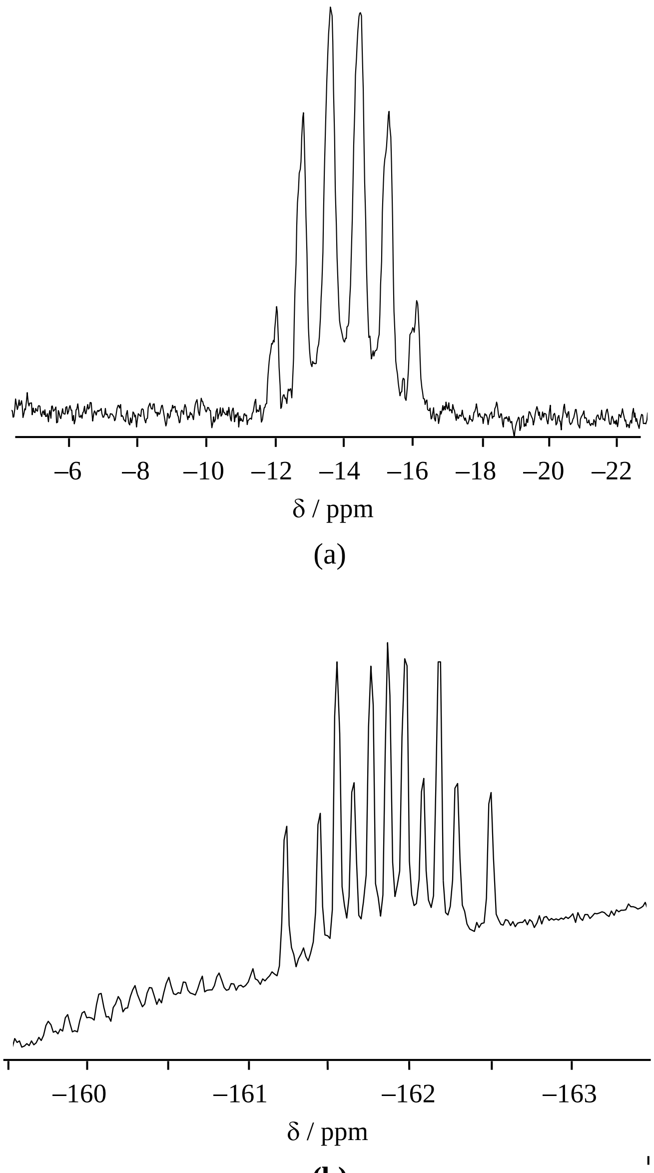
Table 4 Selected NMR spectroscopic data for $[BX_2\{o\text{-}C_6H_4(EMe_2)_2\}]^+$ (E = P, As; X = F, Cl, Br, I)

Complex Cation	^1H δ(CH_3)	$^{31}P\{^1H\}$	^{11}B	$^{19}F\{^1H\}$
$[BF_2\{o\text{-}C_6H_4(PMe_2)_2\}]^{+a}$	2.33 (br s)	–14.3 (qt) $^1J_{PB}$ = 140 Hz $^2J_{PF}$ = 121 Hz	+6.4 (tt) $^1J_{BF}$ = 81 Hz	–161.9 (qt)
$[BCl_2\{o\text{-}C_6H_4(PMe_2)_2\}]^{+b}$	2.06 (t)	+7.5 (q) $^1J_{PB}$ = 125 Hz	–3.17 (t)	-
$[BBr_2\{o\text{-}C_6H_4(PMe_2)_2\}]^{+b}$	2.23 (t)	+7.7 (q) $^1J_{PB}$ = 119 Hz	–14.02 (t)	-
$[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}]^{+b}$	2.35 (m)	+7.2 (q) $^1J_{PB}$ = 110 Hz	–43.5 (t)	-

$[BF_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^{+a}$	2.91 (s)	-	+0.3 (s)	–149.8 (s)
$[BCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^{+b}$	2.08 (s)	-	–1.16(s)	-
$[BBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^{+b}$	2.17 (s)	-	-14.25(s)	-
$[BI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^{+b}$	2.10(s)	-	–74.3(s)	-

All spectra recorded at 295 K – see Experimental for low temperature data; [a] CD_3NO_2; [b] CD_2Cl_2

As indicated above, the $[BF_2\{o\text{-}C_6H_4(PMe_2)_2\}][BF_4]$ is soluble only in $MeNO_2$ and decomposes on standing in this solvent, but multinuclear spectra obtained immediately from freshly prepared solutions show NMR spectra consistent with an AM_2X_2 system for the cation, with A = ^{11}B, M =^{31}P, X= ^{19}F (Fig. 7).



(a)

(b)

Figure 7 (a) $^{31}P\{^{1}H\}$ NMR spectrum and (b) ^{19}F NMR spectrum of [$BF_2\{o\text{-}C_6H_4(PMe_2)_2\}$][$BF_4$] ($CD_3NO_2$, 295 K) (note that the rolling baseline is due to the Teflon in the probe).

Cationic complexes with the diarsine ligand *o*-$C_6H_4(AsMe_2)_2$

The first boron halide complexes of a diarsine ligand were isolated using *o*-$C_6H_4(AsMe_2)_2$, which like the diphosphine analog, is pre-organized for chelation. The reaction of [$BCl_3(SMe_2)$] with *o*-$C_6H_4(AsMe_2)_2$ in a 2:1 molar ratio in CH_2Cl_2 solution yielded a few colorless crystals of [$BCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}$][$BCl_4$] (Fig. 8), with a pseudo-tetrahedral cation and a tetrahedral anion.

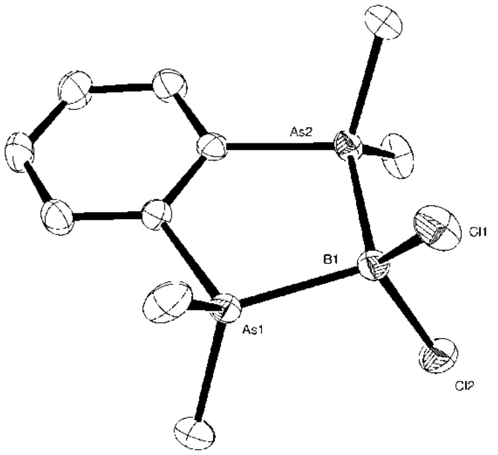


Figure 8 The structure of the cation in [$BCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}$][$BCl_4$]showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–Cl1 = 1.819(3), B1–Cl2 = 1.815(3), B1–As1 = 2.067(3), B1–As2 = 2.083(3), Cl1–B1–Cl2 = 114.51(16), As1–B1–As2 = 99.57(13).

The coordination environment around the boron centre in [$BCl_2\{o\text{-}C_6H_4(EMe_2)_2\}$]$^+$ (E = P, As) is virtually unaffected by the change in donor atom from phosphorus to arsenic; the cations feature similar angles around the boron centre, and the differences in *d*(B–Cl) are small and the *d*(B–As) and *d*(B–Cl) are comparable to those seen for [$BCl_3(AsMe_3)$],[22] whilst comparison of d(B–P) and d(B–As) for [$BCl_2\{o\text{-}C_6H_4(EMe_2)_2\}$]$^+$ reveals an increase of *ca*. 0.08 Å from E = P to E = As. Attempts to isolate bulk samples of [$BX_2\{o\text{-}C_6H_4(AsMe_2)_2\}$]$^+$ from CH_2Cl_2 solutions containing the diarsine and [$BX_3(SMe_2)$] (X = F or Cl) or BX_3 (X = Br or I) failed, but white powdered samples of all four complexes precipitated from n-hexane solutions using the appropriate BX_3 as the boron source. The microanalyses for the three heavier halide complexes were consistent with the formulations [$BX_2\{o\text{-}C_6H_4(AsMe_2)_2\}$][$BX_4$] (X = Cl or Br) and [$BI_2\{o\text{-}C_6H_4(AsMe_2)_2\}$]I, and these are also consistent with the IR and multinuclear NMR spectroscopic data (Table 4). The ^1H NMR spectra of these three complexes in CD_2Cl_2 all show a mixture of the complex and uncoordinated *o*-$C_6H_4(AsMe_2)_2$, due to dissociation in solution, the amount of free diarsine increasing I < Br < Cl, which may explain why the complexes could not be isolated from this solvent, whereas they are insoluble in n-hexane, resulting in immediate precipitation. Several batches of the BF_3-diarsine adduct had consistent analyses which fitted the composition [$BF_2\{o\text{-}C_6H_4(AsMe_2)_2\}$][$B_2F_7$] rather than [$BF_2\{o\text{-}C_6H_4(AsMe_2)_2\}$][$BF_4$], perhaps not unreasonable since the synthesis used excess BF_3. As found for the diphosphine analog described above, this salt is insoluble in or decomposed by most common solvents; it dissolves in CD_3NO_2 with extensive decomposition, although the ^1H, ^{11}B and ^{19}F NMR resonances of the cation can be identified in the solution (Table 4). Notably, the spectra show singlets in the ^{11}B and ^{19}F spectra, consistent with rapid exchange. There are strong $[BF_4]^-$ resonances in the spectra, some of which come from decomposition of the salt. The $[B_2F_7]^-$ ion is known to be unstable in solution (exchanging with $[BF_4]^-$ and F^-) and the NMR data do not resolve the question of its presence in the complex. The IR spectrum of the solid shows bands at 1240 and 830 cm^{-1} which may be due to $[B_2F_7]^-$.[37] The diarsine complexes are the first examples of boronium salts with arsenic donor ligands, but are markedly less stable than the phosphine analogs. This can be attributed to a poorer match of orbital size and energy between the larger, softer arsenic and the boron centre.

Phosphine oxide complexes

Phosphine oxide complexes of BX_3 are well known,[38] but there are no reported complexes with diphosphine dioxides, and so reactions with $Ph_2P(O)CH_2(P(O)Ph_2$ were briefly explored to provide comparisons with the diphosphines. The reaction of $[BCl_3(SMe_2)]$ with $Ph_2P(O)CH_2P(O)Ph_2$ in a 2:1 molar ratio in CH_2Cl_2 yielded crystals of $[(BCl_3)_2\{\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2\}]$ (see ESI). The reactions involving BF_3 proved more complex. A *n*-hexane suspension of $Ph_2P(O)CH_2P(O)Ph_2$ saturated with excess BF_3 gas, produced a white powder formulated as $[(BF_3)_2(\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2)]$ on the basis of the spectroscopic and microanalytical data (see Experimental section). In contrast, reacting $[BF_3(SMe_2)]$ and $Ph_2P(O)CH_2P(O)Ph_2$ in CH_2Cl_2 in a 2:1 molar ratio gave a mixture containing both the $[(BF_3)_2(\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2)]$ and a second product. A few crystals grown from the reaction were shown by a single crystal X-ray study to be the ionic complex $[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}][B_2F_7]$ (Fig. 9). The cation features a BF_2 moiety with an almost symmetrically chelating $Ph_2P(O)CH_2P(O)Ph_2$ ligand, giving a slightly distorted tetrahedral boron centre. The anion is a rare example of a crystallographically authenticated $[B_2F_7]^-$ salt.[22,39] It is composed of a single fluorine atom bridging between two BF_3 fragments, the terminal *d*(B–F) range from 1.326(7) to 1.406(7) Å, while the bridging *d*(B–F) are 1.499(7) and 1.532(8) Å and the B2–F6–B3 angle is 128.6(4)°, consistent with the literature. The reaction was repeated varying the $[BF_3(SMe_2)]$: $Ph_2P(O)CH_2P(O)Ph_2$ ratio, but always produced mixtures of the two complexes, although in varying amounts, and fractional crystallisation failed to separate bulk quantities of the ionic species, which is clearly in equilibrium with the dimer in solution.

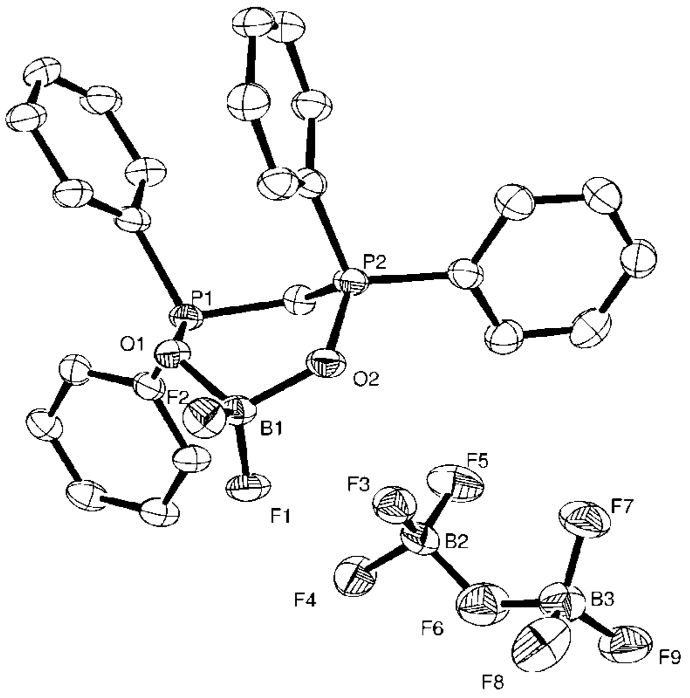


Figure 9 View of the structure of $[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}][B_2F_7]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–O1 = 1.517(6), B1–O2 = 1.512(6), B1–F1 = 1.353(5), B1–F2 = 1.351(6), P1–O1 – 1.538(3), P2–O2 = 1.542(3), F1–B1–F2 = 114.7(4), O1–B1–O2 = 107.6(4), B1–O1–P1 = 127.6(3), B1–O2–P2 = 127.5(3).

Multinuclear NMR data for the $[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}]^+$ (taken from the mixture) revealed a $^{31}P\{^1H\}$ NMR resonance as a triplet ($^3J_{PF}$ = 9 Hz) at $\delta = 50.0$, $^{19}F\{^1H\}$ NMR spectrum consists of a triplet ($^3J_{PF}$ = 9 Hz) at $\delta = -138.2$. The sharp singlet for $[BF_4]^-$ is located at $\delta = 0.15$ in the ^{11}B NMR spectrum, next to a broad resonance centred at $\delta = 0.51$; here separate peaks for the ionic and neutral complexes (which are thought to have similar chemical shifts) cannot be distinguished.[40]

Conclusions

The boron(III) halides have been shown to complex to a number of neutral phosphine ligands, with several novel four-coordinate diphosphine complexes having been synthesized and characterized both structurally and spectroscopically. The X-ray crystal structure of $[BF_3(PMe_3)]$ has been solved for the first time, allowing structural comparisons to be made with $[BX_3(PMe_3)]$ (X = Cl, Br, I).[17] It was shown that with the flexible diphosphine ligands $R_2P(CH_2)_2PR_2$ (R = Me, Et) the only complexes observed were the neutral bridging ligand complexes $[(BX_3)_2\{\mu\text{-}R_2P(CH_2)_2PR_2\}]$ (X = F, Cl, Br, I), and for $Et_2P(CH_2)_2PEt_2$, crystal structure determinations were obtained for all four halides. Ionic complexes are exclusively formed however with sterically small and rigid bidentate ligands that are pre-organized for chelation, and this work includes the first structurally authenticated examples of ionic boron(III) halide complexes with chelating neutral diphosphine and diarsine ligands, $[BX_2\{o\text{-}C_6H_4(PMe_2)_2\}]^+$ (X = Cl, Br, I) and $[BCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^+$, which possess C_{2v} symmetry at boron. The phosphine complexes all show very large high frequency shifts relative to free ligand in their $^{31}P\{^1H\}$ NMR spectra, which are much larger in magnitude than those observed in the corresponding AlX_3 systems.[28] In the ^{11}B NMR spectra $^1J_{BP}$ decreases as the atomic number of the halogen increases, a trend that has been reported for a number of neutral phosphine adducts of BX_3.[20,25,26] Although the differences are sometimes small (and individually may not be considered statistically significant), for all the X-ray structures reported the d(B–P) decrease as the halide gets heavier, which is consistent with the order of Lewis acidity towards neutral phosphine and arsine ligands being $BI_3 > BBr_3 \sim BCl_3 >> BF_3$.

The behavior of BX_3 (X = F, Cl) towards the neutral diphosphine dioxide ligand $Ph_2P(O)CH_2P(O)Ph_2$ has also been investigated and, unexpectedly for a flexible bidentate ligand, the X-ray crystal structure of the ionic chelating ligand complex $[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}][B_2F_7]$ was obtained. However multinuclear NMR spectroscopic data showed that in solution the ionic complex was actually in equilibrium with the neutral bridging ligand complex $[(BF_3)_2\{\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2\}]$. In the BCl_3 system there was no evidence of the ionic complex forming, and so its existence in the BF_3 system was attributed to the formation of the unusual $[B_2F_7]^-$ anion.

The phosphine complexes with BX_3 (X = Cl, Br, I) were found to be robust, showing little sign of oxidation or hydrolysis in CH_2Cl_2 solution or when stored over time under an inert atmosphere. Complexes with BF_3 were found to be more prone to hydrolysis in solution.

Experimental Section

All preparations were carried out under rigorously anhydrous conditions *via* a dry dinitrogen atmosphere and standard Schlenk and glove-box techniques. Boron trifluoride was obtained from Fluorochem. Other boron trihalides were obtained commercially (Aldrich) and used as received. The $[BF_3(OEt_2)]$, $[BF_3(SMe_2)]$, $[BCl_3(SMe_2)]$ and the ligands were obtained commercially (Strem or Aldrich), apart from $o\text{-}C_6H_4(PMe_2)_2$ and $o\text{-}C_6H_4(AsMe_2)_2$ which were made by the literature methods.[41] Solvents were dried by distillation from CaH_2 (CH_2Cl_2, MeCN) or sodium benzophenone ketyl (n-hexane, toluene). IR spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 spectrometer over the range 4000−200 cm^{-1}. ^1H, ^{11}B, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded using Bruker AV400 spectrometer and referenced to the residual solvent resonance, external $[BF_3(OEt_2)]$, $CFCl_3$ and external 85% H_3PO_4 respectively. Microanalytical measurements were performed by London Metropolitan University.

$[BF_3(PMe_3)]$ (1): To a solution of PMe_3 (0.098 g, 1.29 mmol) in CH_2Cl_2 (5 mL) was added $[BF_3(SMe_2)]$ (0.170 g, 1.31 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2.5 h. The solvent volume was reduced to about 5 mL *in vacuo*, onto which n-hexane (8 mL) was layered. Colorless crystals suitable for single crystal X-ray diffraction study formed. These were isolated by filtration and dried *in vacuo* to give a white powder. Yield: 0.089 g (48%). Anal. Calc. for $C_3H_9BF_3P$: C, 25.0; H, 6.3. Found: C, 24.9; H, 6.2%. ^1H NMR (CD_2Cl_2, 295 K): δ 1.41 (d, $^2J_{HP}$ = 11.3 Hz, CH_3). $^{19}F\{^1H\}$ (CD_2Cl_2, 295 K): δ –140.1 (dq,

$^1J_{BF}$ = 50 Hz , $^2J_{PF}$ = 236 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295K): δ –28.5 (qq, $^1J_{PB}$ = 176 Hz, $^2J_{PF}$ = 236 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 1.88 (dq, $^1J_{BF}$ = 50 Hz, $^1J_{BP}$ = 176 Hz). IR (Nujol): ν = 1060 (vs, br), 860(s), 635 (vs) (BF) cm^{-1}.

[$BF_3(AsMe_3)$] (2): Trimethylarsine (0.12 g, 1.0 mmol) was dissolved in n-hexane (25 mL) and a slow stream of BF_3 gas was bubbled through the solution for 5 min., during which a flaky white solid precipitated. The BF_3 stream was turned off and the suspension stirred for 30 min. producing a white powder, which was filtered off and dried *briefly* in *vacuo* (prolonged pumping in *vacuo* leads to loss of the sample). Yield 0.075g, 40%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.19 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ –148.4 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 0.06 (s). IR (Nujol): ν = 1059 (vs), 820 (m), 641(m) (BF) cm^{-1}.

[$(BF_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (3): $Et_2P(CH_2)_2PEt_2$ (0.10 g, 0.5 mmol) was dispersed in n-hexane (20 mL) and a slow stream of BF_3 gas was bubbled through the solution for 5 min. An immediate white precipitate formed. After allowing the mixture to stand for 30 min., the solvent and excess BF_3 were removed *in vacuo*, leaving a fine white powder which was rinsed with n-hexane (5 mL), the powder separated by filtration and dried *in vacuo*. Yield: 0.26 g, (75%). Anal. Calc. for $C_{10}H_{24}B_2F_6P_2$: C, 35.1; H, 7.1. Found: C, 35.2; H, 6.8%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.21 (t, [12H], $^3J_{HH}$ = 10 Hz, CH_3), 1.84 (br s), 1.91 (br s, overlapping, total [12H], CH_2). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ –130.6 (br m, ill-defined couplings); (245 K): δ –131.3 (dq, $^1J_{BF}$ = 53 Hz, $^2J_{PF}$ = 220 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –3.8 (br, s); (223 K): δ –2.7 (br m - see text). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +2.09 (dq, $^1J_{BF}$ = 53 Hz, $^1J_{PB}$ = 176 Hz); (223 K): δ +1.96 (dq). IR (Nujol): ν = 1076 (vs), 876 (vs), 621 (s) (BF) cm^{-1}. *Crystals were obtained as follows:* to a solution of [$BF_3(SMe_2)$] (0.128 g, 0.99 mmol) in CH_2Cl_2 (5 mL) was added $Et_2P(CH_2)_2PEt_2$ (0.102 g, 0.49 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2 h. The solvent volume was reduced to about 5 mL *in vacuo*, then the solution was layered with n-hexane (8 mL) whereupon small colorless crystals suitable for single crystal X-ray diffraction study grew. Attempts to obtain a bulk sample by this route were unsuccessful, an oily residue being obtained upon further concentration.

[$(BCl_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (4): To a solution of [$BCl_3(SMe_2)$] (0.130 g, 0.72 mmol) in CH_2Cl_2 (5 mL) was added $Et_2P(CH_2)_2PEt_2$ (0.075 g, 0.36 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2 h. The solvent volume was reduced to about 2.5 mL *in vacuo* whereupon a white powder precipitated out. The powder was isolated by filtration and dried *in vacuo*. Yield: 0.082 g (51%). Anal. Calc. for $C_{10}H_{24}B_2Cl_6P_2$: C, 27.3; H, 5.5. Found: C, 27.4; H, 5.6%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.30 (dt, [12H], $^3J_{HH}$ = 8 Hz, $^2J_{PH}$ = 12 Hz, CH_3), 2.02-2.17 (m, [8H], CH_2), 2.36 (d, [4H], $^3J_{PH}$ = 12 Hz, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ 3.0 ($^1J_{PB}$ = 155 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 3.39 (d, $^1J_{PB}$ = 155 Hz). IR (Nujol): ν =710 (vs), 389 (m) (BCl) cm^{-1}. Small colorless crystals suitable for single crystal X-ray diffraction study were obtained from layering the filtrate above with n-hexane.

[$(BBr_3)_2\{\mu$-$Et_2P(CH_2)_2PEt_2\}$] (5): To a solution of BBr_3 (0.124 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was added $Et_2P(CH_2)_2PEt_2$ (0.053 g, 0.26 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2 h.

The solvent volume was reduced to about 3 mL *in vacuo* whereupon a white powder precipitated out. The powder was isolated by filtration and dried *in vacuo*. Small colorless crystals suitable for single crystal X-ray diffraction study were obtained from layering the filtrate with hexane (7 mL). Concentrating the filtrate *in vacuo* to about 3 mL afforded a second crop of white powder, which was isolated by filtration and dried *in vacuo*. The overall yield was 0.110 g (63%). Anal. Calc. for $C_{10}H_{24}B_2Br_6P_2$: C, 17.0; H, 3.4. Found: C, 17.1; H, 3.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.34 (dt, [12H], $^3J_{HH}$ = 8 Hz, $^3J_{PH}$ = 16 Hz, CH_3), 2.13-2.28 (m, [8H], CH_2), 2.55 (d, [4H], $^2J_{PH}$ = 4 Hz, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ –0.8 ($^1J_{PB}$ = 146 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –14.82 (d, $^1J_{PB}$ = 146 Hz). IR (Nujol): ν = 613 (vs) (BBr) cm^{-1}.

[$(BI_3)_2$\{*μ*-$Et_2P(CH_2)_2PEt_2$\}] (6): To a solution of BI_3 (0.114 g, 0.29 mmol) in CH_2Cl_2 (5 mL) was added $Et_2P(CH_2)_2PEt_2$ (0.031 g, 0.15 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2 h. The solvent volume was reduced to about 3 mL *in vacuo*, then the solution was layered with n-hexane (5 mL). Large colorless block crystals suitable for single crystal X-ray diffraction study were obtained. The solvent volume was reduced to about 2 mL *in vacuo*, and the resulting white powder was isolated by filtration and dried *in vacuo*. Yield: 0.089 g (62%). Anal. Calc. for $C_{10}H_{24}B_2I_6P_2$: C, 12.1; H, 2.5. Found: C, 12.3; H, 2.5%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.41 (dt, [12H], $^3J_{HH}$ = 8 Hz, $^3J_{PH}$ = 16 Hz, CH_3), 2.29-2.45 (m, [8H], CH_2), 2.82 (d, [4H], $^2J_{PH}$ = 4 Hz, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ –11.6 ($^1J_{PB}$ = 129 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ – 72.11 (d, $^1J_{PB}$ = 129 Hz). IR (Nujol): ν = 559 (vs), 535 (vs) (BI) cm^{-1}.

[$(BF_3)_2$\{*μ*-$Me_2P(CH_2)_2PMe_2$\}] (7): To a solution of [$BF_3(SMe_2)$] (0.130 g, 1.00 mmol) in CH_2Cl_2 (5 mL) was added $Me_2P(CH_2)_2PMe_2$ (0.075 g, 0.50 mmol) in CH_2Cl_2 (5 mL) which immediately led to the precipitation of a white solid. The reaction was stirred for 1 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.053 g (37%) Anal. Calc. for $C_6H_{16}B_2F_6P_2$: C, 25.2; H, 5.6. Found: C, 25.0; H, 5.7%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.37 (br s, [12H], CH_3), 1.84 (br s, [4H], CH_2). ^{19}F NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –137.2 (br d); (273 K): δ –137.2 (dq, $^1J_{FB}$ = 51 Hz, $^2J_{FP}$ = 229 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –17.7 (br s); (223 K): δ –20.4 to –13.0 (m). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 2.08 (br s); (223 K): δ 1.90 (dq, $^1J_{BF}$ = 51 Hz , $^1J_{PB}$ = 176 Hz). IR (Nujol): ν = 1039 (vs), 852 (s), 634 (s) (BF) cm^{-1}. The complex was also made from BF_3 and $Me_2P(CH_2)_2PMe_2$ in n-hexane as described for [$(BF_3)_2$\{*μ*-$Et_2P(CH_2)_2PEt_2$\}], whereby it precipitates from the reaction mixture. Yield 94% (on the diphosphine). The sample was spectroscopically identical to that made from [$BF_3(SMe_2)$].

[$(BCl_3)_2$\{*μ*-$Me_2P(CH_2)_2PMe_2$\}] (8): To a solution of [$BCl_3(SMe_2)$] (0.119 g, 0.66 mmol) in CH_2Cl_2 (5 mL) was added $Me_2P(CH_2)_2PMe_2$ (0.050 g, 0.33 mmol) in CH_2Cl_2 (5 mL), which immediately led to the precipitation of a white solid. The reaction was stirred for 1 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.072 g (56%). Anal. Calc. for $C_6H_{16}B_2Cl_6P_2$: C, 18.7; H, 4.2. Found: C, 18.8; H, 4.1%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.63 (d, [12H], $^2J_{PH}$ = 11 Hz, CH_3), 2.36 (d, [4H], $^2J_{PH}$ = 5 Hz, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ –4.5 ($^1J_{PB}$ = 160 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 3.42 (d, $^1J_{PB}$ = 160 Hz). IR (Nujol): ν = 699 (vs), 408 (s) (BCl) cm^{-1}.

$[BF_2\{o\text{-}C_6H_4(PMe_2)_2\}][BF_4]$ (9): *Method 1*: To a solution of $[BF_3(SMe_2)]$ (0.140 g, 1.08 mmol) in CH_2Cl_2 (5 mL) was added *o*-$C_6H_4(PMe_2)_2$ (0.104 g, 0.52 mmol) in CH_2Cl_2 (5 mL) which caused the immediate precipitation of a white solid. The reaction was stirred for 1.5 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.108 g (61%). Anal. Calc. for $C_{10}H_{16}B_2F_6P_2$: C, 36.0; H, 4.8. Found: C, 36.0; H, 4.8%. ^{1}H NMR (CD_3NO_2, 295 K): δ 2.23 (br s, [12H], CH_3), 8.01-8.06 (m, [4H], *o*-C_6H_4). ^{19}F{^{1}H} NMR (CD_3NO_2, 295 K): δ –151.8 (s, [4F]), –161.9 (qt, $^1J_{BF}$ = 81 Hz, $^2J_{PF}$ = 121 Hz, [2F]). ^{31}P{^{1}H} NMR (CD_3NO_2, 295 K): δ –14.3 (qt, $^2J_{PF}$ = 121 Hz, $^1J_{PB}$ = 140 Hz). ^{11}B NMR (CD_3NO_2, 295 K): δ +6.4 (tt, $^1J_{BF}$ = 81 Hz, $^1J_{PB}$ = 140 Hz), + 0.5 (s, [B]). IR (Nujol): ν = 1054 (vs, br) ($[BF_4]^-$), 1039 (sh), 923 (s), 655 (s) (BF), 520 ($[BF_4]^-$) cm^{-1}.

Method 2: The N_2 atmosphere inside a Schlenk containing a drop of *o*-$C_6H_4(PMe_2)_2$ in n-hexane (5 mL) was replaced with BF_3 gas, which caused the immediate precipitation of a large amount of white powder. The reaction was allowed to stand overnight. After returning the Schlenk atmosphere to N_2, the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.054 g. Anal. Calc. for $C_{10}H_{16}B_2F_6P_2$: C, 36.0; H, 4.8. Found: C, 35.8; H, 4.7%. Spectroscopic data on the white powder were as for Method 1.

$[BCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][BCl_4]$ (10): To a solution of $[BCl_3(SMe_2)]$ (0.096 g, 0.53 mmol) in CH_2Cl_2 (5 mL) was added *o*-$C_6H_4(PMe_2)_2$ (0.051 g, 0.26 mmol) in CH_2Cl_2 (5 mL) to give a colorless solution which was stirred for 2 h. The solvent volume was reduced to about 3 mL *in vacuo*, onto which n-hexane (6 mL) was layered. Colorless crystals suitable for single crystal X-ray diffraction study formed. These were isolated by filtration and dried *in vacuo* to give a white powder. Concentrating the filtrate to dryness *in vacuo* afforded a second crop of the product. Yield 0.072 g (65%). Anal. Calc. for $C_{10}H_{16}B_2Cl_6P_2$: C, 27.8; H, 3.7. Found: C, 27.6; H, 3.6%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.06 (t, $^{2+5}J_{PH}$ = 6.0 Hz, [12H], CH_3), 8.03-8.13 (m, [4H], *o*-C_6H_4). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 7.5 (q, $^1J_{PB}$ = 125 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –3.17 (t, $^1J_{PB}$ = 125 Hz), 8.05 (s, $[BCl_4]^-$). IR (Nujol): ν = 700 (vs) (BCl), 667 (vs) ($[BCl_4]^-$), 477 (m) (BCl) cm^{-1}.

[**$BBr_2\{o\text{-}C_6H_4(PMe_2)_2\}][BBr_4]$ (11):** To a solution of *o*-$C_6H_4(PMe_2)_2$ (0.050 g, 0.25 mmol) in n-hexane (8 mL) was added BBr_3 (0.129 g, 0.51 mmol) which immediately led to the precipitation of a white solid. The reaction was stirred for 2 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.157 g (89%). Anal. Calc. for $C_{10}H_{16}B_2Br_6P_2$: C, 17.2; H, 2.3. Found: C, 17.3; H, 2.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.23 (t, $^{2+5}J_{PH}$ = 6.0 Hz, [12H], CH_3), 8.02-8.45 (m, [4H], *o*-C_6H_4). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 7.7 (q, $^1J_{PB}$ = 119 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ –14.02 (t, $^1J_{PB}$ = 119 Hz), –23.27 (s, $[BBr_4]^-$). IR (Nujol): ν = 607 (vs) ($[BBr_4]^-$), 595 (vs), 584 (vs) (BBr) cm^{-1}. Small colorless single crystals of $[BBr_2\{o\text{-}C_6H_4(PMe_2)_2\}][BBr_4]$ were grown from n-hexane was layered onto a filtered CH_2Cl_2 solution of the reagents.

$[BI_2\{o\text{-}C_6H_4(PMe_2)_2\}]I$ (12): To a solution of BI_3 (0.121 g, 0.31 mmol) in CH_2Cl_2 (5 mL) was added *o*-$C_6H_4(PMe_2)_2$ (0.031 g, 0.16 mmol) in n-hexane (5 ml) which immediately led to the precipitation of a white solid. The reaction was covered and stirred for 1.5 h, then the white powder was isolated by filtration and dried *in vacuo*. Yield: 0.048 g (51%). Anal. Calc. For $C_{10}H_{16}BI_3P_2$: C, 20.4; H, 2.7. Found: C, 20.4; H, 2.6%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.34-2.37 (m, $^{2+5}J_{PH}$ = 7.0 Hz, [12H], CH_3), 7.99-8.50 (m, [4H], *o*-C_6H_4). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 7.2 (q, $^1J_{PB}$ = 110 Hz). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −43.5 (t, $^1J_{PB}$ = 110 Hz). IR (Nujol): ν = 551 (s) (BI) cm^{-1}. Small yellow single crystals of [BI_2{*o*-$C_6H_4(PMe_2)_2$}][I_3] were grown from layering the filtered CH_2Cl_2 solution of the reagents with n-hexane (7 mL).

[BF_2{*o*-$C_6H_4(AsMe_2)_2$}][BF_4] (13): *o*-$C_6H_4(AsMe_2)_2$ (0.29 g, 1 mmol) was dispersed in stirred n-hexane (15 mL) and BF_3 gas bubbled slowly into the solution, resulting in the rapid formation of a white powdery precipitate. The BF_3 was stopped, and the mixture stirred for 1h, after which the mixture was concentrated to ~ 5 mL and the white precipitate was isolated by filtration and dried to a very fine white powder *in vacuo*. Yield: 0.345 g, (82%). Anal: Calc. $C_{10}H_{16}As_2B_2F_6$, C, 28.5 H, 3.8. Calc. for $C_{10}H_{16}As_2B_3F_9$, C, 24.5; H, 3.3. Found: C, 25.0; H, 3.7% (see text). The complex is insoluble in CH_2Cl_2, decomposed by MeCN, dmf and dmso and decomposes quite rapidly in CD_3NO_2. NMR data were obtained from freshly prepared CD_3NO_2 solution (~ 30% decomp to free diarsine). Powder turns into a glass in ~12h in the glove box- ^{1}H NMR (CD_3NO_2, 295 K): δ 2.91 (s, [12H], CH_3), 7.9-8.2 (m, [4H], *o*-C_6H_4) (+ free *o*-$C_6H_4(AsMe_2)_2$ at 1.32, 7.3-7.6). ^{19}F{^{1}H} NMR: (CD_3NO_2, 295 K): δ −149.8 (br s), −151.1 (s); (253 K): δ −149.6 (br) −151.4 (s). ^{11}B NMR (CD_3NO_2, 295 K): δ + 0.30 (s), +0.05 (sh); (253 K): δ + 0.31 (s, BF_2), +0.16 (s, BF_4). IR (Nujol): ν = 1094 (s), 1060 (vbr, s, [BF_4]$^-$), 1023 (s, BF), 530 (BF).

[BCl_2{*o*-$C_6H_4(AsMe_2)_2$}][BCl_4] (14): *o*-$C_6H_4(AsMe_2)_2$ (0.29 g, 1 mmol) was dispersed in stirred n-hexane (15 mL) and BCl_3 gas slowly bubbled into the solution for 5 min., resulting in the rapid formation of a white powdery precipitate. The BCl_3 was stopped, and the mixture stirred for 1h, after which further BCl_3 was passed for 2 min. The mixture was concentrated to ~ 5 mL and the white precipitate was isolated by filtration and dried to a very fine white powder *in vacuo*. Yield: 0.345 g, (66%). Anal. Calc. for $C_{10}H_{16}As_2B_2Cl_6$: C, 23.1 H, 3.1. Found: C, 23.2; H, 3.1%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.08 (s, [12H], CH_3), 7.94 (br, [4H], *o*-C_6H_4. ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ +8.03 (s, BCl_4), −1.16 (s, BCl_2). IR (Nujol): ν = 698 (vs), 667 (s [BCl_4]$^-$), 466 (m) (BCl). A few small colorless crystals were obtained from a CH_2Cl_2 solution of [$BCl_3(SMe_2)$] and *o*-$C_6H_4(AsMe_2)_2$ layered with n-hexane. Work up of this solution gave an impure waxy solid.

[BBr_2{*o*-$C_6H_4(AsMe_2)_2$}][BBr_4] (15): *o*-$C_6H_4(AsMe_2)_2$ (0.29 g, 1 mmol) was dispersed in stirred n-hexane (15 mL) and BBr_3 (0.50g, 2 mmol) added dropwise. An immediate white precipitate appeared. The suspension was stirred for 1h, the white precipitate filtered off, rinsed with hexane (5 mL) and dried *in vacuo*. Yield: 0.55 g, (70%). Anal. Calc. for $C_{10}H_{16}As_2B_2Br_6$: C, 15.3 H, 2.1. Found: C, 15.5; H, 2.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 2.17 (s, [12H], CH_3), 7.97-8.06 (m, [4H], *o*-C_6H_4). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ −14.25 (s, BBr_2), −23.4 (s, [BBr_4]$^-$). IR Nujol): ν = 605 (vs, [BBr_4]$^-$), 594 (vs) 585 (sh) (BBr).

[BI_2{o-$C_6H_4(AsMe_2)_2$}]I (16): Powdered boron triiodide (0.20 g, 0.5 mmol) was suspended in n-hexane (20 mL) and vigorously stirred whilst *o*-$C_6H_4(AsMe_2)_2$ (0.29 g, 1 mmol) in n-hexane (5 mL) was added dropwise, producing an immediate white precipitate. The mixture was stirred for 2h, and then the fine precipitate filtered off, rinsed with n-hexane and dried *in vacuo*. Yield: 0.29 g (87%). Calc. for $C_{10}H_{16}As_2B_2I_3$: C, 17.7, H, 2.4. Found: C, 17.5; H, 2.3%. ^{1}H NMR (CD_2Cl_2): δ 2.10 (s, [12H], CH_3), 7.90 (br, [4H], *o*-C_6H_4) ^{11}B NMR (CD_2Cl_2): δ –74.3(s).

[$(BF_3)_2$(μ-$Ph_2P(O)CH_2P(O)Ph_2$)] (17): $Ph_2P(O)CH_2P(O)Ph_2$ (0.42 g, 1.0 mmol) was suspended in anhydrous n-hexane (10 mL) and the solution saturated with BF_3 gas. The mixture was stirred for 30 min., then more BF_3 bubbled through the solution. The solvent was removed *in vacuo*, leaving a white powder, which was rinsed with dry diethyl ether (5 mL) and dried *in vacuo*. Yield: 0.47 g (85%). The fine powder becomes sticky on brief exposure to moist air. Anal. Calc. for $C_{25}H_{22}B_2F_6O_2P_2$: C, 54.4; H, 4.0. Found: C, 54.8; H, 4.1%. ^{1}H NMR (CD_3CN, 295 K): δ 4.55 (t, [2H], $^3J_{PH}$ = 12 Hz, CH_2), 7.48–7.90 (m, [20H], Ph). ^{19}F{^{1}H} NMR (CD_3CN, 295 K): δ –137.6 (t, $^3J_{PF}$ = 9 Hz). ^{31}P{^{1}H} NMR (CD_3CN, 295 K): δ = 53.5 (s).

Reaction of [$BF_3(SMe_2)$] with $Ph_2P(O)CH_2P(O)Ph_2$ forming (17) and [$BF_2(Ph_2P(O)CH_2P(O)Ph_2)$][$B_2F_7$] (18): The reaction of [$BF_3(SMe_2)$] (0.125 g, 0.06 mmol) with $Ph_2P(O)CH_2P(O)Ph_2$ (0.20 g, 0.48 mmol) in CH_2Cl_2 (10 mL) gave a clear solution, which was concentrated to ~5 mL and layered with n-hexane (10 mL). Some clear crystals deposited after about 2 d, one of which was shown by an X-ray study to be [$BF_2(Ph_2P(O)CH_2P(O)Ph_2)$][$B_2F_7$] **(18)**. The remaining solvent was removed *in vacuo*, and the residue washed with diethyl ether (10 mL) and dried. NMR analysis showed the presence of both [$(BF_3)_2${μ-$Ph_2P(O)CH_2P(O)Ph_2$}] and [BF_2{$Ph_2P(O)CH_2P(O)Ph_2$}][B_2F_7]. *NMR data for (18) taken from the mixture*: ^{1}H NMR (CD_2Cl_2, 295 K): δ 4.40 (t, [2H], $^2J_{PH}$ = 9 Hz, CH_2), 7.48–7.90 (m, [20H], Ph). ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): δ –142.6 (s), –149.8 (br). ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2, 295 K): δ 44.2 (s). ^{11}B NMR (CH_2Cl_2/CD_2Cl_2, 295 K): 0.15 (s, $[BF_4]^-$), 0.51 (br s).

X-ray Crystallography

Selected crystallographic parameters are presented in Table 6. Single crystal X-ray data were collected using a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF or HF Varimax optics (70 or 100 µm focus), with the crystal held at 100 K (N_2 cryostream). Structure solution and refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013,[42] with H atoms bonded to C placed in calculated positions using default C–H distances. Distance restraints were used in [$BF_3(PMe_3)$] to stop hydrogen atoms disordering across the mirror plane. Where additional restraints were required, details are provided in the cif file for each structure.

Supporting Information

Preparation and X-ray crystal structure of $[(BCl_3)_2\{\mu\text{-}Ph_2P(O)CH_2P(O)Ph_2\}]$, together with the crystallographic details for the new structures reported in this manuscript (CCDC 1480550-1480559). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Table 6: X-Ray Crystallographic Data

Compound	$[BF_3(PMe_3)]$ **(1)**	$[(BF_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ **(3)**	$[(BCl_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ **(4)**
Formula	$C_3H_9BF_3P$	$C_{10}H_{24}B_2F_6P_2$	$C_{10}H_{24}B_2Cl_6P_2$
M	143.88	341.85	440.55
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/m$ (11)	$P2_1/c$ (14)	$P2_1/c$ (14)
a /Å	5.838(6)	6.636(2)	11.138(6)
b /Å	9.170(9)	19.987(8)	6.934(4)
c /Å	6.675(7)	6.556(2)	13.505(8)
α /°	90	90	90
β /°	113.359(11)	108.286(9)	110.741(7)
γ /°	90	90	90
U /Å^3	328.1(5)	826.9(5)	975.5(9)
Z	2	2	2
μ(Mo-K$_\alpha$) /mm^{-1}	0.373	0.308	1.032
F(000)	148	356	452
Total no. reflns	2502	3715	8022
R_{int}	0.132	0.038	0.068
Unique reflns	611	1860	2212
No. of params, restraints	49, 3	93, 0	93, 0
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.097, 0.226	0.035, 0.085	0.029, 0.057
R_1, wR_2 (all data)	0.123, 0.240	0.048, 0.091	0.032, 0.058

Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°.

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$.

Table 6: cont.

Compound	$[(BBr_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ **(5)**	$[(BI_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ **(6)**	$[BCl_2\{o\text{-}C_6H_4(PMe_2)_2\}]\text{-}[BCl_4]$ **(10)**
Formula	$C_{10}H_{24}B_2Br_6P_2$	$C_{10}H_{24}B_2I_6P_2$	$C_{10}H_{16}B_2Cl_6P_2$
M	707.31	989.25	432.49
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group (no.)	$P2_1/c$ (14)	P-1 (2)	$Cmc2_1$ (36)
a /Å	11.412(7)	10.7029(19)	10.3485(15)
b /Å	7.255(4)	11.820(2)	13.475(2)
c /Å	14.002(9)	19.582(4)	13.740(2)
α /°	90	85.694(6)	90
β /°	112.219(7)	85.145(6)	90
γ /°	90	77.051(5)	90
U /Å^3	1073.2(11)	2401.6(7)	1916.1(5)
Z	2	4	4
μ(Mo-K$_\alpha$) /mm^{-1}	11.362	7.885	1.049
F(000)	668	1768	872
Total no. reflns	9120	21164	4450
R_{int}	0.052	0.030	0.037
Unique reflns	2452	10864	1590
No. of params, restraints	93, 0	369, 0	102, 1
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.025, 0.055	0.019, 0.039	0.028, 0.069
R_1, wR_2 (all data)	0.030, 0.056	0.022, 0.040	0.030, 0.069

Table 6: cont.

Compound	[BBr$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}][BBr$_4$] **(11)**	[BI$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}][I$_3$] **(12)**	[BCl$_2${*o*-C$_6$H$_4$(AsMe$_2$)$_2$}]-[BCl$_4$] **(14)**
Formula	$C_{10}H_{16}B_2Br_6P_2$	$C_{10}H_{16}BI_5P_2$	$C_{10}H_{16}As_2B_2Cl_6$
M	699.25	843.48	520.39
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group (no.)	Pnma (62)	$P2_1/c$ (14)	$P2_12_12_1$ (19)
a /Å	14.745(4)	9.702(2)	8.277(3)
b /Å	10.796(3)	17.454(3)	14.406(4)
c /Å	13.068(3)	12.615(2)	16.214(5)
α /°	90	90	90
β /°	90	97.751(4)	90
γ /°	90	90	90
U /Å^3	2080.3(9)	2116.7(7)	1933.3(10)
Z	4	4	4
μ(Mo-K$_\alpha$) /mm^{-1}	11.721	7.484	4.272
F(000)	1304	1504	1016
Total no. reflns	17176	18682	17649
R_{int}	0.081	0.045	0.055
Unique reflns	2491	4150	4421
No. of params, restraints	102, 0	167, 0	185, 0
R_1, wR_2 [$I > 2\sigma(I)$]^a	0.032, 0.070	0.028, 0.060	0.021, 0.041
R_1, wR_2 (all data)	0.045, 0.073	0.040, 0.065	0.023, 0.041

Table 6: cont.

Compound	$[BF_2\{Ph_2P(O)CH_2P(O)Ph_2\}][B_2F_7]$ **(17)**
Formula	$C_{25}H_{22}B_3F_9O_2P_2$
M	619.80
Crystal system	Triclinic
Space group (no.)	P-1 (2)
a /Å	10.446(4)
b /Å	10.871(4)
c /Å	12.470(5)
α /°	71.531(13)
β /°	86.113(14)
γ /°	85.936(15)
U /Å^3	1338.2(9)
Z	2
μ(Mo-K$_\alpha$) /mm^{-1}	0.250
F(000)	628
Total no. reflns	12131
R_{int}	0.083
Unique reflns	6040
No. of params, restraints	370, 0
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.080, 0.198
R_1, wR_2 (all data)	0.149, 0.240

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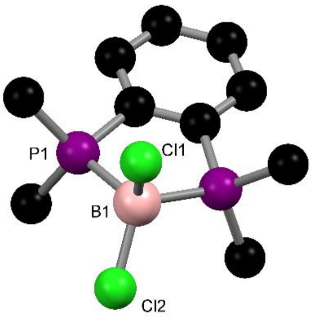
Systematics of BX_3 and BX_2^+ Complexes (X= F, Cl, Br, I) with Neutral Diphosphine and Diarsine Ligands

Jennifer Burt, James W. Emsley, William Levason, Gillian Reid* and Iain S. Tinkler



Dihaloboronium cations with neutral diphosphine and diarsine coordination are obtained from reaction of BX_3 (X = F, Cl, Br, I) with rigid *o*-phenylene based ligands, whilst the aliphatic analogs produce ligand bridged complexes, $[(BX_3)_2\{\mu\text{-}R_2P(CH_2)_2PR_2\}]$; Lewis acidity in these systems follow F << Cl ~ Br < I.